219. *Potassium Fluoaluminates.*

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The chemical composition of potassium cryolite, the synthetic analogue of the naturally-occurring (sodium) cryolite, does not correspond to the theoretical K_3AlF_6, and certain manufactured batches have been found to be abnormally acid. Preliminary experiments had indicated that the salt was not stable in water; it was therefore desirable that the chemistry of the double fluorides of potassium and aluminium should be studied more fully, and the effect of water on potassium cryolite elucidated. Under normal conditions of manufacture, from aluminium and potassium fluorides or potassium hydroxide and " hexafluoaluminic acid " in aqueous solution, it is impossible to prepare a stable material corresponding to the true potassium hexafluoaluminate. A well-defined pentafluoaluminate, K_2AlF_5, has been shown to exist, and evidence has been obtained for the existence also of a tetrafluoaluminate, $KAlF_4$. When it is expected that the hexafluoaluminate would be formed, there usually results a material in which the molecular ratio of potassium fluoride to aluminium fluoride is slightly less than 3 : 1. This is in agreement with some recently published work. The effect of water upon potassium cryolite has been shown to be, first, dissociation of the double salt into potassium fluoride and potassium pentafluoaluminate, followed by solution of the latter if the concentration of potassium fluoride in the aqueous phase is less than 0·15%. The concentration of potassium fluoride necessary to inhibit dissociation of potassium cryolite is of the order of 0·55%. The high acidities associated with some batches are to be attributed to the presence of an acid salt and not to hydrolytic effects.

During the examination of commercially prepared samples of potassium cryolite, nominally K_3AlF_6, it was found that the potassium contents were much lower, and the aluminium contents much higher, than those calculated. In view of this discrepancy, a review was made of the possible methods of analysing such a substance, and many of them were tried with a view to ascertain whether the unexpected values were the result of unsuitable procedures. Since considerable significance has been attached to the results finally obtained, this review is given in an appendix. Table I gives the results of the examination of typical batches, in which allowance has been made for moisture and traces of sodium present, in comparison with the expected proportions. From the figures it will be seen that the molecular ratio of potassium fluoride to aluminium fluoride is less than the 3 : 1 expected.

Table I.

Sample	1.	2.	3.	4.	5.	6.	Calc., %.
Potassium	43·5	43·6	44·0	44·2	44·5	44·3	45·4
Aluminium	11·1	11·3	11·3	11·3	11·4	11·1	10·5
Fluorine	45·4	45·1	44·7	44·5	44·1	44·6	44·1

A review of the literature (Mellor, " Inorganic and Theoretical Chemistry ", Vol. V, pp. 306, 307; Gmelin, " Handbuch der Anorganische Chemie ", Vol. 35, p. 450) shows that until recently potassium penta- and hexa-fluoaluminates have been regarded as stable compounds, slightly soluble in water, containing potassium and aluminium fluorides in the molecular ratios 2 : 1 and 3 : 1, respectively. Apart from the relative proportions of water of crystallisation present in the salts, there had been no suggestion that any differences existed between the fluoaluminates prepared by melting together the components and those obtained by precipitation from aqueous solutions. During the course of the present investigation, a paper appeared (Brosset, *Chem. Abs.*, **1943**, **37**, **13**), demonstrating from crystallographic studies that while potassium penta-fluoaluminate is first formed on adding potassium fluoride to solutions containing aluminium and fluoride ions, the compound produced in the presence of excess of potassium fluoride is not K_3AlF_6 but $K_{3-x}AlF_{6-x},xH_2O$, *i.e.*, potassium cryolite in which part of the potassium fluoride in the crystal lattice has been replaced by water. Brosset (*loc. cit.*) states that the only stable compounds obtainable by mixing aqueous solutions are K_2AlF_5 and $K_{2\cdot8}AlF_{5\cdot8}$.

EXPERIMENTAL.

