CLXVIII.—*The Parachor and Chemical Constitution. Part XIII. Some Compounds of Titanium and Tin.*

By FREDERICK BASIL GARNER and SAMUEL SUGDEN.

THE chief object of the investigation described below was the elucidation of the structure of the additive compound of stannic chloride and phosphorus oxychloride described by Casselman (*Annalen*, 1854, **91**, 242; 1856, **98**, 217). As a preliminary step it was necessary to measure the parachors of a few simple tin compounds in order to determine the atomic parachor of this element. The results in Table I (which includes the parachor of titanium tetrachloride) give for the atomic constants Sn = 56·7 and Ti = 45·3.

TABLE I.

Atomic Parachors of Tin and Titanium.

Substance.	[*P*] obs.	*Σ* [*P*].	Atomic parachor.
Tin tetrachloride	272·8	217·2	55·6
Tin tetrabromide	325·8	272·0	53·8
Tin tetraethyl	441·1	380·4	60·7
			Mean 56·7
Titanium tetrachloride	262·5	217·2	45·3

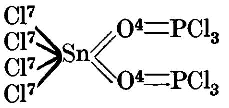
These values are in harmony with those of other elements of group IV which have so far been determined and give the sequence :—

C.	Si.	Ti.	Ge.	Zr.	Sn.	Hf.	Pb.
2·8	*ca.* 25	45·3	—	—	56·7	—	76·4

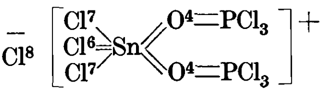
The compound of stannic chloride and phosphorus oxychloride is formed at once with considerable evolution of heat when the components are mixed in suitable proportion. Casselman (*loc. cit.*) describes it as melting at 55° and boiling at 180°, and gives its composition as $SnCl_4,POCl_3$. We have been unable to isolate a compound of this composition and boiling point but from all the mixtures used have obtained a substance which, after careful purification, melts at 54·5° (corr.) and boils at 118—119° (corr.)/760 mm. On analysis this substance was found to have the formula $SnCl_4,2POCl_3$ and thus falls into line with the corresponding compounds of zirconium and hafnium, namely, $Zr(Hf)Cl_4,2POCl_3$, and $Zr(Hf)Cl_4,2PCl_5$. The analytical results are shown below.

	Calculated for		Found.	
	$SnCl_4,POCl_3$.	$SnCl_4,2POCl_3$.	I.	II.
Sn	28·68%	20·92%	21·00%	21·20%
P	7·49	10·92	10·62	10·97
Cl	59·98	62·50	—	62·10

The structure suggested for this substance by one of us (Sugden, J., 1927, 1182), when modified to account for the presence of two phosphorus oxychloride molecules in the complex, is shown by formula (I) and contains four singlet linkages. The parachor calculated for this structure is 665·5, whereas the value found experimentally is 691·6, which is 26 units too high. This result may be accounted for in two ways. In the first place the substance distils with some decomposition at ordinary pressure and the first runnings always contain an excess of stannic chloride. It is therefore possible that, in the liquid state, the compound is partly dissociated into its generators, so that only a portion of it has the structure (I). It may be noted here that, if the octet rule holds and the substance has an open-chain non-polar structure, then at least four singlet linkages must be present in the molecule. This can be proved in the following manner: The total number of valency electrons in the molecule is 96. If the 15 atoms in the molecule all attain an octet, the number of shared electrons is $8 \times 15 - 96 = 24$. The minimum number of bonds which will link the 15 atoms to form a non-polar molecule is 14, so that the 24 shared electrons must be distributed between 10 duplet links and 4 singlets. The introduction of double bonds or ring structures necessitates the use of a still larger number of singlets in order to provide the necessary number of bonds.



[P] calc., 665·5.
(I.)



[P] calc., 688·7.
(II.)

