XXVII.—*Action of Hydrogen Fluoride on Compounds of Selenium and Tellurium. Part I. Selenium Dioxide.*

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THE action of hydrofluoric acid on selenious compounds does not appear to have been studied, except perhaps with negative results, no doubt on account of the unstable and corrosive nature of the reagents and of such compounds as they might be expected to form. Hydrofluoric acid probably does not form a definite product as it does with tellurium dioxide. A solid oxyfluoride of selenium was prepared by Moissan (" Le Fluor," p. 123) by the action of fluorine on selenium, but was not analysed. In the present research anhydrous hydrogen fluoride was used.

A remark of Ditte (*Compt. rend.*, 1876, **83**, 225) bears on the present research, *viz.*, that hydrofluoric acid is energetically absorbed by selenium dioxide; the product, however, was not examined.

Preparation of the Selenium Dioxide.—The method used was substantially that of Divers and Haga (J., 1899, **75**, 537). The selenium was dissolved in concentrated nitric acid and after several evaporations to dryness with water the product was transferred hot to a long glass tube and sublimed in a current of oxygen dried by calcium chloride and phosphoric oxide. The product was white or pink and we consider that it was dry; the test for dryness described by Prideaux and Green (*J. Physical Chem.*, 1924, **28**, 1274) was applied. The oxide, dissolved in dry alcohol, did not immediately redden litmus paper. Also a sample, heated with anhydrous copper sulphate, gave no blue colour.

Preparation of Hydrogen Fluoride—Commercial sodium hydrogen fluoride of high quality and practically dry was finely ground and strongly heated before each distillation. This was carried out in a copper apparatus. The still, still-head, and receiver were made by Mr. E. R. Walter, B.Sc.Eng., whose skill and advice have been much appreciated. The still-head was fitted with an additional tube through which a current of dry air could be blown. The straight condenser cooled by ice-water was succeeded by a spiral condenser cooled by ice and salt. After the first runnings the liquid hydrofluoric acid was colourless and immediately gelatinised filter-paper. The receiver was then screwed on. It contained a platinum crucible, in which the acid collected, and was cooled by ice or a freezing mixture. The vapour passing on was dry, as the condensed acid would retain any traces of water. It passed over the selenium dioxide, which was usually contained in a platinum bottle supplied with platinum inlet and outlet tubes. The vapour then passed through a bubble-counter containing dry chloroform, and finally through a soda-lime tube.

The hydrogen fluoride was rapidly absorbed by the selenium dioxide, which liquefied and became warm. The liquid first formed was not analysed, but it contained quite a small proportion of hydrogen fluoride, the selenium dioxide being very soluble. As the hydrogen fluoride bubbled into the liquid it was continually absorbed. The experiment was stopped usually when the liquid contained 40 to 50% of hydrogen fluoride. This does not represent the limit of absorption from the acid vapour at a pressure somewhat below one atmosphere. In one experiment, a boat gained weight until the hydrogen fluoride was 75% of the total weight.

Properties of the Product.—The liquids formed were colourless and mobile. They fumed strongly and at the ordinary temperature the fumes consisted of hydrogen fluoride only. No volatile selenium compound was trapped in the chloroform (or alcohol) bubble-counter. The liquid does not mix with chloroform, but forms a layer below it. It rapidly attacks copper, forming a dark substance. In absence of water it slowly attacks glass. When allowed to evaporate in a desiccator with reagents which absorb water and hydrogen fluoride, it slowly dries up to a syrup. If water is present, as it was in some of our earlier experiments, crystals of selenious acid are formed, retaining less than ½% of hydrogen fluoride.

Distillation.—The product was distilled from the platinum bottle and condensed in a long platinum tube cooled with ice-water. Distillation began at about 65°, continued freely to about 85°, then fell off; little was obtained above 100° until much higher temperatures were reached. The distillate contained more selenium dioxide than can be accounted for by its vapour pressure, which is 12·5 mm. at 70° and 40·6 mm. at 199° (Jannek and Meyer, *Z. anorg. Chem.*, 1913, **83**, 60). An analysis of the distillate is given in the first line of the table. The residue in the flask was analysed by the volumetric method. The distillate was treated with dry ether, which gave an immediate white precipitate. After washing with more ether, this contained 96 mol.% of selenium dioxide and 4 of hydrogen fluoride. In another experiment the residual liquid, from which much solid had been frozen, was distilled with sulphuric acid (the monohydrate). A yellow, fuming liquid came over at 120° to 130°. This reacted violently with water, giving a solution which contained both selenious and hydrofluoric acids, but no sulphuric acid.