In order to test the truth of Brosset's statement, potassium aluminium fluorides were prepared under carefully controlled conditions, and the resulting materials analysed by the methods detailed in the appendix. As a confirmation, conductometric titrations of aluminium fluoride with potassium fluoride in aqueous solution were conducted in the hope that these would reveal the existence of definite compound formation. These experiments are described below. Although the majority of samples of commerical potassium cryolite examined were essentially neutral in reaction, some were found to be abnormally acid, in that their suspensions in water required considerable additions (up to 60 mg. of potassium hydroxide per g. of solid) to render them neutral. The cause of this acidity has also been investigated. It had been anticipated, by analogy with sodium cryolite, that the solubility of potassium cryolite would be very low; reference may be found (Mellor, *op. cit.*) to figures quoted as solubilities of potassium cryolite, and as nothing is said to the contrary, it must be assumed that these refer to what were believed to be true solutions of the cryolite. It was found, however, that in certain circumstances, up to 22% by weight of potassium cryolite could be extracted by water, and qualitative and quantitative tests have indicated that this extractable material is potassium fluoride. In fact, an instance was brought to the authors' notice, in which the high solubility of potassium cryolite was explained on the assumption that the material consisted, not of the double salt, but of a mechanical mixture of the two components, from which water dissolved the more soluble potassium fluoride. In view of the fact that potassium cryolite is normally prepared from aqueous solution, it was decided to investigate fully the action of water on the compound. The results are reported later.

Except in the analytical procedures, it was found necessary to use paraffin-waxed glass or platinum vessels, since many of the reagents employed dissolved glass, etc., to an inconvenient extent.

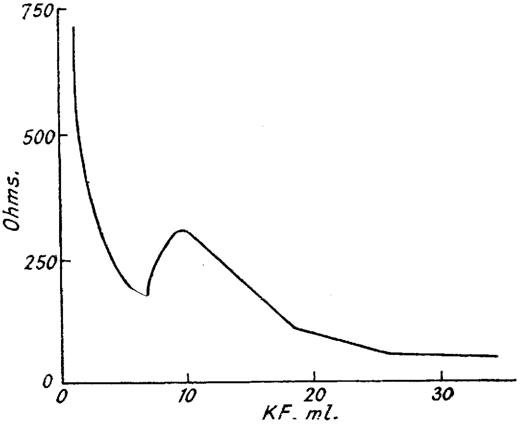
Preparation of Potassium Fluoaluminates.—(i) *From potassium aluminate and hydrofluoric acid.* Solutions were prepared of potassium aluminate in potassium hydroxide in which the molar ratios of potassium to aluminium were 3 : 1 and 2 : 1. To avoid the presence of other anions, the solutions were made by dissolving weighed amounts of pure aluminium foil in standardised potassium hydroxide. These solutions were titrated with hydrofluoric acid, and the end-points determined potentiometrically with a calomel–antimony electrode combination. As would be expected, the end-points corresponded with the production of K_3AlF_6 and K_2AlF_5, since the potential of the antimony–antimony oxide electrode was influenced only by the hydrogen-ion concentration of the systems. The precipitated solid phases were filtered off, washed with the minimum of cold water, dried, and analysed. The constitutions corresponded to the empirical formulæ $K_{2\cdot9}AlF_{5\cdot9}$ and $K_{1\cdot9}AlF_{6\cdot6}$, respectively. This indicates that although K_3AlF_6 and K_2AlF_5 may have been formed initially, the hexafluoaluminate after brief washing had lost potassium fluoride, whilst the pentafluoaluminate had absorbed, from the finally acid solution, some hydrofluoric acid which had not been removed by washing and drying.

A solution of potassium aluminate (K : Al = 3 : 1) was neutralised with hydrofluoric acid, the potential of the antimony electrode then having a value corresponding to the middle of the potential–volume curve found in the first titration. This potential corresponded very closely with the change-point of methyl-red indicator. Similarly, hydrofluoric acid was neutralised with potassium aluminate. Finally, the aluminate was slightly over-neutralised with the acid. The solid phases produced in each case were filtered off, washed briefly, and dried. 1 G. of each was stirred with 100 ml. of cold water and titrated with N/20-potassium hydroxide solution, the end-points being determined potentiometrically. The acidities of the samples were found to correspond to 0·8, 2·7, and 56·8 mg. of potassium hydroxide per g., respectively. This indicates that in the presence of excess of hydrofluoric acid, potassium cryolite absorbs acid and does not readily part with it. This is probably due to the formation of a small proportion of an acid salt. This acid salt may be considered to be formed by the replacement of part of the potassium fluoride in the crystal lattice by hydrofluoric acid, in the same manner as Brosset (*loc. cit.*) has suggested for the replacement of potassium fluoride by water. The acidities observed in some commercial batches of potassium cryolite are thus to be ascribed to the presence of an acid salt, produced by the addition of slight excess of hydrofluoric acid, and not to hydrolysis. It has been found that a solution of aluminium fluoride in water is not acid.

(ii) *From potassium hydroxide and " hexafluoaluminic acid ".* Addition of potassium hydroxide to " hexafluoaluminic acid " (a solution of aluminium fluoride or hydroxide in hydrofluoric acid in the correct proportions) and *vice versa* produced solids having properties, chemical and physical, identical with those of the products obtained above.

