

CXXIV.—*Hydrofluozirconic Acid and the Analysis of Zirconium Fluoride.*

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THIS investigation was undertaken with the object of verifying, or disproving, the existence of an acid fluoride of zirconium, or a hydrofluozirconic acid. Preliminary work on the ordinary hydrated fluoride led to results which do not altogether agree with those previously recorded. These previous results, so far as they are

relevant, may be summarised as follows. The evaporation of a solution of zirconium dioxide in hydrofluoric acid yields triclinic tablets, which, when dried to constant weight in air, consist of the trihydrate,  $ZrF_4 \cdot 3H_2O$  (Chauvenet, *Compt. rend.*, 1917, **164**, 727). This compound begins to be dehydrated at  $100^\circ$ ; at  $140^\circ$  it loses 2 mols. of hydrogen fluoride, giving the dihydrate  $ZrOF_2 \cdot 2H_2O$ , and above  $140^\circ$  it becomes converted into  $ZrOF_2$ . In the cold, this absorbs hydrogen fluoride, giving the monohydrate or  $ZrOF_2 \cdot 2HF$ . A solution of the latter in water slowly deposits a substance which, when dried to constant weight, has the composition  $ZrOF_2 \cdot 2H_2O$ , and at  $120^\circ$  is converted into  $ZrOF_2$ .

Our experience supplements, and leads us to criticise, these results. Evaporation of solutions containing fluorides of zirconium yields only powders of indefinite composition, unless the evaporation is carried out at the ordinary temperature and under reduced pressure. The large crystals thus obtained cannot be dried in air to constant weight without decomposition of the surface layer, since they continually give off hydrogen fluoride. They must therefore be dried quickly and kept enclosed in waxed tubes. Compounds intermediate between the trihydrate and the oxyfluoride may exist, but the isolation of these would require a careful study of the partial pressures of hydrofluoric acid and water. Compounds of constant composition are not likely to be isolated simply by drying or heating to constant weight in contact with the atmosphere. The oxyfluoride is not obtained by heating the trihydrate in air above  $140^\circ$  for any reasonable time; the weight may become constant, but is greater than is required for this compound (*vide infra*). Further, it cannot be considered that the composition of any of these compounds is established by means of the zirconia content alone. There is no evidence in the work of Chauvenet (*loc. cit.*) that any analysis has been attempted beyond the obvious and comparatively easy estimation of zirconia. We have found that none of the methods of estimating hydrogen fluoride was satisfactory in the presence of dissolved zirconium compounds. It has been necessary to devise a new method, which was first tested with potassium hydrogen fluoride and then applied to the best authenticated compound,  $ZrF_4 \cdot 3H_2O$ . This compound, crystallised under the conditions mentioned above, appears as transparent or translucent, polygonal plates, the sides of which contain characteristic angles,  $109^\circ$ ,  $113^\circ$ ,  $121^\circ$ ,  $126^\circ \pm 1^\circ$ .

*Analysis.*—The calcination of this compound to oxyfluoride, with subsequent ignition to dioxide, requires some care, since a part may sublime, if it is heated too rapidly, either as the oxyfluoride or the tetrafluoride. After being gently heated in a covered crucible,

it was converted into the sulphate and then ignited to constant weight. Freshly-prepared crystals gave, as the mean of five analyses, 36.3% Zr, the extreme values being 34.4 and 38.0%. They thus appear to be more highly hydrated than the trihydrate, which requires 41.0%, or even than the tetrahydrate, which would require 38.0% Zr. Later preparations agreed more closely with the composition of the trihydrate. The necessity for determining another constituent was evident, and an apparatus was constructed in which the hydrogen fluoride could be volatilised. This consisted of a copper tube having an internal diameter of about  $\frac{1}{2}$  inch, which was cut with a special reamer and ground to fit a conical platinum stopper. This was continued as a platinum delivery tube which dipped in standard alkali. The platinum boat containing the compound to be analysed was placed in the copper tube close to, and partly entering, the platinum stopper. A current of dry air, or, in later experiments, superheated steam, was passed through the tube. The hydrofluoric acid evolved was absorbed in the alkali without loss, as was proved by analyses of potassium hydrogen fluoride.