The residue in the bottle after distillation (without sulphuric acid) contained slightly more than 5 mols. of hydrogen fluoride to 1 of selenium dioxide. This is the composition at which the vapour pressure of the hydrogen fluoride sinks to low values. At higher temperatures, the liquid would probably distil as a whole, with dissociation.

Separation of Solid.—Preliminary experiments showed that when the liquid was strongly cooled by alcohol–solid carbon dioxide, a white solid separated which had a composition similar to that of the liquid left after the distillation of the more volatile part. The cooling curves of this system were determined in various forms of apparatus. The arrests were variable and not well marked. This was probably due, partly to the nature of the liquid, which can be greatly supercooled, and partly to the difficulty of securing good heat transference and suitable thermal capacity in apparatus which contained so corrosive a liquid.

The freezing points were therefore determined by observation of the contents of the platinum bottle or crucible in which was placed the thermometer in a protecting tube. A portion of solution B, containing about 4·5 mols. of hydrogen fluoride to 1 of selenium dioxide, was poured into a crucible, which was cooled by direct immersion in alcohol–carbon dioxide at —70°. When crystallisation had once started, it proceeded very rapidly. The solid was allowed to melt slowly in a second crucible cooled externally. The temperature was constant at —17·5°, when about one-third was solid, and fell slowly to — 18°, when about three-quarters was solid.

Methods of Analysis.—From what is known of the strengths of hydrofluoric and selenious acids it should be possible by a volumetric method to determine approximately the amounts of each in a mixture; the greater part of the hydrofluoric acid being titrated with the first hydrion of the selenious acid with *p*-nitrophenol as indicator, and the second with an indicator of alkaline end-point. According to the results of Willcox and Prideaux (J., 1925, **127**, 1543) the end-point in a titration of 0·05 *N*-selenious acid is at $p_{\mathrm{H}} = 10{\cdot}35$; the corresponding value from Blanc's second constant is 9·70 (*loc. cit.*). Our solutions were about normal, and from the equation $2p_{\mathrm{H}} = p_k + p_{kw} + \log c$, putting $\log c = 0$ and using our second constant $k_2 = [\mathrm{H}^{\cdot}][\mathrm{SeO_3}'']/[\mathrm{HSeO_3}'] = 0{\cdot}87 \times 10^{-8}$, the end-point will be at $p_k = 11{\cdot}0$. The most suitable indicator available was thymolphthalein, the transition interval of which is 9·3 to 10·5. Titrations to a full blue should still be slightly below the correct end-point of the dibasic acid. This was confirmed with 10 c.c. of solutions of selenious acid.

1st end-point × 2	11·7	11·6	10·8
2nd end-point	11·6	11·5	10·65

Hydrofluoric acid is usually titrated with phenolphthalein on account of the lower degree of the second dissociation of H_2F_2. Titrations first with *p*-nitrophenol and then with phenolphthalein showed that most of the acid was neutralised at the change-point of the former indicator, the factor for converting the former into the latter titres being (on the average of several results) 1·03. The effect of the short titration with thymolphthalein on the total acid titre is negligible, and it is completely overcome by the more important error in the *p*-nitrophenol end-point of the mixed acids, which makes the volumetric estimation of selenious acid too high. The necessary corrections were determined by the following titrations of known mixtures.

	Acids separately.		Acids together.	
C.c. of alkali with *p*-nitrophenol	(*a*) 13·04	(*b*) 13·98	(*a*) 12·90	(*b*) 13·80
,, ,, thymolphthalein	(*a*) 18·45	(*b*) 19·39	(*a*) 18·40	(*b*) 19·30

Thus the result of the *p*-nitrophenol titration must be multiplied by a factor, 1·01, to give the sum of the titrations of the acids separately, *i.e.*, of the hydrofluoric acid and the first hydrion of the selenious acid. This corrected titration subtracted from the total titration (with thymolphthalein) gives the amount of selenious acid. This difference, subtracted from the corrected titration with *p*-nitrophenol, gives the amount of hydrofluoric acid estimated by this indicator; and the latter, multiplied by 1·03, gives the amount of hydrofluoric acid estimated by phenolphthalein. The corrected ratios of hydrogen fluoride to selenious acid so obtained are lower than those determined gravimetrically. We have not been able to determine the reason of this discrepancy. It is possible that the hydrolysis is not quite complete, and that there is some complex formation even in aqueous solutions which diminishes the " strong acid " titration.

