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1. *The Acid Fluorides of the Alkali Metals. Part I. The Acid Fluorides of Rubidium.*

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OUR knowledge of the acid fluorides of rubidium was principally due to Eggeling and Meyer (*Z. anorg. Chem.*, 1905, **46**, 174), who described the preparation of the bifluoride, RbF,HF, and of a mixed salt of RbF,2HF (containing also some RbF,3HF) and gave an account of the apparent stability and solubility of these substances. Since some of their statements, especially those referring to the insolubility of RbF,2HF and its apparent great stability towards heat, were rather improbable, it was decided to examine the matter further and to prepare the bifluoride, and possibly higher fluorides, in a state of greater purity.

Considerable progress had been made when Meyer and Taube (*ibid.*, 1936, **227**, 337) reported that the supposed insoluble acid fluoride of rubidium is really the silicofluoride Rb_2SiF_6 (see also Finbak and Hassel, *ibid.*, 1936, **226**, 175). They proved that an acid fluoride can be prepared from rubidium carbonate and aqueous 40% hydrogen fluoride. Any insoluble silicofluoride at first precipitated is removed, and the filtrate evaporated until it sets to a solid mass on cooling. The residue, on being heated at 150° in a drying oven, lost only 4·62% of its weight. The solid, when ground, and kept over concentrated sulphuric acid in a glass desiccator for several days, gave, on analysis: Rb, 59·2, 59·3; HF, 26·61, 26·94 (Calc. for RbF,2HF : Rb, 59·16; HF, 27·67%). We have confirmed and extended these results.

Higher Acid Fluorides of Potassium and its Congeners.—Prior to Moissan's work on the isolation of fluorine, potassium bifluoride (Frémy's salt) was the only known acid fluoride of potassium. Moissan (*Compt. rend.*, 1888, **106**, 548) obtained KF,3HF from the bifluoride either by cooling its solution in anhydrous hydrogen fluoride to −23°, or by warming it with the calculated quantity of hydrogen fluoride in an oil-bath at 85°. The product, which set to a hard mass at 68°, was deliquescent and evolved hydrogen fluoride in a moist atmosphere, but was stable in dry air. The pressure of hydrogen fluoride at 100° was found to be 30—50 mm. by Wartenberg and Klinkott (*Z. anorg. Chem.*, 1930, **193**, 409). On electrolysis of this fused salt, fluorine was obtained by these workers, and also by Lebeau and Damiens (*Compt. rend.*, 1925, **181**, 917). By suitably altering the proportion of hydrogen fluoride in his second method, Moissan prepared KF,2HF, for which Lebeau gives m. p. 70°, and Cady (*J. Amer. Chem. Soc.*, 1934, **56**, 1431) m. p. 71·7°. The latter investigator, from measurements of vapour pressures and freezing points of the system KF–HF, reported two further acid fluorides, KF,4HF and 2KF,5HF.

For the preparation of fluorine by the electrolysis of fused acid fluorides, those of potassium had generally been used, but when cæsium became more readily available, Mathers and Stroup (*Trans. Amer. Electrochem. Soc.*, 1934, **66**, 113) utilised its acid fluorides for this purpose because they were more readily fusible. From the carbonate and the aqueous acid, both CsF,1½HF, m. p. 30°, and a product of approximate composition CsF,2HF, m. p. 19°, were obtained. CsF,HF had previously been described by Chabrie (*Compt. rend.*, 1901, **132**, 680).

Experimental.

Preparation of KF,2HF.—It would be very convenient if the more fusible higher fluorides of potassium could be prepared without the use of anhydrous hydrogen fluoride, since their high content of hydrogen fluoride and ready fusibility make them valuable for studying the action of hydrogen fluoride upon various materials at moderate temperatures, as Moissan pointed out. In spite of repeated trials, we have been unable to prepare any fluoride higher than KF,HF by evaporation of aqueous solutions by heat. More success attended evaporation over sulphuric acid in a desiccator (cf. Prideaux and Millot, J., 1929, 2703), whereby, from KF,HF and 40% hydrogen fluoride, crystals were obtained, which contained HF, 38·39 (mean of two results) (Calc. for KF,2HF : HF, 40·82%); m. p. *ca.* 80°. This product contained, however, a small quantity of silicofluoride derived from the glass of the desiccator, which cannot be completely protected by any coating—in this instance, wax (ceresin) was used, but was not entirely satisfactory. Further examination of this compound is therefore postponed until the work can be repeated in apparatus free from glass.

