CI.—*Selenium Oxyfluoride.*

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By the action of fluorine on selenium, Moissan (" Le Fluor," p. 123) obtained white fumes and a white solid, which were not further examined. If the fluorine contained electrolytic oxygen (as is often the case) or was mixed with air, it is possible that the fumes contained an oxyfluoride, and the residue would then have consisted of selenium dioxide, or selenious acid containing a little hydrofluoric acid. Lebeau (*Compt. rend.*, 1907, **145**, 190) reported a gaseous fluoride of selenium which he considered to be the hexafluoride previously discovered by one of us (J., 1906, **89**, 316), but since this contained about 2% of selenium in excess of the theoretical proportion, the presence of an oxyfluoride was suspected. In our opinion this is improbable because the gas had been kept in a gas-holder over mercury, which would have decomposed an oxyfluoride. Lebeau also stated that separation of oxyfluoride from hexafluoride by fractional distillation would have been difficult, but we now know that there is a sufficient difference between the boiling points, for the hexafluoride sublimes at — 39°.

No definite oxyfluoride of selenium had therefore been described until our preliminary experiments (J., 1927, 928) showed that it was probably produced by the interaction of selenium oxychloride and silver fluoride. These results are now confirmed and amplified.

EXPERIMENTAL.

Conditions of the Reaction.—The selenium oxychloride, supplied by the British Drug Houses, did not require redistillation. The silver fluoride was prepared by the method of Ruff (" Das Fluor "), or by evaporating a solution of the acid fluoride and drying the product in a heated desiccator; the latter material was reactive, but still contained a little acid, probably as silver hydrogen fluoride, since the acid came over first in the subsequent distillation.

When the vapour of selenium oxychloride was passed over heated silver fluoride contained in a platinum boat, the fluoride was quickly converted into chloride, a white sublimate of selenium dioxide was observed, and the glass was strongly etched. Reaction occurred in dry carbon tetrachloride with similar results. Experiments were then carried out in a platinum bottle with platinum condenser tube, but little if any gas was produced. When the bottle was heated to about 140° on a sand-bath, the reaction suddenly began with the production of copious fumes; these condensed in the platinum tube to a colourless liquid, the analysis of which proved that it was selenium oxyfluoride, $SeOF_2$. The yield was low because some vapour escaped owing to the rapidity of the reaction, and some remained in the bottle at the end of the distillation. Even with excess of silver fluoride, the reaction was sometimes incomplete because the grains of fluoride were coated with silver chloride, as proved by the fact that, although the aqueous extract of the residue contained no soluble silver, some was found in the filtrate obtained when the residue was dissolved in ammonia and reprecipitated with nitric acid.

Preparation.—Selenium oxychloride (9—10 g.) and about 3 times its weight of silver fluoride were thoroughly mixed with a platinum stirrer, and heated until the commencement of the violent reaction, which was moderated as required by cooling the bottle. Alternatively, the silver fluoride was added in two or three portions to the oxychloride, the mixture being well stirred and heating being continued until a portion showed no ionic chlorine after reaction with water. The whole was then distilled between 140° and 200° and the distillate was collected in a platinum crucible with a tight lid; the analyses of successive portions have already been given (*loc. cit.*), and the properties were constant. After removal of the residue from the platinum bottle, this was used for storage, being tightly closed and kept in a desiccator with calcium chloride.

In later experiments, the compounds were mixed in a large platinum crucible which was contained in a monel-metal pot of $1\frac{3}{4}$ inches internal diameter. (This was made to our specification by Mr. E. R. Walter, B.Sc., to whose skill we are also indebted for the other pieces of apparatus made of monel metal.) The screw cover of the pot was provided with an inlet tube through which a current of dry air was passed at the end of the distillation. The products of several experiments were then collected in the platinum bottle, and a sufficient quantity was thus obtained for the determination of the melting point.

Analysis.—The previous methods of analysing mixtures of hydrofluoric and selenious acids (J., 1926, 167) have now been further improved and tested on mixtures of known composition. The procedure is briefly as follows: The solution of the two acids was titrated with $N/10$-alkali (free from carbonate) to the end-point shown by *p*-nitrophenol, which falls somewhat short of the point corresponding to sodium fluoride and sodium hydrogen selenite.

[The factor for this correction of the observed titre (V c.c.) was 1·03 in the particular mixture under investigation, *i.e.*, $2HF + H_2SeO_3$.] Rather more than $2/3V$ c.c. of $N/10$-silver nitrate were added, and the precipitation of silver selenite was completed by the addition of further alkali until the yellow colour of the indicator reappeared. The precipitate was then collected in a waxed funnel, and the titration completed on the filtrate and washings in the presence of phenolphthalein. The total alkali used gave correctly the sum of the acids. The silver selenite, preferably precipitated from a separate portion, was washed, finally with alcohol, and dried at 110—120°. The selenium so found agreed with that determined as element.