Selenium was determined gravimetrically by the usual method, *i.e.*, by precipitation with sulphur dioxide from rather concentrated hydrochloric acid. In the later experiments the modification of Lenher and Kao (*J. Amer. Chem. Soc.*, 1925, **47**, 772) was employed. The selenium was precipitated from dilute hydrochloric acid, filtered off as red selenium in the cold, washed successively with concentrated hydrochloric acid, water, alcohol, and ether, dried at 30—40°, then to constant weight at 120—130°. Under these conditions, no water or salts are included in the precipitate.

Analysis.—Attempts were made to determine the fluorine also as calcium fluoride in the presence of calcium selenite. These gave rather variable results which were low in fluorine compared with those of the two methods on which we placed most reliance. Some of the results are given in brackets under the gravimetric results in column 6 of the table, which are based on the weight of solid taken and the gravimetric selenium. Column 7 is obtained by subtracting the equivalents of selenium (gravimetric) from the total equivalents of the two acids given by the thymolphthalein titrations. The difference gives the weight of hydrogen fluoride. The sum of the selenium dioxide and the hydrogen fluoride should be equal to the weight of the solid taken. Results in which there was not a fair agreement have not been included.

Preparation *A* consisted of 19·43 g. of liquid which contained 69·3% HF. The molar ratio by increase of weight was 12·5 : 1. This was used to determine cooling curves. The first marked arrest on the cooling curve was at − 54°, the last on the heating curve, at − 29°. The liquid was then distilled up to + 85°. The analysis of the distillate is given in the table. The residue, by titration only, contained hydrogen fluoride and selenium dioxide in the ratio 4·9. Two samples of solid separated from the mother-liquor and titrated without weighing gave ratios of 4·9 and 4·93.

Preparation *B* weighed 21·91 g. and the molar ratio by increase of weight was 4·425. The initial arrest on the cooling curve was at − 22·5°. The solid B_1 was frozen out and analysed. The residue in the bottle, which had now been reduced to 14·8 g., was poured into a crucible and the freezing point determined as described above. The remaining samples of *B* were then taken and analysed.

The filtration of B_1 was done in the usual way, except that the crucible was surrounded by a glass tube, containing lumps of solid carbon dioxide and closed at the top by a stopper in which was a calcium chloride tube to dry the incoming air. The platinum Gooch crucible contained dried asbestos fibre, above which was a false bottom of platinum foil perforated with needle holes. The liquid which had run through the asbestos was rejected. The solid was removed quickly and weighed in a closed crucible. Sample

B_2 was pressed on the Gooch crucible with the false bottom but without the asbestos. It was kept cold inside another crucible in the freezing mixture. Sample B_3 was washed with dry cold chloroform by decantation and dried with filter-paper until strong fuming began. Preparation C, 17·54 g., had a molar ratio of 4·62 to 1. The fractions C_1 and C_2 were obtained by partial freezing and decantation of the liquid part; the solid was then broken up, stirred, and dried with filter-paper. C_3 was collected from the hard solid which first formed round the edge at the top.

The use of the analytical results in making the table is exemplified for sample C_1. 1·756 Grams of solid give 0·651 g. or 0·00822 gram-atom of selenium, which is equivalent to 0·915 gram of the dioxide. The difference in weight between the original substance and the dioxide, *i.e.*, 1·756—0·915, is taken as the quantity of hydrogen fluoride (gravimetric) and is 0·04205 mol. The molar ratio of hydrogen fluoride (gravimetric by difference) to selenium dioxide (gravimetric) is therefore 0·04205/0·00822 = 5·1. 1·756 Grams of solid require 58·58 c.c. of 0·988 N-alkali, with thymolphthalein as indicator. By subtracting from the total milliequivalents of acid, *i.e.*, 57·66, the equivalents of selenious acid, *i.e.*, 0·01645, the equivalent of hydrogen fluoride is found to be 0·0412. The ratio hydrogen fluoride (volumetric by difference) to selenium dioxide (gravimetric) is 5·0.

