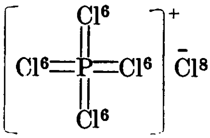
CLXIII.—*The Parachor and Chemical Constitution. Part V. Evidence for the Existence of Singlet Linkages in the Pentachlorides of Phosphorus and Antimony.*

By SAMUEL SUGDEN.

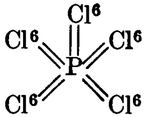
SOME time ago Dr. N. V. Sidgwick suggested to the author that it would be of interest to examine the parachors of substances in which a central atom appears to share electrons with more than four other atoms. Substances of this type have a particular interest from the point of view of the electronic theory of valency, for it is difficult to formulate them satisfactorily without abandoning the octet rule or the conception of the sharing of electrons in pairs.

Three electronic formulæ have been suggested for phosphorus pentachloride. The polar formula (I) (Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 919) is open to many criticisms : phosphorus pentachloride is readily fusible (under pressure) and volatile, its solutions do not conduct electricity, and in general the substance has none of the properties of a salt. For these reasons, Lewis (" Valence and the Structure of Atoms and Molecules," 1923, p. 101) adopts formula (II) and considers that substances of this type are exceptions to the octet rule. On the other hand, Prideaux (*Chem. and Ind.*, 1923, **42**, 672) maintains the rule of eight by discarding the duplet rule for two of the chlorine atoms which are supposed to be bound by sharing one electron each with the phosphorus atom, as shown in formula (III).



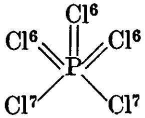
−1·6

(I.)



+7·7

(II.)



−24·8

(III.)

For this method of formulation the author is indebted to Dr. J. D. Main Smith. Each bond indicates a shared electron, whilst the superscript figures give the number of unshared electrons.

This conception of a single-electron linkage (which for brevity will be termed a singlet), in which one electron is held in common by two atoms, played an important part in the earlier electronic theories of Stark ("Atomdynamik," Hirzel, Leipzig, 1916) and was suggested by Thomson (*Phil. Mag.*, 1921, **41**, 510) for the hypothetical NCl_5. More recently, Prideaux's formula for phosphorus pentachloride has been applied by Ingold and Ingold (J., 1926, 1315) to explain certain cases of substitution in the aromatic series. As these authors point out, the singlet linkage in this compound is a semipolar single bond, for it consists of half a covalency and half an electrovalency. If a shared electron is counted as half value for each of the atoms which share it (Lowry, *Trans. Faraday Soc.*, 1923, **18**, 285), there is found to be a positive charge on the phosphorus atom and an effective half negative charge on each of the chlorine atoms held by a singlet. This half charge does not, of course, signify a splitting of the electron, but may be interpreted dynamically on the lines suggested by Højendahl (J., 1924, **125**, 1381) as a statistical average obtained by integrating the field of the electron in the neighbourhood of a particular atom over a time interval which is large compared with the period of revolution in its orbit. From this point of view it is obvious that the effective polarity of a shared electron will only be exactly 0·5 if its orbit lies symmetrically about or between the two atoms which share it; the small variations in polarity discussed by Højendahl on this basis need not be considered here, and, with this reservation, the value 0·5 will be used in calculating polarities.

The most important difference between the point of view expressed by formulæ (II) and (III) is that in (II) the duplet is maintained and the octet rule abandoned, whilst in (III) the octet is completed by violating the rule that electrons are shared only in pairs. It is therefore of interest to inquire what general experimental evidence can be adduced in favour of these two hypotheses. The conception of duplets (Lewis, *loc. cit.*) is based upon (*a*) the occurrence of electrons in pairs at each quantum level throughout the structure of atoms, and (*b*) the presence of an even number of valency electrons in by far the greater number of stable molecules. This, however, can scarcely be regarded as proving the invariable covalency linkage of two electrons. Sufficient " odd " molecules exist to show that the pairing of electrons, although very common, is not necessary for the formation of stable molecules; also pairs of singlet linkages, as in formula (III), may well be present in molecules containing an even number of valency electrons.

