CCIX.—*On Selenium Tetrafluoride.*

By EDMUND BRYDGES RUDHALL PRIDEAUX and CHARLES BERESFORD COX.

BY passing fluorine over selenium contained in a boat and placed in a copper tube, Lebeau (*Compt. rend.*, 1907, **144**, 1042, 1047) prepared a colourless liquid, which, according to his description, had some properties which differed considerably from those we attribute to selenium tetrafluoride, but which bear certain resemblances to those of the oxyfluoride or of the mixture $SeO_2 + 4HF$ (see table).

The analysis of Lebeau's fluoride corresponded closely to the formula SeF_4, and he was not able to understand why the fluorination stopped at this point. It was suggested, however, by Ramsay (*Compt. rend.*, 1907, **144**, 1196) that the presence of copper as a reducing agent might have this effect. On another occasion, Lebeau (*ibid.*, **145**, 190) succeeded in preparing a gaseous mixture, which (when analysed by means of sodium in liquid ammonia) had a composition approximating to SeF_6 but which contained about 2% of selenium in excess of the theoretical. The presence of a little sodium selenite with the selenide which was formed by treatment with sodium, suggested to him the presence of a little selenium oxyfluoride. Although it seems improbable that this would remain after storage over mercury, yet it might very probably have been formed by the reaction, since fluorine as prepared by Moissan's method is always liable to contain ozone and oxygen. It is also difficult to purify the fluorine completely from hydrogen fluoride carried up from the electrolyte, and this together with the oxyfluoride might well have given a mixture having the correct ratio of selenium to fluorine. The analytical results were expressed as a ratio: there is no statement that they were referred to a weighed portion of the liquid, as was done in our analyses.

There is at present, then, some doubt as to the existence of a lower fluoride of selenium. The hexafluoride, a stable gas which did not attack glass, was prepared later in a somewhat impure form by Lebeau, using the same reaction which had previously given the corrosive liquid. The mode of origin and properties of the latter would therefore seem to require further investigation.

We have now prepared the lower fluoride of selenium by another method, *viz.*, the interaction of selenium tetrachloride and silver fluoride. This method excludes the presence of moisture or hydrogen fluoride or a higher fluoride of selenium.

EXPERIMENTAL.

The selenium tetrachloride, prepared in the usual manner from the dry reagents, was kept in sealed sections of glass tube. The silver fluoride was prepared by the method of Ruff (see this vol., p. 739). The fluoride (4—5 parts) and the chloride (1 part) were mixed in the platinum bottle or the platinum crucible contained in the large monel metal pot. The reaction was started by heating to 50—60° and then proceeded vigorously. On distillation, a colourless, fuming liquid passed over, which was analysed in fractions and gave results corresponding to SeF_4 (J., 1927, 928). As in the case of the oxyfluoride, it was necessary to redistil the product from silver fluoride in order to remove the chloride completely. The yields were low for the reasons already given, but in this case were further reduced by the formation of some oxyfluoride. The analysis of our first product showed a surplus of selenium corresponding to a considerable proportion of this compound. Although it is probably the first product of the hydrolysis of the tetrafluoride, we do not consider that more than a very small amount could have been formed by contact with ordinary moist air, which was, of course, avoided as far as possible. The presence of the oxyfluoride was more probably due to the unavoidable presence in the silver fluoride of silver oxide which could give oxyfluoride, either *via* SeO_2 and SeF_4 or *via* $SeOCl_2$ and 2AgF. On account of this difficulty, the physical properties of the tetrafluoride as given in the table have probably not been defined so well as those of the oxyfluoride. In the next preparation, 9·14 g. of selenium tetrachloride gave 5·12 g. of distillate, the last portions of which appeared slightly milky, perhaps owing to the separation of selenium dioxide. On mixing with the rest of the distillate it became clear. On being redistilled below 140° it yielded 4·42 g. of distillate, *i.e.*, 73·5% of that theoretically obtainable from the tetrachloride taken. This product, analysed by different methods, gave 52·1—51·0% of selenium and 47·2—47·7% of fluorine.