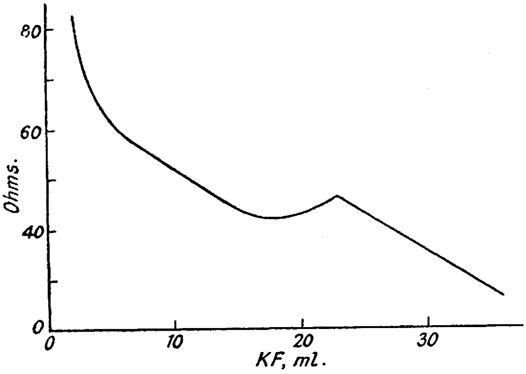
Conductometric Titrations of Potassium Fluoride and Aluminium Fluoride.—A saturated solution of aluminium fluoride in water was titrated with aqueous potassium fluoride and the conductivity of the aqueous phase determined when equilibrium had been established after each addition of titrant. Cell-resistance (*i.e.*, reciprocal of conductivity) was actually measured and plotted against volume of potassium fluoride. The concentration of potassium fluoride was chosen so that the amount added made no significant change in the total volume. A typical curve obtained in this way is shown in Fig. 1. At the stage corresponding to 7·0 ml., precipitation of solid phase commenced, and the sudden rise in resistance at that point is to be attributed to the deposition of salt and not to the formation of a compound. The breaks at 9·3, 18·65, and 26·05 ml. correspond to the formation of $KAlF_4$, K_2AlF_5, and $K_{2\cdot8}AlF_{5\cdot8}$ respectively. This is in agreement with Brosset's work. It is noteworthy that Russian workers have examined synthetic and natural cryolite. Tananaev and Lelchak (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, XLI, **3**, 144) report that the ratio NaF : AlF_3 for Greenland cryolite is in the range 2·7—2·8. They suggest a formula, for the natural and synthetic material, of $11NaF,4AlF_3$, which corresponds to $Na_{2\cdot75}AlF_{5\cdot75}$. Yatlow (*J. Gen. Chem. Russia*, 1937, **7**, 2439) states that sodium cryolite is formed as a result of a reaction between the tetrafluoaluminate, yielded initially by solutions of sodium fluoride and aluminium fluoride, and sodium fluoride. As the proportion of sodium fluoride is increased, the ratio of NaF to AlF_3 in the composition of the precipitate increases from 1 to 2·8. Yatlow has demonstrated the existence of sodium tetra- and penta-fluoaluminates, but states that attempts to synthesise cryolite from aqueous solutions yielded a material of the composition 2·7—2·8NaF,AlF_3. The analogy with potassium fluoaluminates is thus complete.

FIG. 1.



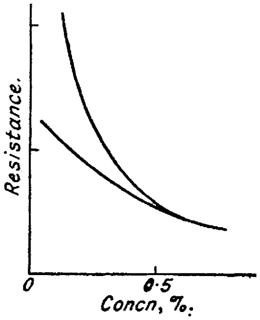
Conductometric titration of aluminium fluoride solution with potassium fluoride.

FIG. 2.



Conductometric titration of potash alum solution with potassium fluoride.

FIG. 3.



Conductivity of potassium fluoride solutions as influenced by addition of potassium cryolite.

No evidence was found for the formation of the hexafluoaluminate when an aqueous solution of potash alum was titrated with potassium fluoride (see Fig. 2), the only significant break in the curve, at 23·2 ml., corresponding to formation of potassium pentafluoaluminate. After the addition of 18 ml. of potassium fluoride solution, solid commenced to separate; the subsequent rise in resistance is to be attributed to this fact. This observation is not in accord with that of Berzelius (*Pogg. Ann.*, 1824, **1**, 43) that potassium cryolite is formed from potash alum in the presence of excess of potassium fluoride. This point requires further examination, but it is of interest that a commercially prepared material, reputed to be potassium cryolite and made from potash alum and potassium fluoride, was found to consist of the hydrated pentafluoaluminate, K_2AlF_5,H_2O.

The Effect of Water on Potassium Fluoaluminates.—A suspension of potassium cryolite (5 g. in 87·5 ml. of distilled water) was kept at 35° and stirred continuously, with precautions against loss by evaporation. At hourly intervals portions of the suspension were withdrawn, the solid phase removed, and the solution analysed. In every instance the only compound in solution was potassium fluoride. Its concentration increased gradually with time, until after about 6 hours it had become constant. At this stage there was present in every 10 ml. of solution 0·063 g. of potassium fluoride, *i.e.*, a 0·63% solution of potassium fluoride inhibited further dissociation of the hexafluoaluminate to pentafluoaluminate and fluoride.