A mixture corresponding to $SeO_2 + 2HF$ was made by distilling 4 mols. of the anhydrous acid on to a weighed quantity of the dioxide and adding the necessary additional amount of dioxide. The analyses of the mixture and of the compound followed the same course. The sample was weighed quickly in a platinum crucible with a tightly fitting lid; this was then immersed in water contained in a large platinum basin, and rolled about so as to admit the water so slowly that no fumes escaped at any stage. As an example of the results obtained, we quote the analysis of a sample taken from the preparation which was used in the determination of the melting point: 0·9132 g. was dissolved to give 97·88 g. of solution in a ceresined flask; 44·25 g. of this solution gave 0·2440 g. of selenium (as element) and hence the selenium content of the sample was 59·1%. 12·23 G. of the solution required altogether 40·0 c.c. of $N/10$-alkali (*i.e.*, before and after precipitation of silver selenite); of this, the selenious acid required 19·8 c.c., as calculated from a gravimetric determination, and therefore the hydrofluoric acid required 20·2 c.c., corresponding to 28·9% of fluorine in the sample (Calc. for $SeOF_2$: Se, 59·5; F, 28·5%).

Physical Properties.—On account of the corrosive action of this compound, especially upon glass, it has only been possible to determine the density, the boiling point, and the melting point. The preparations used in these determinations all gave satisfactory analyses by the above methods.

Density. A thick-walled tube, made by drilling out a rod of monel metal, was fitted with two lids which could be screwed down against a flange inside and also against a lead washer, which was held between the lid and the top of the tube. Two similar tubes of this pattern were used, one as a density bottle, the other as a boiling-point and reaction bottle. The lid of the density bottle was centrally bored with a hole 1/32 inch in diameter and was prolonged into a plunger below the screw thread. The bottle was calibrated with water in the usual way. Its capacity was about 0·5 c.c. Found: d = 2·70, 2·64, 2·66; mean 2·67.

Boiling point. This was determined by the method of Smith and Menzies (*Z. physikal. Chem.*, 1911, **75**, 494). The monel-metal bottle was closed by a lid carrying a piece of tubing of $\frac{1}{8}$ inch internal diameter, which was bent through 180°. The end (below the bottom of the boiling-point bottle) was drilled to 3/16 inch diameter. Into this end was fitted a short length of platinum tube, the other end of which was sealed into a capillary glass tube, in which could be observed the fluctuations of the vapour pressure. The bottle was about three-quarters filled with the selenium oxyfluoride, attached to a thermometer, and heated in a bath of bromonaphthalene or medicinal petroleum. The temperature at which a steady stream of bubbles first appeared was about 100°, but this did not correspond to the true boiling point, since the temperature of the bath rose much higher, and liquid was still found on opening the bottle. A number of readings were made of the temperature at which the liquid sucked back; this point was determined about a dozen times as 121—129°, with 5 readings at 124°.

Melting point. In anticipation of a low value, a pentane thermometer was used, which had also been found accurate at the ordinary temperature. In the first two determinations, which gave rather higher values than that stated below, the bulb of the thermometer was protected by a thin glass tube coated with sulphur. The lag, however, was too great to allow of trustworthy readings, especially with the small quantity of liquid then available The bulb was therefore sheathed in platinum foil, wound tightly round, and pressed together at the bottom. The liquid was poured into the smallest platinum vessel, which was placed in the bottom of a thinly vaselined glass tube, tightly closed by a rubber bung bearing the thermometer and a drying tube. The liquid was solidified, not too quickly, by immersion of the outer tube in a mixture of alcohol and carbon dioxide snow, being thus obtained as a clear, dark mass, like ice. This was allowed to melt slowly by placing the tube inside a vacuum cylinder. A heating curve was taken from the time when liquid was first observed; in the presence of solid and liquid, the temperature fluctuated irregularly between 4·5° and 4·7° for 10 minutes, and then rose slowly; hence melting point = 4·6°.

Chemical Reactions.—Glass is rapidly attacked by the liquid or vapour with the formation of a white deposit, consisting principally of selenium dioxide. Silica, as a dry powder, reacts violently with the liquid. An attempt to analyse the compound by means of this reaction showed that the evolution of silicon tetrafluoride is nearly quantitative: $2SeOF_2 + SiO_2 = 2SeO_2 + SiF_4$.

Crystalline silicon is slightly attacked in the cold, readily on warming. The fine powder was added to some of the compound in the boiling-point bottle, which was connected with a nitrometer containing dry mercury. On heating, gas was evolved, some of which was absorbed by water and shown to be silicon tetrafluoride. The residual silicon was coated with red selenium, and also contained selenium dioxide; the amounts of these were 0·078 and 0·166 g., respectively, the theoretical amounts from the 0·400 g. of selenium oxyfluoride taken being 0·119 and 0·167 g. respectively, in accordance with the equation $Si + 2SeOF_2 = SiF_4 + SeO_2 + Se$.

