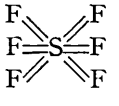
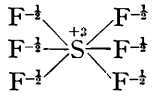
334. *The Electronic Structure of Hexafluorides.*

By THOMAS G. PEARSON and PERCY L. ROBINSON.

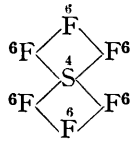
IN the theory of valency, the electronic configuration of the hexafluoride molecules is of considerable importance (Sidgwick, " The Electronic Theory of Valency," Oxford, 1927, p. 62). For sulphur hexafluoride, a typical case, no less than five structures (I—V) may be postulated (Sugden, " Parachor and Valency," London, 1930, p. 136). Of these, the polar formula (IV) is at once excluded on account of the properties of the compound, but chemical methods are not available for discriminating between the remaining alternatives. This may, however, be done through the parachor, which not only distinguishes between those structures containing singlet links (II, III, and V), but would also identify the duodecet in the covalent structure (I).

(I.) 

(204·8.)

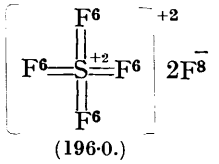
(II.) 

(123·8.)

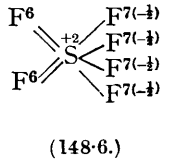


(III.)

(128·6.)

(IV.) 

(196·0.)



(V.)

(148·6.)

Professor Whytlaw-Gray, learning of our interest in the problem, kindly furnished us with about two litres of his very pure sulphur hexafluoride, the surface tension and liquid density of which we have measured. The parachor deduced therefrom, 143·3, is in reasonable agreement with that computed from the accepted atomic and structural constants for the configuration (V), *viz.*, 148·6.

Although the liquid densities of the hexafluorides of selenium and tellurium have been measured, values for their surface tensions are not available, and in the absence of supplies of these materials, we have had recourse to a formula proposed by Walden (*Z. physikal. Chem.*, 1909, **65**, 224), *viz.*, $\gamma_{b.p.} = [T_{b.p.} \times 2{\cdot}15 \log T_{b.p.}]/MV_{b.p.}$, wherefrom the surface tension may be calculated from the boiling point together with the liquid density at that temperature. We have tested this relationship for a large number of simple inorganic compounds by means of data mainly collected in this laboratory, and have found it to be trustworthy within $\pm$ 2% for unassociated liquids, and, where association is slight, to an accuracy sufficient for parachor purposes. Fortunately, the hexafluorides, as judged by Trouton's constant (Table I), are normal liquids, and, with the aid of the Walden formula, we have calculated from the density determinations of Klemm and Henckel (*Z. anorg. Chem.*, 1932, **207**, 73) the molecular parachors. These are collected in Table I, and in Table II are compared with those computed from the accepted atomic and structural data (S = 48·2, Se = 62·5, Te = 81·0, singlet = — 11·6, semipolar singlet = —12·4, polar bond = — 1·6, 4-membered ring = + 11·6, 12-electron shell = + 11·6 approx.). It is seen that,

TABLE I.

Compound.	Trouton's constant.	B. p., Abs.	$D_{b.p.}$, g. per c.c.	$d_{b.p.}$, g. per c.c.	γ, dynes per cm.	Parachor.
SF_6	22	205·0°	1·975	0·009	13·78	143·1
SeF_6	19	224·0	2·34	0·011	13·71	159·5
TeF_6	19	234·7	2·67	0·013	13·23	173·4

TABLE II.

	Parachor, calc. for structure					Parachor, found from	
Compound.	(I).	(II).	(III).	(IV).	(V).	b. p.	surface tension.
SF_6	204·8	123·8	128·6	196·0	148·6	143·1	143·3
SeF_6	219·1	138·1	132·9	210·3	162·9	159·5	—
TeF_6	237·6	156·6	151·4	228·8	181·4	173·4	—

as with the sulphur compound (the values for which, calculated by aid of the Walden relationship, are included for comparison), the parachors agree most closely with those anticipated for the type of structure of which (V) is an example, *i.e.*, one in which two fluorine atoms are covalent, and the rest united to the sulphur atom by semipolar singlet linkages. The alternative interpretation of the value for the parachors which would reconcile these results with the covalent formula (I) was discussed in the case of the pentachlorides by Sugden (*op. cit.*, p. 133) and shown to involve the assumption that the sharing of an electron causes a contraction of 11·6 units, but was rejected by him on account of data for mercury and thallium compounds (*ibid.*, p. 111) and of the difficulty with non-polar and triple bonds. On the basis of Sugden's argument, the covalent formula (I) must be rejected.

EXPERIMENTAL.

The sulphur hexafluoride had been made from its elements and purified by passage through aqueous potassium hydroxide, soda–lime, and phosphoric oxide, followed by two fractionations, and a subsequent treatment with sodium–potassium alloy; it was received by us in a 2-litre bottle closed by a mercury-sealed tap. This vessel was connected to a train which was subsequently evacuated, and the material was transferred through a tube freshly charged with phosphoric oxide to a vessel cooled in liquid air. A manometer incorporated in the system showed that the whole of the gas was condensed under these conditions. Without further purification, appropriate quantities of the sulphur hexafluoride were sealed off in the density bulb and the surface tension vessel following the usual procedure employed in this laboratory.

Measurements were made of the density and the surface tension, and the results are recorded in Table III.

TABLE III.

Temp.	D, g. per c.c.	h, mm.	γ, dynes per cm.	Parachor.
− 50°	1·878	2·20	11·63	143·0
− 20	1·722	1·68	8·02	143·7

$r_1 = 0{\cdot}27165$ mm., $r_2 = 0{\cdot}49920$ mm., $g = 981{\cdot}45$.
Temp. coefficient of surface tension 0·1204 dynes/cm./degree.

The liquid densities are in fair agreement with the recent determinations of Klemm and Henkel (*loc. cit.*), but somewhat lower than those of Prideaux (J., 1906, **89**, 376). The coefficient of expansion, 303×10^{-5}, is comparable with that (290×10^{-5}) obtained by the former workers, especially when it is considered that their measurements extended over a range of but 6°. The Ramsay–Shields constant, $d[(Mv)^{2/3}\gamma]/dt$, is 1·8, and, like Trouton's constant, 22, almost normal.

SUMMARY.

(1) The density and the surface tension of suphur hexafluoride have been measured over a range of temperature, and the parachor calculated therefrom indicates that the octet valency rule is maintained in this compound, two fluorine atoms being attached to the sulphur atom by covalent linkages and the remaining four by semipolar singlet links.

(2) The parachors of selenium and tellurium hexafluorides, calculated from their respective liquid densities and boiling points, reveal a structure identical with that found experimentally for sulphur hexafluoride.

Grateful acknowledgment is made to Professor R. Whytlaw-Gray, F.R.S., for his generous gift of the sulphur hexafluoride used, to Capt. F. P. Mills, of the Northumberland and Durham Rescue Brigade, for supplies of liquid air, and to the Research Committee of this College for certain apparatus.

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