The conductivities of solutions of potassium fluoride of various concentrations were determined. To fixed volumes of these solutions was added a standard weight of potassium cryolite (two typical commercial materials, $K_{2\cdot7-2\cdot8}AlF_{5\cdot7-5\cdot8}$ were used). The liquid was stirred until no further change in conductivity occurred. The initial and final conductivities (as resistance of a nominal volume of solution) were plotted against the concentration of the original solutions. The curves for the two samples were identical and are shown in Fig. 3. It will be seen that the two branches of the graph merge at a concentration of 0·55 to 0·60%. Since at concentrations below 0·55% the conductivity of a potassium fluoride solution was increased by the addition of potassium cryolite, it follows that dissociation of the cryolite had occurred. At concentrations of 0·60% and above, no alteration in conductivity was observed; no dissociation of the cryolite had taken place. This value for the inhibiting concentration is in good agreement with that found by analysing aqueous extracts; the conductivity measurements were carried out at 20° as against 35° used in the extraction method.

The above-mentioned samples of potassium cryolite and a sample of anhydrous potassium pentafluoaluminate were used to study further the effect of water. 5 G. of each were suspended in 500 ml. of distilled water and shaken at room temperature until equilibrium was reached. The solid residues were removed and dried. The clear solutions and portions of the solids were analysed. 3 G. of the remaining solids were each suspended in 300 ml. of water and treated as above. The first extraction with water removed from each of the cryolites approximately 22% of potassium fluoride and left a residue with a composition approximating to K_2AlF_5. The first aqueous extraction of the potassium pentafluoaluminate removed only 13·3%, and this was found to be of a composition identical with that of the starting material and of the solid residue. The second extraction removed from each sample 13·2% of pentafluoaluminate, leaving a solid of the same composition. It will thus be seen that the action of water on potassium cryolite is to dissociate and dissolve away potassium fluoride and then to take into solution the pentafluoaluminate. Experiments conducted with solutions of various concentrations of potassium fluoride showed that the concentration required to prevent the solution of the pentafluoaluminate is about 0·15%, *i.e.*, slightly less than the 0·22% resulting from the first water-extraction of the cryolite samples.

Appendix.

Analysis of Potassium Fluoaluminates.—(i) *Potassium.* Any method which involves preliminary separation of aluminium with ammonia or ammonium salts, etc., is liable to give low results owing to losses by adsorption on the precipitated alumina, by spitting during evaporation of solutions to dryness, and by decrepitation during heating to expel ammonium salts. Estimation as perchlorate, without separation of aluminium, avoids these losses, and has been found to give results in general higher than those obtained when potassium is estimated as sulphate, a method subject to the above-mentioned disadvantages. Some comparative figures are:

Sample	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)
K, % (determined as K_2SO_4)	42·9	42·5	43·2	43·5	43·5	43·9
K, % (,, $KClO_4$)	43·4	43·8	43·9	43·8	43·5	44·1

(ii) *Aluminium.* Time is saved if aluminium is determined in the solution as used for the potassium estimation. This can be accomplished by precipitation with 8-hydroxyquinoline. Results are identical with those obtained when the aluminium is estimated as alumina; the use of oxine is to be preferred since the aluminium content of the "oxinate" is much smaller than that of alumina, and accidental impurities in the precipitate are of less importance.

(iii) *Fluorine.* Various modifications of the method involving titration with thorium nitrate have been examined. All suffer from the drawback that the end-point of the titration, using sodium alizarinsulphonate as indicator, may be uncertain and difficult to assess, though in the hands of an experienced operator accurate results are obtainable. The estimation as lead chlorofluoride is simpler; the distillation is easy to control, the weight of the sample taken is fairly large, and the estimation may be finished gravimetrically or volumetrically as desired, identical results being obtained by either method. Volumetric estimation was not employed in view of the consumption of silver nitrate. It should be noted that preliminary melting of the material with fusion mixture, as recommended by certain authorities, is not only unnecessary, but leads, in fact, to low results, as shown by the following figures:

F, % with fusion	44·6	44·0	44·3
F, % without fusion	45·2	44·5	44·3

It was found that fusion of potassium cryolite alone at temperatures above 900° leads to loss in weight, and also that sodium fluoride is volatile on heating.

(iv) *Sodium.* When it is desired to determine sodium content, it is necessary to decompose the cryolite with sulphuric acid, remove the aluminium, and use zinc uranyl acetate as precipitant.

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