The weight of hydrogen fluoride so found (volumetric by difference), *i.e.*, 0·824 g., when added to the selenium dioxide, 0·918 g., gives the weight of product calculated from the volumetric total acid and gravimetric selenium; *i.e.*, 1·739. These are the values in brackets in column 2.

Description of preparation and sample.	Wt. taken. Wt. calc. from analysis in brackets.	Ratio nHF/SeO$_2$ from gravimetric selenium and total wt. of sample.	Ratio nHF/SeO$_2$ from gravimetric selenium and total acid found.
Distillate at 85° and over (p. 168).	0·5435 (0·507)	14·65	12·85
B_1. Solid sucked dry on cooled Gooch.	0·5405 (0·5124)	4·5	4·5
B_2. Solid dried by pressing on Gooch.	3·56 (3·47)	4·93	4·94
B_3. Solid washed with cold chloroform.	1·236 (1·170)	5·3	4·8
C_1. Solid, first fraction dried with filter-paper.	1·756 (1·739)	5·15	5·0
C_2. Solid, second fraction.	0·984 (0·998)	4·55	4·45
C_3. Solid first formed on surface.	0·6695 (0·664)	—	(4·9) Corrected volumetric as on p. 170.
C_4. Liquid, mother-liquor of C_1 and C_2.	2·770 2·83	4·14	4·34

Summary and Conclusions.

The analyses show that the solid frozen out of our liquid product contains constantly about 5 mols. of hydrogen fluoride to 1 mol. of selenium dioxide. The fluctuations are, we consider, due to inclusion of mother-liquor, to the loss of variable quantities of hydrogen fluoride, and to other difficulties inherent in the analysis of so corrosive a substance. This additive compound, $SeO_2,5HF$, is in equilibrium with liquids of various compositions. It dissociates in the vapour phase, giving off small quantities of hydrogen fluoride, the vapour pressure of which is only a small fraction of that of the pure acid. At higher vapour pressures the dissociation of the vapour which contains selenium dioxide is not complete. Thus the same compound is obtained either by distillation of the excess of hydrogen fluoride or by freezing from liquids of different compositions.

The above is one of the few examples of complex formation between hydrogen fluoride and an acid anhydride. Analogous compounds with tellurous anhydride have been prepared by Metzner (*Ann. Chim. Phys.*, 1898, **15**). These were prepared from aqueous hydrogen fluoride. One of them was much hydrated; $2TeF_4,3TeO_2,6H_2O$. The other, given as $TeF_4,TeO_2,2H_2O$, might of course be written as $2TeO_2,4HF$. We have prepared a compound somewhat similar to this from anhydrous hydrogen fluoride which we hope to describe in a later communication. The probabilities of the two formulæ are evenly balanced in the case of tellurium, but in the case of selenium we consider the latter, or additive compound, formula far more probable. The fluoride of so strongly electronegative an element is probably not formed under conditions which involve elimination of water, or at any rate, if there is some anhydrous fluoride in the presence of a large excess of hydrogen fluoride, it would be very difficult to prove its presence and isolate it. Up to the present, no fluorides or oxyfluorides of quadrivalent selenium have been described, with the important exception of the compound, afterwards claimed to be the hexafluoride, described by Lebeau (*Compt. rend.*, 1906, **144**, 1042). His first preparation, the analysis of which corresponded to SeF_4, had the properties to be expected and also resembled our present compound. It was a colourless liquid, boiling at about + 100°, and solidifying at − 80°. It decomposed water, giving hydrofluoric and selenious acids in the molar ratio 4 : 1.

A comparison between the actions of hydrogen fluoride and hydrogen chloride on selenium dioxide is instructive. Hydrogen chloride also gives in the first place an additive compound, which, however, easily loses water, giving the oxychloride $SeOCl_2$ (Lenher, *J. Amer. Chem. Soc.*, 1920, **42**, 2498). Loss of water from our compound did not take place under the conditions tried and is unlikely in the case of the compound obtained from hydrogen fluoride on account of the order of the affinities of fluorine and oxygen for hydrogen.

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