

24. *The Acid Fluorides of the Alkali Metals. Part II. The Higher Acid Fluorides of Rubidium, and the Thermal Diagram of the RbF-HF System.*

By K. R. WEBB and E. B. R. PRIDEAUX.

Further studies on the RbF-HF system have provided conclusive evidence for the existence of the compounds RbF,2HF and RbF,3HF and have made possible the construction of an approximate thermal diagram. In addition, a new substance, RbF,3.5HF, has been prepared, and evidence has been obtained which points to the existence of other acid fluorides.

THE few recorded attempts to obtain thermal diagrams of acid fluorides clearly indicate the difficulties of such work and the necessarily incomplete nature of the results.

Potassium acid fluorides were investigated by Cady (*J. Amer. Chem. Soc.*, 1934, **56**, 1431), who used a closed system, anhydrous hydrogen fluoride being admitted to the potassium acid fluorides in a copper container. The compounds formed were not separated or examined, but their existence was inferred from the nature of the curve of initial freezing points and the calculated compositions of the mixtures. The following compounds were indicated on the thermal diagram: KF, HF (in two forms), KF, 2HF, KF, 2.5HF, KF, 3HF, and KF, 4HF.

Ammonium acid fluorides were investigated by Ruff and Staub (*Z. anorg. Chem.*, 1933, **212**, 399), who used an open system, various quantities of hydrogen fluoride being added to ammonium bifluoride, NH₄F, HF. By means of an approximate thermal diagram, they obtained evidence of NH₄F, 3HF and NH₄F, 5HF. The diagram is incomplete in the neighbourhood of NH₄F, 2HF and it appears that this substance could not be prepared.

The thermal diagram of the RbF-HF system had not hitherto been examined; that of caesium still awaits complete investigation. The work described in Part I (J., 1937, 1) has been continued, pure anhydrous hydrogen fluoride being used.

EXPERIMENTAL.

Quantities of RbF, HF (*ibid.*) were weighed in a covered platinum crucible and hydrogen fluoride (either a middle fraction from a copper still, or, in the majority of the experiments, a sample redistilled in platinum apparatus) was allowed to drop on to the specimen until the total weight increased by the required amount. In this way, various hydrogen fluoride-rich mixtures were prepared.

Cooling curves were taken for mixtures with various proportions of the two fluorides. Since the temperatures characteristic of the present systems were generally considerably lower than those employed in the former work (*ibid.*), a different apparatus was used. It consisted of a copper calorimeter (7×4.5 cm. approx.) containing a waxed cork in which was embedded a bakelite ring of such dimensions that the platinum crucible containing the mixed fluorides could comfortably rest in it completely insulated from direct contact with the metal vessel. The calorimeter was closed by a waxed cork carrying a specially constructed silver thermometer-well and a narrow copper tube, through which passed a silver wire stirrer working in a flexible, soft-rubber joint to exclude moisture. A pentane thermometer, checked against an accurate mercurial one, was used for the lowest temperatures; for higher temperatures, the accurate mercurial instrument was used. The whole apparatus could be supported in a beaker which rested in the neck of a wide Dewar vessel; the beaker contained a suitable cooling mixture, generally of powdered "drikold" and alcohol.

Cooling curves were not as a rule continued from the initial halt-point to the eutectic temperature, partly on account of difficulties connected with the pasty nature of the partly solidified mixture and the relatively small quantity of material available, but principally on account of the importance of isolating and analysing small samples of the solid which separates first and is in equilibrium with the liquid having the total composition at the initial freezing point. This composition could be maintained almost constant for further experiments by avoiding all waste. Collection of the solid on a platinum Gooch crucible (as described in Part I) was abandoned. Instead, the smallest amount of crystals suitable for analysis was removed, and freed from liquid by being quickly pressed between filter-papers. The absorbed mother-liquor could be recovered as $\text{RbF}\cdot\text{HF}$ from the paper by extraction with aqueous ammonia and subsequent evaporation. By practice, the whole operation of crushing and pressing the solid specimens could be performed in a few moments, and the solid transferred to a small capped platinum crucible of known weight and then weighed. Slight losses of hydrogen fluoride sometimes occurred during these operations; however, when the original solid formed hard crystals (as in the case of $\text{RbF}\cdot 3.5\text{HF}$), this loss was quite small. Duplicate analyses, under such conditions, were usually reasonably consistent.