If, however, the substance has a polar structure, the number of bonds required is smaller and the presence of a smaller number of singlet linkages can be admitted. For instance, if one of the chlorine atoms ionises to give the structure (II), only two singlets are necessary to formulate the complex kation and the calculated parachor (688·7) is very nearly equal to the experimental value. This polar structure is, however, difficult to reconcile with the properties of the substance, *viz.*, its fusibility, volatility, and solubility in hydrocarbon solvents. We therefore measured the conductivity of the compound in the fused state, with the results shown below. As the absorption of moisture gives ionisable products, care was taken to expose the substance as little as possible to the atmosphere. Specimen I was recrystallised from ligroin and showed a small conductivity. Specimen II was purified by distillation under diminished pressure and was stored in sealed tubes. After melting, the tube was opened and the contents were rapidly transferred to the stoppered conductivity cell. A much smaller conductivity was found for this specimen, and, after addition of ¼% of water, the conductivity showed a large increase. A 4% solution of the substance in benzene was also examined and had no measurable conductivity ($<10^{-6}$ mho). We conclude that the small conductivity shown by the fused substance is due to traces of moisture and that the molecule must be non-polar. Its structure is probably represented by (I), but the parachor shows that it is largely dissociated into its generators in the liquid state.

Specimen.	Specific conductivity at 60°.
I	0·00136 mho
II	0·000081 ,,
II + ¼% water	0·00132 ,,

EXPERIMENTAL.

Surface tensions were determined by the method of maximum bubble pressure (Sugden, 1922, **121**, 858; 1924, **125**, 27), and densities with a U-shaped pyknometer (J., 1924, **125**, 1171). Since most of the substances studied are rapidly hydrolysed by moisture, long tubes containing phosphoric oxide were used to dry the air entering the bubbler or pyknometer.

The tables below are set out in the same manner as in other papers of this series and do not need further description. The parachor is calculated by the formula $[P] = \gamma^{\frac{1}{4}}M/(D - d)$, where γ is the surface tension in dynes/cm., M the molecular weight, and D and d the densities of the liquid and vapour respectively. For the substances studied in the present paper, d is very small and has been neglected.

Stannic chloride, $SnCl_4$, $M = 260{\cdot}5$, was purified by distillation and had b. p. 114° (corr.)/768 mm. Densities determined : $D_{4^\circ}^{27^\circ}$

2·220, $D^{37\cdot5^\circ}_{4^\circ}$ 2·194, $D^{48^\circ}_{4^\circ}$ 2·169, $D^{55\cdot5^\circ}_{4^\circ}$ 2·152; whence $D^{t^\circ}_{4^\circ} = 2\cdot284 - 0\cdot00239t$.

t	12°	29·5°	40°	51°	58·5°	
γ	31·15	29·01	27·39	26·63	25·02	
D......	2·255	2·213	2·188	2·162	2·144	
[P] ...	272·9	273·2	272·4	273·7	271·7	Mean 272·8

Stannic bromide, $SnBr_4$, $M = 438\cdot5$, was purified by distillation and had m. p. 29·5° (corr.) and b. p. 204° (corr.)/765 mm. Densities determined: $D^{37\cdot5^\circ}_{\circ}$ 3·320, $D^{51\cdot5^\circ}_{4^\circ}$ 3·282, $D^{61^\circ}_{5^\circ}$ 3·253, $D^{71^\circ}_{4^\circ}$ 3·225, $D^{81\cdot5^\circ}_{4^\circ}$ 3·197; whence $D^{t^\circ}_{4^\circ} = 3\cdot427 - 0\cdot00284\,t$.

t	37°	51·5°	64°	75·5°	
γ	37·76	35·32	33·91	32·09	
D....................	3·322	3·281	3·246	3·212	
[P]	326·3	325·8	326·0	325·1	Mean 325·8