On the other hand, the rule of eight can now be supported by a much greater body of experimental evidence. It is an essential feature of Bohr's theory of atomic structure that all the inert gases contain eight electrons of greatest principal quantum number. This conception is retained in the further sub-division into grouplets (Main Smith, " Chemistry and Atomic Structure," Benn, 1924; Stoner, *Phil. Mag.*, 1924, **48**, 719), which has now been shown to give a satisfactory explanation of *X*-ray absorption edges and the complex phenomena of multiplet structure in optical spectra. The volume of physical evidence in favour of the Bohr–Main Smith–Stoner scheme of the distribution of extra-nuclear electrons is now so large that it is highly improbable that any further advance in knowledge will necessitate a serious modification of its main features.

The octet rule has also been shown to predict accurately the occurrence and number of semipolar double bonds in a series of compounds of nitrogen, phosphorus, and sulphur (Sugden, Reed, and Wilkins, J., 1925, **127**, 1525) and further striking evidence for the existence of this type of linkage has been obtained by the preparation of three new types of optically active sulphur compounds by Phillips and his collaborators (J., 1925, **127**, 2522; 1926, 2079; this vol., p. 188). In all these cases the existence of the semipolar double bond indicates that the number of electrons associated with the atoms of nitrogen, phosphorus, and sulphur does not exceed eight.

From these considerations, it appears probable that in compounds of the type of phosphorus pentachloride the rule of eight will still be valid and that (III) represents the structure of this compound better than (II). It is evident, however, that the case for the existence of singlet linkages would be very much strengthened if this rather indirect evidence could be supported by observation of an effect due directly to the presence of singlets. Such evidence is now furnished by the effect of singlets upon the parachor.

The Parachor and Singlet Linkages.

It has been shown (Sugden and Wilkins, this vol., p. 139) that the effect of unsaturated linkages upon the parachor is very nearly proportional to the excess of electrons above two in the linkage considered. Some of the values found are in Table I; the constants for ring structures are not recorded, but they lie between those found for the non-polar double and the single bond, and they can be predicted with fair accuracy on the assumption that they are proportional to the degree of unsaturation.

TABLE I.

Linkage.	No. of electrons.	Parachor.
Triple bond	6	46·6
Non-polar double bond	4	23·2
Single bond (duplet)	2	(0·0)
Semipolar double bond	2	−1·6
Singlet	1	−11·6
Semipolar single bond	1	−12·4

The duplet linkage (the chemical single bond) is of necessity neglected when the atomic constants are computed and must therefore be regarded as an arbitrary zero or normal level from which the effect of other linkages is measured. For the double and the triple bond and for ring structures, each electron above two adds 11·6 units to the molecular parachor; it seems probable, therefore, that this scale can be extended downwards and that the singlet linkage containing one electron less than the duplet will lower the parachor by 11·6 units. When a half-polar bond is present, as in phosphorus pentachloride, there must be added to this the effect of half a polar linkage, which, by comparison with the value for a semipolar double bond (duplet + polar bond), will be − 0·8. The total effect for a semipolar single bond should therefore be − 12·4 units. The singlet linkage is not always polar (compare the formula for acetylacetone derivatives, VIII, p. 1179) and when neutral would have a value of − 11·6 units; the difference is, however, less than the usual error of experiment. The two singlets in formula (III) should therefore give a change of − 24·8 in the molecular parachor.

The polar bond in formula (I) should produce an effect of − 1·6 units only. This value is obtained from the observed effect of the semipolar double bond which consists of a covalency plus an electrovalency. Since a covalency = 0, it follows that an electrovalency = − 1·6. Further evidence for this value is given by the parachors of the halogen hydrides recorded in Table II, calculated from the observations of Steele, McIntosh, and Archibald (*Z. physikal. Chem.*, 1906, **55**, 145). The surface-tension determinations of these workers are based upon the data of Ramsay and Shields and have therefore been corrected as indicated in an earlier paper (Sugden, J., 1924, **125**, 33). This correction increases the value of the parachor by about 1%.

