222. *The Preparation and Properties of Selenium Tetrafluoride and Oxyfluoride.*

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A preparation of selenium oxyfluoride from the dioxide is described in which there is no accompanying formation of any oxy-compound of sexavalent selenium. At 0° with low concentrations of fluorine, selenium tetrafluoride has been obtained from the element in high yield. Some physical properties of these liquids have been measured. Selenium tetrafluoride shows remarkable solvent properties and gives selenofluorides with alkali fluorides.

SELENIUM oxyfluoride was first obtained by Prideaux and Cox (*J.*, 1927, 929; 1928, 738) by reaction of silver fluoride with selenium oxychloride, and its formation in other reactions has been noted by Wiechart (*Z. anorg. Chem.*, 1950, **261**, 313) and Huckel (*Nachr. Akad. Wiss. Göttingen*, Math.-phys. Klasse, 1946, 36—37). No recent examination of its properties has, however, been made and there is evidence that earlier preparations were not pure.

A new method of preparing selenium oxyfluoride by the action of well-diluted fluorine on selenium dioxide has proved successful. Under ideal experimental conditions, yields of oxyfluoride reaching 80% of the dioxide used are possible. The rest of the selenium appears as a gas, which on condensation and fractionation, proves to be selenium hexafluoride. A second method of preparation, producing satisfactory yields of the oxyfluoride, is the combustion of selenium in a stream of fluorine containing about 60% of oxygen. The oxyfluoride from either source, after redistillation in a vacuum, requires no further purification and does not attack dry glass. Its m. p. is 15·0°, some 10° higher than that previously reported, and its b. p. is 126°. The molecular weight of the vapour is normal. The density at 20° is 2·800 g./c.c. and the surface tension, measured by capillary rise, 42·2 dynes/cm. at 25° The parachor, calculated from the surface tension and density measurements, is abnormal $[(P)_{\text{obs.}} = 121;\ \Sigma(P) = 133{\cdot}9]$. Selenium oxychloride shows a similar abnormality $[(P)_{\text{obs.}} = 179{\cdot}1;\ \Sigma(P) = 191{\cdot}1]$.

Lebeau (*Compt. rend.*, 1907, **144**, 1092, 1196, 1397; **145**, 190) got a liquid fluoride, together with the well-known gaseous selenium hexafluoride, by passing fluorine over selenium contained in a copper boat; he reported the liquid to be the tetrafluoride. Prideaux and Cox (*J.*, 1927, 928; 1928, 1608) obtained a similar material by reaction of silver fluoride with selenium tetrachloride, and determined some of its properties. Yost and Clausen (*J. Amer. Chem. Soc.*, 1933, **55**, 885), in the course of fractionating selenium hexafluoride, collected a liquid which they were unable to analyse as the vessel containing it exploded. They described this substance as an unstable lower fluoride.

We have shown that diluted fluorine reacts with selenium at 0° to give the tetrafluoride. At temperatures above 100°, or with more concentrated fluorine which raises the temperature in the zone of reaction, the main product is the gaseous hexafluoride, so it is necessary, in order to obtain a good yield of the tetrafluoride, to use a very shallow bed of selenium on a well-cooled surface. This precaution also avoids the concurrent formation of oxyfluoride by traces of oxygen in the gas stream. Minute amounts of the latter present in the tetrafluoride considerably affect its m. p.

Pure selenium tetrafluoride melts at $-9{\cdot}5°$ to a colourless liquid which boils at 106°. The molecular weight of the vapour is normal. The density of the liquid is 2·72 at 25°, and the surface tension 34·3 dynes/cm. at 25°, giving a parachor $(P)_{\text{obs.}} = 137{\cdot}2$ $[\Sigma(P) = 165{\cdot}3]$. The compound shows little resemblance to the tetrachloride, which is a solid melting under pressure at 305° ± 3° and subliming at 196°.

The fluorides of sodium, potassium, rubidium, and cæsium dissolve in selenium tetrafluoride to form complexes with a composition approaching $MSeF_5$, a formula different from that of the other complex selenium halides, *viz.*, M_2SeX_6. These substances apparently possess an appreciable vapour pressure of selenium tetrafluoride and dissociate slowly in a vacuum even at room temperature, a behaviour similar to that of potassium iodohexafluoride, KIF_6, described by Emeléus and Sharpe (*J.*, 1949, 2206). Water immediately decomposes them. Thallous fluoride also dissolves in selenium tetrafluoride to form an isolable complex of similar formula, but with silver fluoride, the complex, although evidently formed, is very unstable.