*Results of Analysis.*—Samples A and B were prepared at different times but had the same composition. The rest were all taken from one preparation. A was first heated in air, the rest in steam. The relatively small amount of hydrogen fluoride which can be obtained by heating in air is noteworthy. The manner in which hydrolysis proceeds during the heating was determined by weighing the residues and titrating the hydrofluoric acid at various stages. When the compound was heated in dry air it lost hydrogen fluoride, which was formed by hydrolysis with the contained water, and also some of this water. The residue, when heated in undried air, lost no appreciable weight but gave off more hydrogen fluoride. In this case, more of the fluoride must have been hydrolysed, but by external water, some of which was retained :  $\text{ZrF}_4 + \text{H}_2\text{O} = \text{Zr}(\text{OH})\text{F}_3 + \text{HF}$ .

A portion of the residue was ignited to dioxide as described above. The hydrogen fluoride driven off by this operation may be calculated on the assumption that the compound is hydrolysed (*a*) by its own water, or (*b*) by external water. These two estimates, when added to the hydrofluoric acid titrated, furnish the two values in the last line of the table. The uncertainty arises from the fact that it is not possible, by the strongest heating which the apparatus permitted (between 300° and 400°) in a current of air, to drive off all combined hydrogen and to convert all the compound into  $\text{ZrOF}_2$ . The ratio of the weight of zirconia to that of the product heated in the tube was 0.77 instead of 0.8473 =  $\text{ZrO}_2/\text{ZrOF}_2$ . When steam was used the hydrolysis was more complete. Sample C lost both hydrogen fluoride and water, the ratio of ignited zirconia to steam-

heated product being now 0.823. In the case of sample D, the ratio was 0.836. The percentages of hydrogen fluoride will accordingly be nearer to the higher value in the table. In order to obtain a direct titration of still more hydrofluoric acid, we arranged to hydrolyse at a higher temperature. A small platinum tube, closed at one end by a cap of platinum foil, was placed inside the platinum delivery tube, which was heated to bright redness in a current of superheated steam. Samples B and F were analysed by this method. Sample B yielded 34.0% of hydrogen fluoride when heated in steam below a red heat and a further 3.48% when heated to a bright red heat. The weight of the residue showed that it had been almost completely hydrolysed to oxide. In calculating the results, the quantities of zirconia and hydrogen fluoride were added together, and the water was obtained by difference.

	A.	B.	C.	D.	E.	F.
% ZrO <sub>2</sub> .....	58.8	57.6	53.9	54.0	(54)	(54)
% HF (titrated) .....	8.2	37.5	19.8	22.3	31.2	31.1
% HF total	25.7-	—	30.5-	32.9-	—	—
(estimated) .....	37.8	37.5	39	41.5	—	—

The weighted mean of the zirconia in A and B is 58.5, the hydrogen fluoride is 37.5, the water 4.0; the composition therefore corresponds to  $\text{ZrF}_4 \cdot 2.45\text{H}_2\text{O}$ . The preparation containing 54% of zirconia contains at least 31% of hydrogen fluoride in C and more than 33% in D. We estimate it at 35%, for the reason mentioned on previous page. The water will therefore be 11.0, corresponding to  $\text{ZrF}_4 \cdot 3.4\text{H}_2\text{O}$ . Thus the crystals do contain the tetrafluoride, but the water of crystallisation is proved to be variable.

*The Acid Fluoride.*—Numerous double fluorides have been prepared such as  $2\text{NH}_4\text{F}, \text{ZrF}_4$ ;  $3\text{NH}_4\text{F}, \text{ZrF}_4$ ;  $\text{KF}, \text{ZrF}_4, \text{H}_2\text{O}$ ;  $2\text{KF}, \text{ZrF}_4$  (Marignac, *Ann. Chim. Phys.*, 1860, **60**, 271); also  $2\text{NaF}, \text{ZrF}_4$  (Wells and Foote, *Amer. J. Sci.*, 1866, **3**, 466). The salt  $2\text{KF}, \text{ZrF}_4$  is one of the easiest to prepare, yet even in this case a slight excess of potassium fluoride produces  $3\text{KF}, \text{ZrF}_4$ . The free acid might correspond to any of these salts. An acid salt is said to be deposited on rubbing the walls of a vessel containing a solution of zirconia in hydrofluoric acid (Fischer and Thiele, *Z. anorg. Chem.*, 1910, **67**, 309). This dissolved readily in water, but with difficulty in concentrated hydrofluoric acid. When treated with lead carbonate, it gave a soluble lead salt which was believed to be  $\text{PbZrF}_6$ . Some soluble lead salt is certainly formed when lead carbonate is added to any solution containing zirconium fluoride, for, after removal of the lead fluoride by filtration, more lead may be precipitated from the filtrate by means of hydrogen sulphide, and the second filtrate contains both zirconium and fluorine.