Red phosphorus, which had been extracted with alkali and thoroughly dried, ignited in a few seconds when mixed with the compound. The oxyfluoride was placed in the monel bottle, the bent tube of which was filled with the phosphorus, and connected with a nitrometer containing dry mercury. When the bottle was warmed, the vapour reacted very suddenly, filling the nitrometer with gas and with red fumes of selenium and phosphorus. The gas was very quickly absorbed by dilute alkali, and the resulting solution, after filtration, was shown to contain combined phosphorus; the gas was therefore probably phosphoryl fluoride and not phosphorus trifluoride, for the latter is very slowly absorbed by alkali and not by water. The reaction probably occurs mainly according to the first of the equations given below.

Sulphur (octahedral) as a powder is not attacked in the cold, but on warming, a gas is evolved, and red selenium is deposited.

Alcohol mixes readily with the compound, as it does with both the dioxide and hydrogen fluoride. Carbon tetrachloride forms two layers.

The Solution $SeO_2 + 2HF$.

It has already been shown that under ordinary conditions selenium dioxide does not combine with hydrogen fluoride with the elimination of water (J., 1926, 168). Solutions of the dioxide in hydrogen fluoride resemble in many respects the compound described above, and it was therefore deemed of interest to determine the constants and behaviour of the mixture in the above ratio. The preparation and analysis of this mixture have been described above.

The reaction with phosphorus was even more violent than in the case of the oxyfluoride, and seemed to increase with the concentration of the selenium dioxide, for the mixture $SeO_2 + 4HF$ showed scarcely any action until the excess of acid had evaporated. The reaction was investigated quantitatively in the boiling-point bottle. The gas was first treated with water, which slowly absorbed 4·9 c.c. (POF_3), and then with alkali, which slowly absorbed 6·6 c.c. (PF_3). The reaction therefore probably takes place in two ways:

$$6(SeO_2 + 2HF) + 4P = 4POF_3 + 5Se + H_2SeO_3 + 5H_2O$$
$$6(SeO_2 + 2HF) + 4P = 4PF_3 + 3Se + 3H_2SeO_3 + 3H_2O.$$

Silicon was attacked with steady evolution of gas. Sulphur was hardly affected in the cold, but on heating, a deposit of red selenium was formed, sometimes with inflammation. Monel metal was slightly attacked after a time, with the production of a red solution which probably contained colloidal selenium.

Changes in Volume during Solution and Hydrolysis.—The determination of the densities of this solution and of the compound (see table) furnishes an unusually favourable set of data for the comparison of changes of volume which occur during the course of a complete dissolution and a complete hydrolysis yielding the same product, under isothermal and isobaric conditions. Halides of the non-metals, other than fluorides, on hydrolysis yield gases which can only be kept in the system under high pressures, *e.g.*, phosphorus oxychloride gives off hydrogen chloride, and the mode of combination of the elements in the products of hydrolysis is extremely doubtful. Fluorides of many non-metals are themselves gaseous and cannot be compared under isobaric conditions with the products of hydrolysis. In the present case, however, solids and liquids react to form a solution which almost certainly should be written as $SeO_2 + 2HF$, since it is extremely improbable that hydrogen is removed from direct combination with fluorine. The partial formation of a complex, such as hydrofluoselenious acid, $H_2SeO_2F_2$, is not likely to involve a considerable change of volume. We can compare the volume changes of reactions (1) and (2) by using the densities given in the table, together with those of selenium dioxide (3·954) and hydrogen fluoride (0·988).

$$SeO_2 + H_2F_2 \longrightarrow (SeO_2 + 2HF) \quad . \quad . \quad . \quad (1)$$
$$\text{Molecular volumes } 27{\cdot}55 + 40{\cdot}50\ (= 68{\cdot}05) \longrightarrow 58{\cdot}5$$

$$SeOF_2 + H_2O \longrightarrow (SeO_2 + 2HF) \quad . \quad . \quad . \quad (2)$$
$$\text{Molecular volumes } 49{\cdot}2 + 18{\cdot}0\ (= 67{\cdot}2) \longrightarrow 58{\cdot}5$$

Both of these reactions proceed with considerable evolution of heat from left to right. The contractions, 9·55 and 8·70, are very similar, and if the volume of the SeO, which is common to all the systems, is constant, then the molar volume of H_2O is scarcely altered when its elements are divided between SeO and F_2.

Comparison of Properties.

	$SeOF_2$.	$SeO_2 + 2HF$.
Density.	2·67	$2{\cdot}57_5$
Molar volume.	49·2	58·5
Melting point.	+ 4·6°	Indefinite.
Boiling point.	+124·0°	Indefinite.
Effect of distillation.	Constant distillate; no residue.	Distillate contains much HF and little SeO_2. Residue of SeO_2.
Se content (by analysis).	59·5% (58·0—59·9)	52·4%
Action on sulphur.	Not perceptible in the cold; evolution of gas and deposition of red Se on heating.	Similar.
Action on silicon.	Slight in cold; evolution of SiF_4, deposition of Se on heating.	Steady evolution of SiF_4.
Action on red phosphorus.	Violent, with inflammation; evolution of gaseous fluorides of phosphorus; production of red Se and of SeO_2.	Similar.

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