Barium and lithium fluorides retain some tetrafluoride on drying, suggesting that combination takes place. Lithium fluoride is peculiar in being soluble in cold but not in hot selenium tetrafluoride—a behaviour which is explicable if the complex is stable at the ordinary but not at higher temperatures. Ammonium fluoride dissolves somewhat in the cold, but on being warmed the solution soon becomes brown and selenium is deposited, suggesting that the ammonium salt dissociates. The results of other qualitative reactions are given in the experimental section and these, together with the quantitative evidence, suggest that selenium tetrafluoride may be an ionising solvent. This is being investigated.

EXPERIMENTAL

Selenium Oxyfluoride ($SeOF_2$).—The all-glass (Pyrex) apparatus used allowed for the careful vacuum-drying of the selenium dioxide, for the fractionation of the product in a vacuum, and its distribution, under these rigorous conditions, into vessels appropriate for its analysis and the measurement of its various physical properties. The dry dioxide was treated with a nitrogen stream carrying fluorine at the rate of 2 l. per hour. The crude product was condensed, and subsequently fractionated, in a vacuum, with the removal of head and tail fractions. The final product was analysed by breaking a weighed bulb containing the material under water and determining the selenium as silver selenite and the fluorine as lead chlorofluoride (Found: Se, 59·0; F, 28·6. Calc. for $SeOF_2$: Se, 59·3; F, 28·6%).

The m. p. was observed by freezing a specimen in a water-bath containing ice and allowing the temperature to rise gradually. At 15·0° it was possible to maintain an equilibrium between solid and liquid.

The b. p. was determined by means of a capillary, with its upper end closed, dipping into the liquid which was heated by means of a bath to above the actual temperature and allowed to cool until bubbles ceased to issue from the capillary (Siwoloboff's method). The average value was 126·0°.

Determinations of the relative density of the vapour made by Dumas's method at 150° (24° above the b. p.) indicated a molecular weight of 133·5 (Calc. for $SeOF_2$: 133). Hence the vapour is not associated.

The density and coefficient of expansion were measured by the thermometer-bulb method, the vessel employed having been previously calibrated as to volume by using mercury. Observations made between 21° and 60° on 1·3580 g. of the oxyfluoride were as follows, giving a coefficient of expansion of 0·00114 c.c. per c.c. per degree:

Temp. of bath	21·5°	33·0°	42·0°	59·7°
Volume, c.c.	0·4839	0·4903	0·4949	0·5044
Density, g./c.c.	2·800	2·769	2·744	2·693

The surface tension was observed by sealing some of the liquid in a tube containing two capillaries of different, but uniform, diameters which had been previously calibrated for capillary rise by using water. As the oxyfluoride wets glass only with difficulty, special precautions were taken to flood the capillaries by tilting the whole unit immediately before making the cathetometer readings. But in spite of all precautions, reproducible results were difficult to secure : $\gamma(25^\circ) = 42$ dynes/cm., giving a parachor of 121 (Calc. : 134).

The oxyfluoride is violently hydrolysed by water, attacks phosphorus with inflammation, and gives coloured solids with potassium chloride, bromide, and iodide. Sulphur and selenium dissolve to give, respectively, a brown and a green solution, but there is little dissolution of tellurium.

Selenium Tetrafluoride.—Selenium, spread as a shallow layer on the flat base of a large reaction vessel, was dried at 200° in a vacuum and in part sublimed on to the walls, and was then treated with a 1 : 1 fluorine–nitrogen mixture at the rate of 1 l. per hour, the reaction vessel being cooled in ice. At the completion of the reaction the liquid product, which in the main remained in the reaction vessel, was distilled forward and fractionated in a vacuum. It was analysed exactly as for the oxyfluoride (Found : Se, 51·0 ; F, 48·2. Calc. for SeF_4 : Se, 51·0 ; F, 49·0%).

1. *Physical properties.* The m. p. and b. p. were observed by the methods used for the oxyfluoride, and the b. p. also by measuring the temperature at the head of a fractionating column while the liquid was being distilled in an atmosphere of dry nitrogen. The m. p. appeared to be much affected by the presence of traces of impurity ; m. p. −9·5°, b. p. 106°. A determination of the molecular weight by Dumas's method gave 154 (Calc. for SeF_4 : 155).

The density was found by the method used for the oxyfluoride. Observations made between 12° and 40° with 1·4063 g. of the tetrafluoride were as follows, giving a coefficient of expansion of 0·00092 c.c. per c.c. per degree :

Temp. of bath	12·3°	18·0°	27·9°	32·5°	38·7°
Volume, c.c.	0·5085	0·5114	0·5159	0·5181	0·5210
Density, g./c.c.	2·765	2·750	2·725	2·714	2·699

The surface tension measured by capillary rise averaged 34·3 dynes per cm., which gave a parachor of 137 against a calculated value, assuming four covalencies, of 165.