TABLE II.

Substance.	[*P*]obs.	Σ[*P*].		Polar bond.
HCl	67·8	71·4		−3·6
HBr	85·4	85·1		+0·3
HI	105·3	108·1		−2·8
			Mean	−2·0

It is evident that these substances give the same structural constant as the semipolar double bond within the limits of experimental error (± 2 units). It is possible, of course, to argue that in the liquid state the halogen acids are not polarised and that the hydrogen atom is linked by a covalency. On this view, however, the structural constant for formula (I) would also be negligibly small, for it appears highly improbable that liquid phosphorus pentachloride is polar whilst liquid hydrogen chloride is not. A fuller discussion of this point will be given in a later paper in which the data for fused salts will be discussed.

The effect of the enhanced valency shell in formula (II) is rather more difficult to predict. The relation set out in Table I appears to be interpreted most simply by assuming that the effect of linkages upon the parachor is determined chiefly by the space required to accommodate the orbits of the shared electrons, and is very nearly a linear function of the number of shared electrons. On this view, the effect of the structure in (II) may be estimated roughly as follows. Since two extra electrons are shared between six atoms, the effect should be one-third of that found when two extra electrons are shared between two atoms in the non-polar double bond, *i.e.*, 23·2/3 or + 7·7 units.

The parachors for the pentachlorides of antimony and phosphorus have now been determined and are recorded in Table III. The column headed Σ[*P*] gives the sum of the atomic constants, and the last column shows the difference between [*P*]obs. and Σ[*P*], thus giving the effect of any special structure present in the mole-

TABLE III.

Substance.	[*P*]obs.	Σ[*P*].	Structural constant.
Phosphorus pentachloride ...	282·5	309·2	−26·7
Antimony pentachloride	311·8	337·5	−25·7

cule. It will be seen that for both substances the value found for the structural constant is very close to the predicted effect of two singlet linkages, but differs widely from the expected effect of the structures represented by formulæ (I) and (II).

The atomic constant of phosphorus, used in calculating Σ[*P*], has been determined from a number of compounds of this element for which data have already been recorded (Sugden, Reed, and Wilkins, *loc. cit.*). The constant for antimony was obtained from the data shown in Table IV in which Σ[*P*] is the sum of all the atomic and structural constants in the molecule except that for the antimony atom. The mean value, 66·0, can scarcely be in error by more than ± 2 units.

TABLE IV.

Substance.	[*P*]obs.	Σ[*P*].	Antimony.
Antimony trichloride	227·4	162·9	64·5
Triphenylstibine	637·4	570·0	67·4
		Mean	66·0

It should be mentioned that the anomaly exhibited in Table III cannot be accounted for by association of the liquid pentachlorides. Highly associated liquids, *e.g.*, alcohols, have a parachor which is only a few units below the predicted value and which increases as the temperature rises, but the pentachlorides examined show no signs of association—the parachor is nearly independent of temperature and the molecular weights of these substances in organic solvents are normal.

The difference between [*P*]obs. and Σ[*P*] is therefore real, and since the additive nature of the parachor has been verified for a large number of substances, the conclusion seems inevitable that in these pentachlorides a type of valency linkage is present which has not been encountered in earlier work. It is submitted that by far the simplest interpretation of this result, which is in harmony with the established effect of well-known types of valency linkage, is the hypothesis that two singlet linkages are present in the molecule.

If this conclusion is accepted, it follows that the existence of singlet linkages can be detected, and their number determined, by means of the parachor. The extension of the electronic theory of valency to include singlet linkages, or more generally odd-electron linkages, can therefore be subjected to a direct experimental test and has no longer a purely speculative basis; it opens up a wide field for future investigation, as will be seen from the following brief account of the more important theoretical consequences.

Applications of the Theory of Odd-electron Linkages.

