LXXIX.—*Fluosulphonic Acid.*

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LIQUID hydrogen fluoride, as Gore has shown, acts with great violence upon liquid sulphur trioxide; when care is taken to mix the two substances in the proper proportions, and at as low a temperature as possible, we find that the product is a mobile, colourless liquid, which comports itself like the chlorosulphonic acid discovered by Williamson, and which therefore may be conveniently termed *fluosulphonic acid.*

In order to prepare fluosulphonic acid, we made use of the platinum apparatus already employed by one of us, in conjunction with Mr. F. J. Hambly, in the preparation of the liquid hydrogen fluoride required for the experiments on the vapour density of this substance (Trans., 1889, **55**, 163). A quantity of sulphur trioxide, obtained by gently heating a mixture of sulphuric anhydride (procured from Messrs. Chapman and Messel) and phosphoric oxide, was distilled into the receiver, the weight of which was known. After again weighing, by which the amount of sulphur trioxide present was ascertained, the receiver was connected with the retort in which was heated a quantity of the double fluoride of hydrogen and potassium. The condensing tube and receiver were cooled by a mixture of ice and calcium chloride. The double fluoride was used in such quantity that the presence in the receiver of an excess of hydrogen fluoride, over and above the amount needed to form the compound $SO_2(OH)F$, could be ensured, as demonstrated by again weighing the receiver. In order to remove the uncombined hydrogen fluoride, the receiver and its contents were heated to a temperature between 25° and 35°, and a stream of dry carbon dioxide was passed through the liquid. In one of the preparations a sample weighing about 60 grams lost in weight by this treatment as follows:—After $4\frac{1}{2}$ hours, 2·1 grams; after 6 hours more, 0·85 gram; after 2 hours further treatment, 0·4 gram; and after 6 hours additional treatment, during which time the current of carbon dioxide was occasionally very rapid, 1·5 grams. A portion of this loss, especially at the later stages, is doubtless due as much to the volatilisation of the fluosulphonic acid as to the dissipation of any dissolved hydrogen fluoride. After the second period, an analysis of the liquid showed that the ratio of SO_3 to HF was 1 to 1·15. After the last period, the mean of two concordant analyses gave the ratio 1 to 1·13.

The analysis of fluosulphonic acid is attended with some little difficulty, owing to the extraordinary energy with which the substance reacts with water; the decomposition, indeed, is almost explosive in violence. The best method of operating we found to be as follows:—About 1 c.c. of the liquid was poured into a small platinum tube, which was allowed to slide into distilled water, contained in a platinum bottle of such dimensions that the water did not come in contact with the liquid so long as the bottle remained vertical. The bottle was then tightly closed by means of a caoutchouc stopper, and surrounded by ice. After some time the bottle was carefully tilted in such a manner that the liquids were caused to mix. After the violent reaction was at an end, and after standing for some time, the solution was poured into a platinum dish, and its acidity determined by titration with a standard solution of pure soda, after which the sulphuric acid was precipitated by the addition of barium chloride and hydrochloric acid. The barium sulphate after weighing was tested for any admixed fluoride; if present, its amount was determined by heating with pure sulphuric acid, igniting, and again weighing. The increase in weight was due to the conversion of BaF_2 into $BaSO_4$, so that by subtracting the weight of BaF_2 equivalent to this change from the first weight of the precipitate, the real amount of $BaSO_4$ was obtained, and hence the amount of SO_3. The total acidity of the solution was determined in terms of SO_3; the difference gave the SO_3 equivalent of the hydrofluoric acid. The amount of barium fluoride precipitated with the barium sulphate varied between 0·8 and 1·5 per cent. of the weight of the precipitate.

The results of an analysis made by this method gave—

SO_3................	1·0891 grams.
HF................	0·3053 „

Or 1 mol. SO_3 to 1·11 mols. HF.

Of a later preparation two analyses gave—

SO_3	0·8797 gram.	0·7871 gram,
HF	0·2516 „	0·2196 „

being in the proportion of 1 mol. SO_3 to 1·14 and 1·12 mols. HF respectively.

In order to determine the boiling point of the fluosulphonic acid, a small platinum retort was fitted to the condensing tube of the hydrofluoric acid apparatus. The retort was provided with a neck into which was ground a thin platinum tube closed at the bottom, to serve as a case for the thermometer. When distilling water in this apparatus, the thermometer used indicated 99·3° under a barometric pressure of 764·6 at 17°. As the true boiling point of water under these conditions is 100·2°, the correction was +0·9. About 30 grams of fluosulphonic acid was poured into the retort, and carefully heated. The temperature, as read from the thermometer, rose rapidly to 158°, and then slowly increased to 160°, at which temperature almost the whole of the liquid distilled over. The results of four different distillations corrected for scale error and emergent column gave—

(1) 163·3°; (2) 162·3°; (3) 162·0°; (4) 162·9°.

Hence the boiling point of fluosulphonic acid may be taken without sensible error as 162·6°, the mean value of the foregoing determinations.

In reality fluosulphonic acid, like chlorosulphonic acid, cannot be distilled without more or less decomposition. It then in all probability forms a greater or less quantity of sulphuryl difluoride, analogous to the sulphuryl dichloride obtained by Behrend by heating chlorosulphonic acid under pressure—

$$2SO_2{\cdot}O{\cdot}HF = SO_2F_2 + SO_4H_2.$$

The evidence for this supposition is furnished by the facts that the ratio of HF to the SO_3 in the distillate is continually increased by successive distillations, and that there is invariably a residue of sulphuric acid left in the retort at the conclusion of the operation. SO_2F_2 on decomposition by water would, of course, yield the ratio $1SO_3$ to 2HF.

Thus, after expulsion of excess of HF by dry carbon dioxide, the ratio of SO_3 to HF was 1 to 1·1; after several distillations, the ratio was 1 to 1·37. In a second series of observations, the ratio of SO_3 to HF before distillation was 1 to 1·13; after distillation it was 1 to 1·32 and 1·30 (2 analyses). The redistilled liquid was found to pass over at 163·6, which is but slightly higher than the mean of the several boiling points given above.

We have little doubt that sulphuryl difluoride might be readily obtained by Behrend's method; that is, by heating fluosulphonic acid in a sealed platinum vessel to a sufficiently high temperature.

Fluosulphonic acid is a thin, colourless liquid, which fumes in the air, and boils with slight decomposition at 162·6°. It has a faint, pungent smell, and has but little action on the dry skin; it feels greasy to the touch, and is without the intense blistering action of hydrogen fluoride. It slowly attacks glass, more rapidly in presence of moist air; it quickly acts on lead, forming lead sulphate and fluoride.

It is noteworthy that fluosulphonic acid boils at a considerably higher temperature than its analogue chlorosulphonic acid, the boiling point of which was found by one of us (Thorpe, Trans., 1880, **37**, 358) to be 155·3°. This fact is possibly connected with the relatively high boiling point of hydrogen fluoride as compared with that of hydrogen chloride.