Two methods were used for progressively decreasing the hydrogen fluoride content of the initially rich mixtures: (a) hydrogen fluoride was expelled gradually by heating the mixture for some time at an appropriate temperature; (b) the mixture was treated with weighed amounts of rubidium bifluoride. The latter method was less suitable than the former, since the added $\text{RbF}\cdot\text{HF}$ only dissolved slowly in the mixture unless heat were applied, whereupon there was risk of losing more hydrogen fluoride and so rendering the material poorer in this constituent than had been intended.

Methods of Analysis.—(a) The back-titration volumetric method previously described was abandoned in later experiments, since the recovered residues were found to contain considerable amounts of rubidium chloride which is not easily convertible into the fluoride.

(b) Direct titration of the acid fluoride dissolved in carbon dioxide-free distilled water with pure, freshly-standardised ammonia solution, using bromothymol-blue as indicator, yielded very satisfactory results, especially when, by experience, the exact coloration corresponding to the true end-point had been ascertained. The method was checked against the standard procedure (titration of a pure hydrofluoric acid solution with pure sodium hydroxide solution, phenolphthalein being used as indicator) and found to be very exact (difference about 0.25%).

(c) A gravimetric method was also used, in which hydrogen fluoride was expelled by heating a weighed quantity of $\text{RbF}\cdot x\text{HF}$, and the residual rubidium fluoride weighed. The salt was heated in a small platinum crucible with a slip-on lid, the usual precautions taken in volatilising an acid being observed. The greater part of the hydrogen fluoride is quickly lost below 400° , and prolonged heating to a high temperature causes appreciable volatility of the normal fluoride.

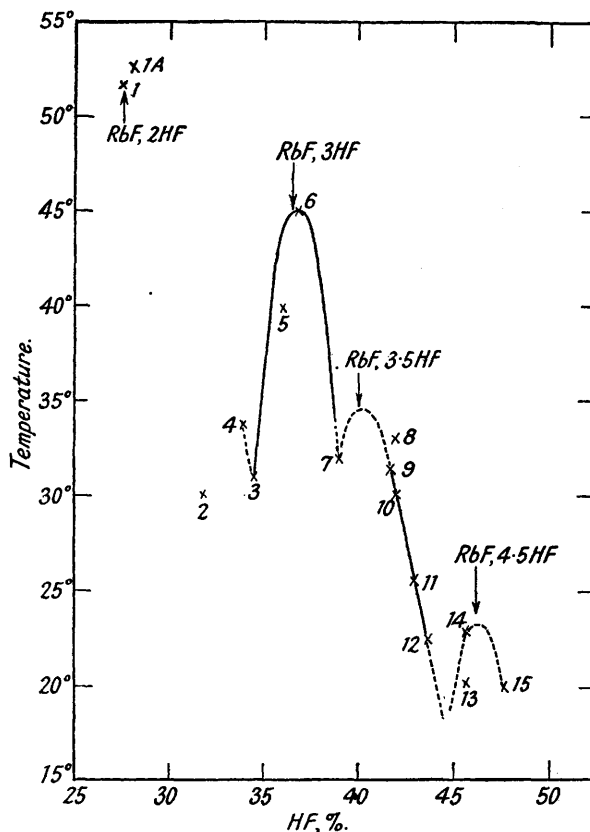
This method, checked against the titration procedures, was found to give slightly high results; e.g., 27.96% of hydrogen fluoride was found by method (b), and 28.15, 28.40% by method (c). This discrepancy was ascribed to the very deliquescent nature of the higher acid fluorides, since absorption of a little moisture would increase the loss in weight on heating but diminish the acid content. The method was checked, therefore, on non-deliquescent potassium bifluoride: the loss on heating was 25.57% (Calc. : 25.64%).

Details of a few experiments are given below.