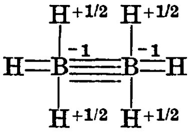
The formulæ suggested below are based upon the following three rules :

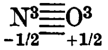
(1) The number of electrons associated with each atom (except hydrogen) does not exceed, and wherever possible is equal to, eight (the octet rule of Lewis).

(2) Atoms may share 1, 2, 3, 4, 5, or 6 electrons with another atom.

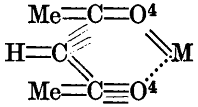
(3) The polarity of an atom in a compound is calculated by reckoning shared electrons at half their value, as proposed by Lowry (*loc. cit.*). When alternative formulæ are possible, the one showing the smallest development of polarity is the more probable.

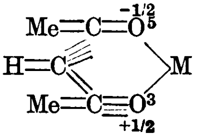
Simple Compounds.—The application of the theory of odd-electron linkages to compounds of the type of SF_6, SCl_4, IF_5, ICl_3, OsF_8, etc., is obvious and has already been discussed by Prideaux (*loc. cit.*). Less obvious is the fact that borethane (IV) and nitric oxide (V) can be formulated with complete octets. Thomson's symmetrical formula for benzene (compare Sugden and Wilkins, J., 1925, **127**, 2518) also involves triplet linkages.

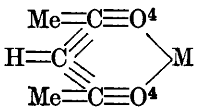
(IV.)


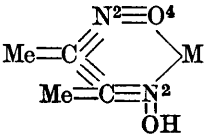

$\underset{-1/2}{N^3}\equiv\underset{+1/2}{O^3}$
(V.)

Chelate Linkages.—Singlet linkages give a simple explanation of the hypothetical residual valency bonds assumed to exist in many chelate groups. The oxalyl radical and ethylenediamine can, of course, be linked by two duplets, but in acetylacetone derivatives the metal is supposed to be attached to the second oxygen atom by a residual valency often indicated by a dotted line. This is shown in (VI) in which M represents one equivalent of a metal. The metal can, however, be attached to both oxygen atoms by singlets as in (VII); this formula contains polar oxygen atoms which can be neutralised by replacing the two double bonds by four triplets as in (VIII), in which all the atoms are neutral.

(VI.)



(VII.)

(VIII.)



(IX.)

Formula (IX) represents in similar fashion the structure of derivatives of dimethylglyoxime, and gives a neutral molecule in which all the atoms, except hydrogen, have complete octets. It will be seen that the metal is co-ordinated with oxygen and nitrogen; if it is co-ordinated with the two oxygen atoms it incurs unlikely polarities.

Co-ordination Compounds.—In the older form of the electron theory of valency the existence of co-ordination numbers higher than 4 seemed to necessitate the abandonment of the octet rule. If singlet linkages are used, co-ordination numbers of 5, 6, 7, and 8 can readily be accounted for by the presence of 2, 4, 6, and 8 singlet linkages, respectively.

The cobaltammines and similar compounds can easily be formulated by building up an octet in the valency shell of the ion of the metal. This involves the assumption, first put forward by Lewis (*J. Amer. Chem. Soc.*, 1916, **38**, 762) and elaborated by Bury (*ibid.*, 1921, **43**, 1602), that the electronic structure of the transition elements is not uniquely determined. This suggestion has been verified by recent work on optical spectra, and the table of electronic configurations compiled by McLennan, McLay, and Smith (*Proc. Roy. Soc.*, 1926, **112**, 76) contains a number of examples of alternative structures which give rise to different groups of lines in the spectra of one element.

The structures of hexamminocobaltic chloride and potassium hexachlorocobaltiate are represented on this view by (X) and (XI). The polarities of the atoms are indicated in the formulæ, and it will be seen that in both cases the central cobalt atom has a net charge of -1, since its original charge of $+3$ is more than neutralised by sharing 8 electrons with the co-ordinated groups. The net charge of the complex ion as a whole is predicted correctly by summing the polarity of each group as indicated in the formulæ.