Physical Properties.—The *density* was determined in the monel bottle (this vol., p. 739). It was slightly higher than that of the oxyfluoride and much higher than that of the corresponding mixture of selenium dioxide and hydrogen fluoride.

The *boiling point* was determined in the monel metal bottle. A rapid stream of bubbles began at 91·0° and continued steadily as the temperature was slowly raised to 95°. Heating was continued, until at 124° the bubbles recommenced and continued steadily at that temperature. Since this is the boiling point of selenium oxyfluoride, it is evident that the very small quantity of liquid taken (about 0·4 c.c.) had gained more oxyfluoride by hydrolysis at some stage.

Melting point. The liquid solidified rapidly and completely at —70°. As only 1·476 g. were available for this determination, it was carried out by inspection in a very small platinum crucible which was contained in a glass tube coated inside with a transparent varnish. The pentane thermometer, protected with platinum foil, was inserted so that the bulb was just covered, and the liquid was frozen quickly and allowed to warm slowly. No liquid was seen at —13·0°, whilst all was liquid at —10°. On taking temperature–time readings, a halt was noticed, with oscillations, at —13·0°. The plotted curve showed an inflexion beginning slightly below this point and the melting point from the graph appeared at about

−13·5°. It was therefore much lower than that of the oxyfluoride but much higher than that of Lebeau's preparation.

Chemical Properties.—With silicon (crystalline) an immediate reaction was observed in the cold. This was then carried out in the monel metal boiling-point bottle, which was connected with a nitrometer filled with mercury. The gas collected was silicon tetrafluoride. There was a residue of red selenium in the bottle.

Sulphur gave no reaction in the cold.

Red phosphorus gave a strong reaction with the production of gaseous fluorides, apparently both PF_3 and POF_3, and a residue of red selenium and selenium dioxide. The preparation of selenium fluoride, however, contained some oxyfluoride.

The chemical properties common to selenium tetrafluoride, selenium oxyfluoride, and solutions of selenium dioxide in hydrogen fluoride are:

(1) Strong and complete attack of glass.

(2) Complete hydrolysis by water with evolution of heat and formation of selenious and hydrofluoric acids.

(3) No effect, or only a very slight one, on clean copper.

The chemical properties which show differences are:

(1) The attack on silicon seemed to be directly proportional to the amount of combined fluorine. For a given ratio of fluorine to selenium, it was much greater when the fluorine was present as hydrogen fluoride.

(2) The attack on red phosphorus seems to be proportional to the amount of selenium present in combination or solution, and is inhibited by an excess of hydrogen fluoride.

Properties of the lower fluorides of selenium and of a solution of selenium dioxide in hydrogen fluoride.

	SeF_4 (authors).	SeF_4 (Lebeau).	$SeO_2 + 4HF$.	$SeOF_2$.
Density.........	2·77	—	2·09	2·67
M. p...............	−13·2°	Solid at −80°.	Below about −30° $SeO_2,5HF$ crystallises.	+4·6°
B. p.	+93°	Above 100°.	Indefinite.	+124°
Effect on Si....	Strong, giving SiF_4 and Se.	None at b. p.	Strong, giving SiF_4 and Se.	Very slight in cold; on heating, gives SiF_4 and Se.
Effect on S. ...	None in cold.	None at 100°.	Similar to $SeOF_2$.	None in cold; on heating, gives a gas and Se.
Effect on P. ...	Red P. Strong action. Gaseous fluorides, Se and SeO_2. (Sample contained $SeOF_2$.)	White P. Vivid action: gaseous fluorides and Se.	None until excess of HF boils off, then strong.	Very strong in cold: PF_3, POF_2, Se, and SeO_2 formed.

There are still outstanding points in connexion with these compounds which we hope to investigate.

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UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, April* 23*rd*, 1928.]