Experiment I. 5.8 G. of $\text{RbF}\cdot\text{HF}$ (1 mol.) were treated with about 5.6 g. (6 mols.) of pure hydrogen fluoride redistilled from platinum. No solid separated from this solution when it

was cooled to between -20° and -30° . By warming, about 3 g. of hydrogen fluoride were evaporated; the resulting solution solidified completely when cooled in solid carbon dioxide-ether. The liquid showed an initial halt-point at $+22.9^{\circ}$, the whole mass becoming solid at this temperature (point 14—see figure). After standing for some time sealed up out of contact with the air, the solid formed a mass of clear, colourless, transparent crystals, together with some mother-liquor. The solid was crushed, dried, and analysed (Found: HF, 39.9, 39.15. $\text{RbF}, 3.5\text{HF}$ requires HF, 40.11%). It is considered that $\text{RbF}, 4.5\text{HF}$ decomposes on standing (Expt. II).

The hydrogen fluoride content of the total material was reduced to 38.97%; the initial halt-point found for this material was $32-33^{\circ}$ (point 7). Rubidium bifluoride was added to the residual *substance*, so that the composition approximated to that of $\text{RbF}, 3\text{HF}$. The resulting mixture formed a clear, water-white liquid with a slight odour of hydrogen fluoride; it remained



Partial thermal diagram of the system RbF-HF .

supercooled at room temperature, but solidified when chilled in solid carbon dioxide. The substance thus produced showed only a slight tendency towards surface fusion at room temperatures and remained solid for a considerable time.

On standing for several days, it changed to a mush, probably owing to slow access of moisture. On long standing, a clear mother-liquor was formed, in which were seen clear crystals, some plates and some blunt needles [Found (by titration): HF, 27.96; (by heating): HF, 28.15, 28.40. Calc. for $\text{RbF}, 2\text{HF}$: HF, 27.68%].

This experiment demonstrated the replacement of hydrogen fluorides in the higher acid fluorides by water, and also the possibility, previously reported, of preparing $\text{RbF}, 2\text{HF}$ from concentrated solutions containing some water. The experiment, as a whole, pointed to the existence of $\text{RbF}, 3.5\text{HF}$ and gave indirect evidence of the existence of $\text{RbF}, 3\text{HF}$.

Experiment II. A rubidium fluoride-hydrogen fluoride mixture was prepared which was calculated to contain 47.7% of the latter. The initial halt-point of the mixture was at 20°

(point 15). The solid which separated was pressed and analysed (Found : HF, 40.0. Calc. for $\text{RbF},3\cdot5\text{HF}$: HF, 40.1%); hence, if $\text{RbF},4\cdot5\text{HF}$ exists (see diagram), it must be unstable, readily losing hydrogen fluoride and passing into $\text{RbF},3\cdot5\text{HF}$. After some hydrogen fluoride had been expelled by heating, the residue contained 42.8% of hydrogen fluoride : the halt-point was at $25\cdot5^\circ$ (point 11) and the separating solid approximated to $\text{RbF},3\cdot5\text{HF}$ (Found : HF, 38.9%).

The hydrogen fluoride content was then reduced to 36.8%, *i.e.*, to approximately that of $\text{RbF},3\text{HF}$ (Calc. : HF, 36.47%); the initial halt-point was 45° , and may be taken as almost the true m. p. of $\text{RbF},3\text{HF}$. The separating solid had 36.6% of hydrogen fluoride, and the whole, when solidified, formed a homogeneous, friable, crystal mass, consisting of practically pure $\text{RbF},3\text{HF}$. This experiment, therefore, provided additional evidence for the existence of $\text{RbF},3\cdot5\text{HF}$ and $\text{RbF},3\text{HF}$.

In all, in addition to the preliminary experiment indicating the existence of $\text{RbF},3\text{HF}$ and described in Part I (*loc. cit.*), four complete and separate experiments have been performed on the binary system. From these, 15 points on the thermal diagram of the system have been obtained, in addition to extensive analytical evidence for the existence of the substances $\text{RbF},2\text{HF}$, $\text{RbF},3\text{HF}$, and $\text{RbF},3\cdot5\text{HF}$. There is evidence also, especially from the thermal diagram, of the probable existence of $\text{RbF},4\cdot5\text{HF}$, but it has not been satisfactorily isolated. The thermal diagram also indicates the possible existence of $\text{RbF},2\cdot5\text{HF}$; point 3 is a eutectic one and may show the composition and the m. p. of the eutectic between $\text{RbF},3\text{HF}$ and $\text{RbF},2\cdot5\text{HF}$. The evidence is rather fragmentary, however.