Method of Analysis.—Since only small amounts of the rubidium compounds (see below) were available, it was necessary to devise a method of analysis which would allow the rubidium to be recovered from all residues in a convenient form, free from alkali metals. Therefore, the free acid was neutralised with excess of ammonia, and the excess determined by back-titration with hydrochloric acid, bromothymol-blue being used as indicator. A good end-point was obtained at p_H about 7·5, and control experiments with dilute hydrogen fluoride solutions showed that the results by this method agreed within the limits of experimental error in titration (0·3%) with those given by direct titration with carbonate-free sodium hydroxide and phenolphthalein as indicator.

Acid Rubidium Fluorides.—Materials. The source of rubidium was the carbonate, supplied by the Burbach-Kaliwerk A.G. and guaranteed chemically and spectroscopically pure. In view of the known deliquescence of potassium carbonate, the loss on ignition of a specimen of the rubidium carbonate was found : it was 0·75%.

The dilute hydrofluoric acid used was 36—40% A.R. quality, supplied in ceresin bottles. The anhydrous hydrogen fluoride was prepared by heating sodium bifluoride of good quality free from silicofluoride. The salt was previously dried by heating at 100—110° for some hours, and cooling in a desiccator. The distillation of the bifluoride was conducted in the copper apparatus previously described (Prideaux and Millott, J., 1926, 167); external joints were luted with glycerol–litharge cement, and addition of a little lead fluoride seemed to improve its properties at higher temperatures. Platinum vessels were used exclusively for the preparation and manipulation of the acid fluorides.

Rubidium bifluoride, RbF,HF. This was easily prepared by dissolving rubidium carbonate in a slight excess of the 36% acid. A clear solution was obtained, showing the absence of silicofluoride, and was evaporated to a small bulk. On cooling, it set to a hard white mass (Found : HF, 16·54; whence Rb, 68·3.* Calc. : HF, 16·07; Rb, 68·6%), the weight of which agreed closely with the theoretical. The salt was therefore purer than that prepared by Eggeling and Meyer (*loc. cit.*), which had Rb, 66·7%. They attributed the discrepancy to the deliquescent nature of the bifluoride. This would, however, be in strong contrast to the property of the potassium analogue, which at most is only slightly hygroscopic. We have found, in fact, that exposure to ordinary atmospheric conditions for an hour leads to no gain in weight, and the gain even from a moist atmosphere in a similar time was less than 1%. The saturation pressure of hydrogen fluoride over this compound is low, probably lower than that of potassium bifluoride, but, in agreement with Meyer and Taube, we find that the acid is completely volatilised below red heat, with production of neutral rubidium fluoride. The m. p. of the substance is undoubtedly lower than that of the potassium compound : by heating a little of the substance in a platinum crucible in an oil-bath, it was found to be about 207°. A more accurate determination was made by heating a larger quantity in a platinum crucible to 220° in an oil-bath and allowing the liquid to cool whilst being stirred with a thermometer protected by a silver sheath (not appreciably attacked by the melt) made for the purpose : the value thus found by several trials was 204—205°.

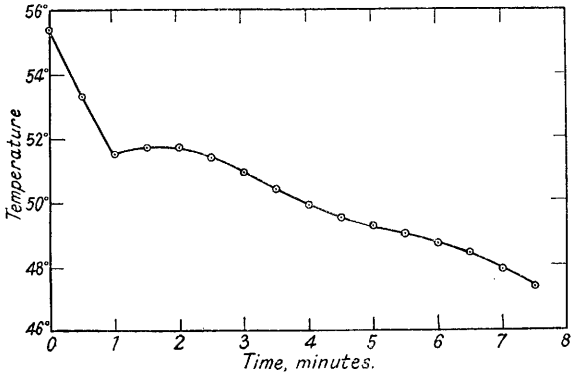
RbF,2HF. This compound was prepared in the waxed desiccator (see above) by evaporation of a solution of the bifluoride in 36—40% acid with greater ease and in a purer condition than the potassium compound. It is not necessary to segregate the solid material which separates round the edges of the dish, as in the case of potassium : the whole mass is allowed to become solid and dry, the compound, surrounded by an atmosphere rich in hydrogen fluoride, resulting

* RbF is found by difference.

(Found : HF, 26·76. Calc. : HF, 27·68%. Meyer and Taube found 26·78%). In agreement with Meyer and Taube, we attribute the low result to the presence of a small quantity of silicofluoride. Excessive corrosion of the desiccator under the ceresin is also evident in some cases in the preparation of salts of this type. In the dry state, as a solidified melt, RbF,2HF has only a slight pressure of hydrogen fluoride, and even in the fused state above 60° the loss of the fluoride is very slow; at about 100—110°, it is appreciable, especially after repeated fusions. The substance is deliquescent, and after a little moisture has been absorbed, the loss of hydrogen fluoride on heating appears to be greater. Meyer and Taube report that it is converted into RbF,HF at 150—190° after some hours.