2. *Reactions with metallic fluorides.* The metallic fluorides were dissolved in the selenium tetrafluoride and the compounds formed were allowed to crystallise from excess of the solvent. In some cases, however, most of the liquid tetrafluoride present had to be removed (in a vacuum at room temperature) before crystallisation could take place.

(*a*) Lithium fluoride was soluble in the cold (0·05 g. in 10 g. of solvent), but on warming, a flocculent precipitate appeared which redissolved as the solution cooled. Only a trace of selenium tetrafluoride remained associated with the solid on evaporation of the liquid.

(*b*) Sodium fluoride (0·02 g.) dissolved slowly in boiling selenium tetrafluoride (6 g.). White crystals of the double *fluoride* slowly separated on cooling, which after removal of excess of solvent at 25° were creamy-white and dissolved in water with decomposition and evolution of heat (Found : Se, 38·9 ; F, 48·0 ; Na, 13·1% ; NaF : SeF_4 = 1·18 : 1. $NaSeF_5$ requires Se, 40·1 ; F, 48·2 ; Na, 11·7%).

(*c*) Up to 0·15 g. of potassium fluoride dissolved readily in 10 g. of tetrafluoride on warming. On cooling the solution, a precipitate slowly separated which was recrystallised by redissolving it in a smaller quantity of solvent and cooling it slowly. The crystals of the double *fluoride* were isolated by removing excess of solvent in a vacuum at 25° (Found : Se, 35·4 ; F, 44·5 ; K, 18·9% ; KF : SeF_4 = 1·05 : 1. $KSeF_5$ requires Se, 37·1 ; F, 44·6 ; K, 18·3%).

(*d*) Rubidium fluoride (0·1 g.) dissolved in 10 g. of tetrafluoride in the cold, and, after some of the solvent had been removed, as with potassium fluoride, the complex *fluoride* crystallised (Found : Se, 28·7 ; F, 36·3 ; Rb, 34·1% RbF : SeF_4 = 1·18 : 1. $RbSeF_5$ requires Se, 30·4 ; F, 36·6 ; Rb, 33·0%).

(*e*) Cæsium fluoride was readily soluble in the cold (0·3 g. in 10 g. of solvent) and most of the solvent had to be removed before crystallisation started. The double *salt* formed in this case was more stable than the others and showed only slight decomposition after 24 hours in a high vacuum at room temperature (Found : Se, 24·9 ; F, 30·7 ; Cs, 43·6% ; CsF : SeF_4 = 1·01 : 1. $CsSeF_5$ requires Se, 25·7 ; F, 30·9 ; Cs, 43·4%).

(*f*) Thallous fluoride proved to be as soluble as potassium fluoride. After the solution had cooled and excess of solvent had been removed, a well-crystallised white solid remained which had a slight vapour pressure of selenium tetrafluoride (Found : TlF : SeF_4, 1·03—1·15 : 1 ; Tl, 57·2—58·5 ; Se, 18·8—20·7. $TlSeF_5$ requires Tl, 54·0 ; Se, 20·9%).

(*g*) Barium fluoride gave a residue with a ratio $BaF_2 : SeF_4$ 1·40 : 1, suggesting that a compound is formed which is not very stable.

(*h*) Silver fluoride dissolved on warming (0·05 g. in 10 g. of solvent) and gave a white precipitate on cooling the solution. As the solvent was removed, however, it began to decompose : an examination at an intermediate stage suggested the formula $AgSeF_5$. After 1 hour at 100° in a vacuum the material was visibly decomposed and the ratio $AgF : SeF_4$ was as low as 1 : 0·26. The best intermediate analysis gave the ratio $AgF : SeF_2$ = 1·3 : 1.

(*i*) Calcium fluoride, practically insoluble, retained only a trace of tetrafluoride after excess had been removed.

3. *Other observations.* Selenium tetrafluoride is decomposed violently by water and attacks phosphorus as does the oxyfluoride. It is miscible in all proportions with sulphuric acid, alcohol, ether, and iodine pentafluoride, and dissolves appreciable quantities of carbon tetrachloride, chloroform, bromine, iodine, sulphur, and selenium. Selenium tetrafluoride dissolves and reacts with all the potassium halides and some of the higher metallic and non-metallic oxides such as phosphoric oxide, vanadium pentoxide, and chromium trioxide. These reactions are in the course of quantitative investigation.

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