Supercooling was very persistent in the RbF -HF system, especially in the case of the mixtures richer in hydrogen fluoride. It is probable, therefore, that the halt-points obtained for some of these rich mixtures are somewhat too low. No satisfactory means of eliminating the supercooling was devised. However, the plotting of initial setting-points (which are more or less affected by supercooling) against total composition has been used to determine the thermal diagrams of many binary mixtures, and these diagrams have been recognised as being substantially correct. In the present case, several points showed *no* supercooling (see table), while, of the remainder, some being near to maxima, the compositions of the liquid and the solid are nearly the same, so that the separation of moderate amounts of solid will hardly affect the composition of the whole. This will also be the case near to minima, which are end-points of crystallisation. For instance, points 2, 3, 5, 6, 9, and 10 are hardly affected by supercooling. The remaining points, in which supercooling might affect the composition of the liquid, are in

Data for Thermal Diagram.

No. of point.	Initial halt-point.	Super-cooling (S) or not (N).	Total compn. of material, HF, %.*	Compn. of first separating solid, HF, %.*	Remarks.
1	51.7°	slight S	—	—	Specimen prepared from dilute HF (Part I).
1A	52.5	slight S	28.1 D	—	Specimen prepared from pure, anhydrous HF.
2	30.2	slight S	31.91 D	33.4 D	? " $\text{RbF},2\cdot5\text{HF}$ " (HF, 32.4%) separating.
3	31.1	S	34.71 D	34.75 D	? Eutectic between $\text{RbF},3\text{HF}$ and " $\text{RbF},2\cdot5\text{HF}$."
4	33.8	S	34.13 C	—	—
5	40.0	N	ca. 36.0 D	35.9 D; 36.98 H	Mixture closely approximated to $\text{RbF},3\text{HF}$.
6	45.0	S	36.83 H	36.6 H	Substance practically <i>pure</i> $\text{RbF},3\text{HF}$.
6A	—	—	38.48 D	36.0 D	Not shown on thermal diagram.
7	32.0	S	38.97 B	—	This point lies near eutectic between $\text{RbF},3\text{HF}$ and $\text{RbF},3\cdot5\text{HF}$.
8	33.0	N	41.8 C?	37.86 H	The removal of some mother-liquor (HF, 43.3%) reduced the total HF content, and during this manipulation, the solid, which had the appearance of $\text{RbF},3\cdot5\text{HF}$, probably lost HF.
9	31.4	N	41.64 D	—	—
10	30.1	N	42.0 D	—	—
11	25.5	S	42.8 D	38.93 D; 41.3 H	$\text{RbF},3\cdot5\text{HF}$ separating solid; second result for crystals after standing.
12	22.5	S	43.7 D	40.33 D	$\text{RbF},3\cdot5\text{HF}$ separated in clear crystals on standing.
13	20.2	S	45.7 D	—	—
14	22.9	S	45.6 C	—	Mass became totally solid at initial halt-point.
15	20.0	S	47.66 C	40.0 D	Solid consisted of $\text{RbF},3\cdot5\text{HF}$, <i>not</i> $\text{RbF},4\cdot5\text{HF}$.

* D = Direct NH_3 titration. B = Excess NH_3 and back-titration with HCl. H = "Heating off" (gravimetric) method, C = Calculated.

good general agreement. Any considerable change in the composition of the liquids due to separation of solids might abolish an apparent maximum at 4, the curve then, however, not agreeing with 5. The minimum between $\text{RbF}, 3.5\text{HF}$ and $\text{RbF}, 4.5\text{HF}$ would also fall at a higher temperature. With regard to reproducibility, it may be mentioned that the points were determined in irregular order during 4 different series, each using newly prepared or well kept and newly analysed material. Thus, two closely situated points may be derived from quite distinct experiments.

The diagram is considered reasonably accurate and is more complete than any published hitherto on acid fluorides, on account of the extent of supporting analytical data available. It indicates maxima corresponding to the compounds which have been described and also their intervening eutectics.

Rate of Loss of Hydrogen Fluoride from the Higher Acid Fluorides.—The systems under investigation at the ordinary temperature have only low pressures of hydrogen fluoride which could best be measured by a dynamic method, *e.g.*, with absorption in standard alkali. After some preliminary experiments in this direction, it was decided that measurements of rate of loss of weight of the substance when confined in a suitable container over a known absorbent would give just as satisfactory information as to the nature of the solid phases present. The substance taken was intermediate between $\text{RbF}, 3.5\text{HF}$ and $\text{RbF}, 3\text{HF}$.