Those authors did not determine the m. p., but an approximate determination by the method already described showed it to be slightly above 50°.

An apparatus for taking cooling curves of such substances was devised. The salt was contained in a small platinum crucible, into which were inserted a silver wire stirrer and a nickel-plated tube which contained a thermometer graduated in 0·1°. The crucible was surrounded by a thin-walled metal pot, which was kept at a suitable constant temperature by immersion in a large vessel of water, covered with a layer of oil. The crucible stood in the metal pot upon an ebonite pad and therefore was not in direct thermal contact with the metal itself.



Cooling curve of RbF,2HF.

The salt was melted by placing the crucible in an oil-bath. The crucible was then inserted in the metal pot, and the temperature read every ½ minute. In early experiments, without stirring, the degree of supercooling was very great, the temperature rising from 46° to 50° as the material solidified. By vigorous stirring it was greatly reduced, as shown in the figure. The closest estimate for the m. p. is 51·6—51·7°. A second slight inflection in the graph, observed at 49°, may be due to transition into another crystalline form or to the separation of a lower fluoride from the melt.

The m. p.'s of various acid fluorides of the alkali metals are given in the table.

Melting Points of Acid Fluorides.

KF,HF	KF,2HF	KF,3HF	RbF,HF	RbF,2HF	RbF,3HF
217° [1]	71·5° [2]	65° [3]	204—205° [4]	51·7° [4]	>0° [4]
	CsF,HF	CsF,1½HF	CsF,3HF	CsF,1½—2HF	
	142° [5]	30° [5]	—	19°	

[1] Dennis, Veeder, and Rochow (*J. Amer. Chem. Soc.*, 1931, **53**, 3263). [2] Cady (*loc. cit.*).
[3] Moissan (*loc. cit.*). [4] Present paper. [5] Mathers and Stroup (*loc. cit.*).

RbF,3HF. The foregoing experiments have shown that very concentrated or anhydrous hydrogen fluoride would be required in the preparation of acid fluorides higher than RbF,2HF, and by using the latter, we have isolated a new *substance* which appears to be RbF,3HF. Anhydrous hydrogen fluoride, prepared in the manner and apparatus already described, was kept cooled in a covered platinum crucible, and about 2 g. of RbF,HF were added, which dissolved with a hissing sound. Some brownish flocculent precipitate, apparently due to organic matter, was filtered off in a platinum Gooch crucible fitted with platinum-gauze pads, and the clear colourless liquid was cooled in a solid carbon dioxide–ether mixture, in which it solidified to a pasty mass, which melted again below 0°. On addition of further quantities of the two

reactants and cooling as before, a fairly hard solid was obtained, which on warming to about 20° gave a mush of transparent crystals. A portion was filtered off and pressed, and about 0·1 g. was rapidly weighed and analysed (Found : HF, 36·98. RbF,3HF requires HF, 36·47%). After standing for a week, the liquid still contained clear colourless crystals, which obviously had the same refractive index as the surrounding liquid. The mother-liquor then contained HF, 37·73%, so it seems that the crystals, being in contact with a liquid of nearly the same composition, had nearly the maximum freezing point, *i.e.*, nearly the m. p. of the pure compound. An attempt is being made to determine more fully the conditions of existence and the physical constants of this highest fluoride. It is probably incapable of existence in the presence of even a small amount of water, since the above solution, which gradually attracted some moisture during manipulation, gave, on careful evaporation by heat, only RbF,2HF (Found : HF, 28·58. Calc. : HF, 27·68%) with a slight excess of hydrogen fluoride. Undoubtedly, RbF,2HF could be prepared in a state of purity by maintaining the higher fluoride in a fused state for some time, with stirring to expel the excess hydrogen fluoride.

Conclusions.

(1) Under suitable conditions, an acid fluoride of potassium approximating in composition to KF,2HF can be obtained from dilute (36—40%) hydrofluoric acid.

(2) The acid fluoride RbF,HF can readily be prepared from dilute hydrofluoric acid and pure rubidium carbonate. It has m. p. 204—205° and is not deliquescent.

(3) The acid fluoride RbF,2HF can be prepared in an analogous manner to that of potassium, but in a purer state, by using the special method described; its m. p. is 51·7°.

(4) From preliminary experiments, the existence of a higher hydrofluoride of rubidium, RbF,3HF, is indicated, but this can only be obtained by using anhydrous hydrogen fluoride.

(5) The acid fluorides of rubidium resemble those of potassium in their general properties and heat stability.

Further work is in progress on the higher acid fluorides of rubidium.

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