727. *Some Properties of Selenium Tetrafluoride.*

By R. D. Peacock.

The vapour pressure and surface tension of selenium tetrafluoride have been determined. Reactions of the compound have been further investigated, and those with mercury and some oxides and oxy-compounds of both metals and non-metals are described.

In a recent paper (Aynsley, Peacock, and Robinson, *J.*, 1952, 1231) the preparation of selenium tetrafluoride was described and values for the density and melting and boiling points were given. Only one approximate value for the surface tension was obtained; this and also the vapour pressure have now been measured over a range of temperatures. As previously indicated, selenium tetrafluoride is remarkable in its chemical behaviour and exhibits unexpected compound formation and solvent properties towards a number of substances

The vapour pressure can be conveniently measured by what is essentially the isoteniscope method. The logarithm of the vapour pressure gave a straight line when plotted against the reciprocal of the absolute temperature except for below 20°. Between that temperature and 70° the vapour pressures are given by the equation $\log P = 9{\cdot}44 - 2457/T$ (where T = temperature in °K), from which the boiling point found by extrapolation is 101·6° (cf. 106° experimentally determined). A latent heat of vaporisation of 11,240 cal. per mole, and a Trouton's constant of 30·0 can be deduced. If the relation $T_{\text{B.p.}}/T_c = 0{\cdot}6$ is assumed to apply, the critical temperature is approximately 290°.

The surface tension referred to above had been obtained by observing capillary rise. This method is not satisfactory because the liquid does not readily wet glass, and a method based on the measurement of maximum bubble pressure was used instead. Between $-10°$ and 100° the surface tension is given by the equation $\gamma = 38{\cdot}40 - 0{\cdot}124t$ dynes/cm., where t = temperature in °C. Extrapolation to the boiling point gives $\gamma = 25{\cdot}80$ dynes/cm., and further extrapolation to zero surface tension suggests a critical temperature of 310°, which is of the same order as that deduced above from vapour-pressure data.

A further examination of the reaction of selenium tetrafluoride with mercury shows that the attack is slow at 20° but much more rapid at the boiling point and can be completed by refluxing. The white solid formed, $HgSeF_4$, is slightly soluble in selenium tetrafluoride. On addition of water, the solid evolves heat but does not suffer very obvious change, though some of it goes into solution since the liquid becomes acid and gives a white precipitate with potassium chloride. Alkali causes the compound to blacken immediately, leading to precipitation of the element, and cold concentrated hydrochloric acid turns it a reddish colour which becomes grey and metallic-looking when the liquid in which it is suspended is boiled.

Of the solvent properties of selenium tetrafluoride, the most striking is its ready dissolution of brown vanadium pentoxide to give a colourless solution of considerable concentration from which white crystalline plates of $VOF_3,2SeF_4$ [probably the salt $(SeF_3)_2VOF_5$ (cf. K_2VOF_5)] separate on cooling. Even titanium dioxide and tantalum pentoxide dissolve in the tetrafluoride.

Sulphur trioxide reacts with much heat and, after removal of the excess of selenium tetrafluoride in a vacuum, yields an oily liquid, SeF_4,SO_3, which on cooling solidifies to colourless crystals, m. p. 70°. In the absence of solid the compound readily supercools to room temperature; it may be distilled at about 170° in a vacuum without decomposition. With water, it reacts violently giving among other things fluorosulphonic acid. Again the material most probably has the character of a salt $(SeF_3)SO_3F$.

The vigorous reaction with potassium permanganate is interesting. The green solution first formed almost immediately becomes reddish-brown, evolves oxygen, and deposits a red-brown solid, $KMnF_5$. The reaction is probably represented by $4KMnO_4 + 10SeF_4 \longrightarrow 4KMnF_5 + 10SeOF_2 + 3O_2$.

The reaction with selenium dioxide provides the most convenient method of preparing selenium oxyfluoride yet described. Excess of dioxide is used and the product is fractionated.