A hydrofluozirconic acid is also said to be produced when hydrogen fluoride is absorbed by zirconium tetrafluoride (Chauvenet, *loc. cit.*). The isolation of an acid by either of these methods would appear to be difficult. We consider that the only method which offers any reasonable chance of success is to add much anhydrous hydrogen fluoride to a little zirconium fluoride which is already in solution.

*Preparation.*—The anhydrous acid, prepared by distilling dry sodium hydrogen fluoride in a copper still, was condensed in a platinum bottle or crucible which fitted into a copper receiver. After addition of this to the solution of zirconium fluoride or *vice versa*, a fine, white crystalline solid was usually deposited. This was cooled in a freezing mixture and well stirred. The liquid was then decanted, and the solid washed several times by decantation with dry ether and pressed on filter-paper. This substance has been prepared on five occasions. The appearance of the crystals was always the same, but very different from that of the ordinary fluoride. Under the microscope, they were seen to be of uniform type—long prisms with chisel-shaped ends. On exposure they gave off hydrogen fluoride and became dull on the surface. In a few days the whole crystal became opaque. When they were dissolved in a very little water (in which they are extremely soluble) and treated with a few drops of lead acetate, the liquid remained clear. A drop of hydrofluoric acid produced an immediate turbidity. The hydrofluozirconic acid was therefore not much hydrolysed.

*Analysis of the Acid Fluoride.*—One of the earlier samples, weighed rapidly in a closed platinum crucible with a tightly fitting lid and then converted into zirconia, contained 46.0%  $ZrO_2$ . In the case of the last sample, we were able to determine the hydrogen fluoride separately as described above, and to follow the course of the decomposition: (1) 0.4603 g. was heated in a current of dry air. The loss was 0.1359 g., of which 0.0772 g. was hydrogen fluoride. (2) The residue, 0.3244 g., was heated in steam. The loss was 0.0379 g., and the hydrogen fluoride 0.03619 g. This is the stage in which the hydrolysis proceeds at the expense of water of crystallisation. (3) A portion, 0.0863 g., of the last residue, when heated in steam to a bright red heat, lost 0.0196 g. The hydrogen fluoride was 0.01962 g. (4) Another portion, 0.0911 g., ignited with sulphuric acid, gave 0.0682 g. of dioxide. All quantities being referred to the original weight, the hydrogen fluoride lost in (3) is 0.0658 g., whilst the total loss in (4) is 0.0720 g. Since steaming at a red heat causes conversion nearly into  $ZrO_2$  with a little  $ZrOF_2$ , the final loss,  $0.0720 - 0.0658 = 0.0062$  g., represents hydrogen fluoride produced by the reaction  $ZrOF_2 + H_2O = ZrO_2 + 2HF$ , the water being derived from external sources such as the sulphuric acid. This loss must corre-

spond to a weight of hydrogen fluoride =  $40 \times 0.0062/22 = 0.0113$  g. The weight of zirconia calculated on the original weight of compound is 0.215 g., or 46.59%. On heating in dry air, 1 mol. of the compound loses rather more than 2 mols. of hydrogen fluoride and rather less than 2 mols. of water. On heating in steam, it loses rather more than 1 mol. of hydrogen fluoride, and, at a bright red heat, rather less than 2 mols. of the acid.

*Composition of the Acid.*—0.4603 G. gave 0.1792 g. HF (titrated) and 0.0113 g. (deduced from final loss of weight), total 0.1905 g.; and 0.0548 g. of H<sub>2</sub>O (by difference). The simplest formula calculated from these results is ZrF<sub>4</sub>.1.5HF, 3.74H<sub>2</sub>O, or ZrOF<sub>2</sub>.3.5HF, 2.74 H<sub>2</sub>O. On account of the difficulty in avoiding loss of hydrogen fluoride during the weighing, etc., and of the hygroscopic character of the compound, we consider that, as originally precipitated, it would probably contain the extra 0.5 mol. of hydrogen fluoride and 0.75 mol. less water, and that it would be hydrofluozirconic acid corresponding to the best known potassium salt, with the addition of about 3 mols. of water of crystallisation, *i.e.*, H<sub>2</sub>ZrF<sub>6</sub>.3H<sub>2</sub>O.

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