Tin tetraethyl, $Sn(C_2H_5)_4$, $M = 234\cdot9$, was prepared by the action of excess of magnesium ethyl bromide on stannic bromide (Pfeiffer and Schnurmann, *Ber.*, 1904, **37**, 320) and was purified by distillation. The specimen used had b. p. 180·5—181·5° (corr.)/768 mm. Densities determined: $D^{15^\circ}_{4^\circ}$ 1·202, $D^{28\cdot5^\circ}_{4^\circ}$ 1·187, $D^{40\cdot5^\circ}_{4^\circ}$ 1·172, $D^{52^\circ}_{4^\circ}$ 1·160, $D^{64^\circ}_{4^\circ}$ 1·147; whence $D^{t^\circ}_{4^\circ} = 1\cdot219 - 0\cdot00113\,t$.

t	13·5°	34·5°	46°	55·5°	77·5°	
γ	26·22	24·05	22·98	22·08	20·41	
D......	1·204	1·180	1·167	1·156	1·131	
[P] ...	441·6	440·9	440·8	440·6	441·4	Mean 441·1

Additive compound of stannic chloride and phosphorus oxychloride, $SnCl_4,2POCl_3$, $M = 567\cdot3$. When stannic chloride (1 mol.) and phosphorus oxychloride (2 mols.) are mixed, considerable heat is evolved; on cooling, the mixture solidifies completely. Three methods of purification were attempted. The crude substance was melted and after partial solidification the crystals were separated and drained. Owing to the ready absorption of moisture the melting point could not be raised above 52·5° by this method. By crystallisation from ligroin the pure substance was obtained melting about 2° higher, but the crystals were frequently discoloured or turned brown on keeping. Distillation at atmospheric pressure gave a boiling point of 118—119°, but some decomposition occurred and the first runnings did not solidify completely. The best method of purification was found to be distillation at about 100 mm. pressure. Three distillation flasks with long necks (to minimise contact of the vapours with the rubber bungs) were connected in series and thoroughly dried by heating with a flame in a current of dry air. The compound was introduced into the first flask, and the system connected to the pump through a guard tube containing calcium chloride. The substance readily distilled at 70°/100 mm.

and in one distillation was obtained pure with m. p. 54·5° (corr.). This was unchanged by further distillation or by sublimation in a sealed tube at room temperature.

Analysis. Tin was estimated by precipitation as sulphide and was weighed as oxide. The phosphorus was estimated as magnesium pyrophosphate, and the chloride as silver chloride. The analytical figures are given on p. 1299.

An attempt was made to prepare the substance described by Casselman (*loc. cit.*) by mixing equimolecular quantities of the components. The product, on distillation, gave a first fraction, b. p. 114°, which was chiefly stannic chloride, and a later fraction which partly solidified and on further distillation gave the compound described above. Densities determined : $D_{4°}^{56·5°}$ 1·923, $D_{4°}^{62·5°}$ 1·907, $D_{4°}^{67·5°}$ 1·892 ; whence $D_{4°}^{t°} = 2·090 - 0·00293\,t$.

t	57·5°	64°	67·5°	71·5°	74°	81·5°
γ	29·88	29·12	28·27	27·70	27·27	25·87
D.........	1·922	1·903	1·893	1·880	1·873	1·851
$[P]$	690·2	693·3	690·8	692·1	692·1	691·1
					Mean	691·6

Titanium tetrachloride, $TiCl_4$, $M = 189·9$. A commercial specimen was purified by distillation ; the fraction used was pale yellow and had b. p. 136°/753 mm. Densities determined : $D_{4°}^{15·5°}$ 1·742, $D_{4°}^{26°}$ 1·725, $D_{4°}^{40°}$ 1·701, $D_{4°}^{58·5°}$ 1·673 ; whence $D_{4°}^{t°} = 1·767 - 0·00162\,t$.

t	13°	27·5°	39·5°	52°	75°	
γ	34·03	32·16	30·78	29·08	26·65	
D......	1·746	1·722	1·703	1·683	1·645	
$[P]$ ...	262·8	262·6	262·7	262·0	262·3	Mean 262·5

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BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
FETTER LANE, E.C. 4.

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