When first prepared in this laboratory the tetrafluoride was believed, on visual evidence, not to attack glass; it has since been shown to do so, though quite slowly and even when completely free from hydrogen fluoride. The attack on a borosilicate is surprising. At room temperature silicon tetrafluoride and boron trifluoride are produced in readily measurable pressures after a week, and the inner surface of the glass above the liquid becomes slowly covered with a white deposit of selenium dioxide. The reaction may be represented by $SiO_2 + SeF_4 \longrightarrow SiF_4 + SeO_2$, and correspondingly for boron. These facts do not prevent this compound from being usefully handled in glass since it can be satisfactorily separated from these materials by distillation.

EXPERIMENTAL

Preparation of Selenium Tetrafluoride.—Selenium was allowed to react at 0° with fluorine by the method described by Aynsley, Peacock, and Robinson (*loc. cit.*), which allows of the convenient preparation of up to 300 g. of the tetrafluoride at one time.

Vapour Pressure.—Freshly distilled material, purified in a vacuum, was carefully degassed several times by alternate freezing and melting in a high vacuum. The sample was degassed frequently during the measurements. At low temperatures the vapour pressure was read directly by means of a cathetometer on the isoteniscope which was charged with selenium tetrafluoride. Pressures were converted into mm. of mercury. At higher temperatures the isoteniscope was used as a null instrument through air pressure to a mercury manometer.

Temp.	−11·1°	−5·0°	0°	10·3°	19·8°	25·6°	29·6°	34·5°	40·1°	47·7°	60·0°	69·0°
V. p. (mm.)	0·71	1·31	2·50	5·77	12·02	16·42	21·26	29·11	41·20	61·90	114·5	187·4

Surface Tension.—A suitable modification of the maximum bubble pressure method was used. The Pyrex instrument was calibrated before and after the determination, water being used as the reference liquid.

Temp.	−7·6°	5·0°	17·8°	29·0°	39·6°	50·3°	60·9°	71·8°	77·8°	82·0°	89·2°
γ (dynes/cm.)	39·06	38·21	36·33	34·99	33·30	31·97	30·89	29·20	28·80	28·20	27·51

Reactions.—(a) *With mercury.* Mercury, carefully purified and dried, was refluxed with a large excess of selenium tetrafluoride for 30 hr. The white residual *compound* was dried in a vacuum at 20° (Found: Hg, 57·3; Se, 21·8; F, 20·7%; equiv., 348·4. $HgSeF_4$ requires Hg, 56·4; Se, 22·4; F, 21·2%; equiv., 355·6).

(b) *With vanadium pentoxide.* Vanadium pentoxide was dissolved in warm selenium tetrafluoride, and the solution allowed to cool. The excess of tetrafluoride was removed in a vacuum at 20°, leaving the *salt* (Found: V, 11·5; Se, 35·6; F, 47·9. $VOF_3,2SeF_4$ requires V, 11·7; Se, 36·4; F, 48·2%).

(c) *With sulphur trioxide.* Sulphur trioxide was allowed to react with a large excess of selenium tetrafluoride. The excess of reagent was carefully pumped off, the temperature being raised slowly from 20° to 160°, above which the *compound* itself began to distil (Found: SO_3 34·0; Se, 33·4; F, 32·0. SO_3,SeF_4 requires SO_3, 34·1; Se, 33·6; F, 32·3%).

(d) *With potassium permanganate.* Selenium tetrafluoride was condensed on to a small quantity of solid potassium permanganate. When the frothing had subsided the mixture was refluxed for a short time for completion of the reaction. The excess of solvent was removed in a vacuum at 20°, and the last traces pumped off from the *fluoromanganate* at 160° (Found: Mn, 29·3; F, 49·8. $KMnF_5$ requires Mn, 29·1; F, 50·3%).

(e) *With glass.* About 30 c.c. of selenium tetrafluoride in an evacuated Pyrex system provided with a manometer were kept for several weeks at room temperature. The pressure of gas, which after about a week was 2—3 mm., increased uniformly to 30 cm. after 6 months. After some time a white incrustation began to show on the glass, and a few white crystals appeared in the liquid; analysis showed these to be mainly selenium dioxide. At the end of the experiment the gases were condensed by means of liquid oxygen and proved to be a mixture of silicon tetrafluoride and boron trifluoride.

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INORGANIC CHEMISTRY LABORATORIES,
KING'S COLLEGE, NEWCASTLE-ON-TYNE.

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