The rubidium compound was contained in an open platinum crucible which was enclosed in a copper-plated cylinder with a screw lid. This vessel contained a layer of pure dry sodium fluoride. The tightly closed vessel was stored under approximately constant temperature conditions in a desiccator over concentrated sulphuric acid. The crucible and contents were weighed at intervals during 3 months, and the sodium fluoride stirred occasionally to expose an active absorbing surface. A graph of total weight against time (in days) showed a definite change in direction at about 36.4% of hydrogen fluoride (as found by extrapolation) (Calc. for $\text{RbF}, 3\text{HF} : \text{HF}$, 36.4%), a sharp break at 27.58% (Calc. for $\text{RbF}, 2\text{HF} : \text{HF}$, 27.68%), and another at 16.53% (Calc. for $\text{RbF}, \text{HF} : \text{HF}$, 16.08%). After this, the weight remained practically unchanged, since the vapour pressure of hydrogen fluoride over RbF, HF is very low at ordinary temperatures.

The results of this experiment afford additional evidence for the existence of definite compounds of rubidium fluoride with hydrogen fluoride having different vapour pressures.

Properties and Characters of the Higher Acid Fluorides.— $\text{RbF}, 2\text{HF}$. This substance has been previously described; in the present work, however, a very good specimen of the crystalline solid has been obtained (see above).

$\text{RbF}, 3\text{HF}$. This compound separates from $\text{RbF}-\text{HF}$ mixtures in which the percentage of hydrogen fluoride lies in the region 35—*ca.* 40. Also, from mixtures containing almost the theoretical amount of hydrogen fluoride, the substance is obtained, by chilling the supercooled liquid, in the form of a crystalline solid of rather friable texture, having a low vapour pressure of hydrogen fluoride in absence of moisture. The m. p. is in the neighbourhood of 45°. The thermal diagram delimits the conditions of its existence.

The following analyses have been obtained for the substance (Calc. for $\text{RbF}, 3\text{HF} : \text{HF}$, 36.47%): (a) by excess ammonia and back titration with hydrochloric acid (see Part I), HF 36.98%; (b) by direct titration with ammonia, HF, 35.9, 36.0%; (c) by loss in weight when heated, HF, 36.6, 36.98%.

$\text{RbF}, 3.5\text{HF}$. From $\text{RbF}-\text{HF}$ mixtures containing about 45% of hydrogen fluoride, specimens of a hard crystalline solid of this composition have been obtained on several occasions. Analyses of samples obtained in various experiments were: by method (a), HF, 39.87, 39.15%; by method (b), HF, 40.0, 40.33, 38.93%; by method (c), HF, 41.32% (Calc. for $\text{RbF}, 3.5\text{HF} : \text{HF}$, 40.11%).

The substance forms hard, clear, granular crystals of definite character; the m. p. appears to be between 34° and 40°, but has not been determined exactly on account of the deliquescent nature of the substance and the small quantities available. The vapour pressure is fairly low just above the m. p., since it was found possible to maintain the substance in the liquid state for some time without great loss of hydrogen fluoride taking place.

The existence of $\text{RbF}, 3.5\text{HF}$ in equilibrium with liquids of diverse composition has been proved by points 9, 10, 11, and 12 (see figure), and this evidence, combined with that from point 7, indicates the existence of a maximum m. p. very close to the composition stated.

$\text{RbF}, 4.5\text{HF}$. Points 13, 14, and 15 distinctly suggest a compound of this composition, m. p. *ca.* 23°. However, (see p. 113) it appears to decompose when pressed, passing into $\text{RbF}, 3.5\text{HF}$. No doubt a successful isolation would require more elaborate technique.

Conclusion.—The studies detailed above have shown that, by the use of pure anhydrous hydrogen fluoride, at least two acid fluorides of rubidium containing more hydrogen fluoride than $\text{RbF}\cdot 2\text{HF}$ can be obtained. The approximate thermal diagram shows the possible existence of other acid fluorides also.

The authors are indebted to the Chemical Society for grants.

UNIVERSITY COLLEGE, NOTTINGHAM.

[Received, July 29th, 1938.]