The corresponding derivatives of iron, chromium, and nickel can readily be formulated in a similar manner. The formula for potassium ferricyanide is, *mutatis mutandis*, similar to (XI). The replacement of the ferric ion by the ferrous ion merely alters the charge on the complex ion from -3 to -4 in potassium ferrocyanide. In all these formulæ a definite structure in harmony with the octet rule is assigned to the complex within Werner's square brackets

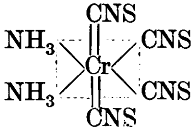
$$\left[(\underset{+1/2}{H_3N^1}—)_4\underset{-1}{Co}(=\underset{+1}{NH_3})_2\right]^{+++}3\overset{-}{Cl}{}^8 \qquad \left[(\underset{-1/2}{Cl^7}—)_4\underset{-1}{Co}(=Cl^6)_2\right]^{---}3\overset{+}{K}$$

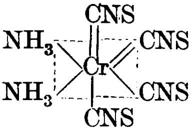
(X.) (XI.)

by substituting singlet linkages for the less clearly-defined " residual affinities." The recent work of Burgess and Lowry (J., 1924, **125**, 2081), Mills and Gotts (J., 1926, 3121), and Mann and Pope (*ibid.*, p. 2675) shows clearly that residual affinities are sufficiently well-defined entities to be capable of bringing about molecular asymmetry, and in all the compounds studied by these investigators singlet linkages can be employed to give a concrete picture of the bonds which are presumed to be responsible for the development of optical activity.

It would appear at first that formula (X) would give too many isomerides for co-ordination compounds containing two or more different radicals within the complex. The restrictions of the polarity rule (p. 1179), which means in this case that the duplet linkages are, wherever possible, associated with negative groups, reduce the number of possible isomerides in most cases to that which would be expected on the usual theory of a symmetrical octahedral structure. One interesting difference is found for substances of the type of Reinecke's salt, $NH_4[Cr(CNS)_4(NH_3)_2]$, which on the singlet theory might exist in two forms, (XII) and (XIII); the second of these, in which the duplets are *cis*, should be resolvable.

(XII.)



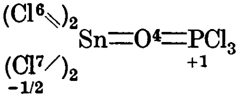


(XIII.)

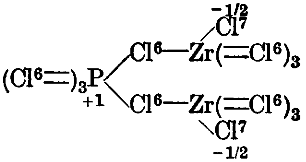
Since, however, a duplet linkage is much more bulky than a singlet, it appears probable that the normal form has the *trans*-structure (XII).

Molecular Compounds.—A large number of additive compounds, formed by the higher halides of Groups IV, V, and VI, are not readily formulated on Werner's co-ordination theory; some of these possess an extraordinary stability, *e.g.*, $SnCl_4,POCl_3$, b. p. 180°; $2ZrCl_4,PCl_5$, b. p. 416°; $2ZrCl_4,POCl_3$, b. p. 363°. All these compounds can be formulated by using singlet linkages. In general, the formulæ are obtained by supposing that two of the halogen atoms in one molecule, which were originally linked by duplets, become linked by singlets; the central atom is then sharing only 6 electrons and can link with a lone pair of electrons in the second compound. Formula (XIV) gives such a structure for $SnCl_4,POCl_3$; similar formulæ account for the well-known series of additive compounds of stannic chloride with ketones which have the composition $SnCl_4,2R_1R_2CO$. In the corresponding series of compounds with antimony pentachloride, the compounds so far described have the compositions $SbCl_5,R_1R_2CO$ or $2SbCl_5,3R_1R_2CO$; these are exactly the compounds to be expected if the linkage between the molecules is made possible by the conversion of halogens linked by duplets into halogens linked by singlets. The very stable compound $2ZrCl_4,PCl_5$ appears to be of a rather different type in which each

(XIV.)



$$\begin{matrix}(Cl^6\diagdown)_2 & & \\ & Sn{=}O^4{=}PCl_3 & \\ (Cl^7\diagup)_2 & \quad\quad +1 & \\ -1/2 & & \end{matrix}$$



$$(Cl^6{=})_3\underset{+1}{P}\begin{matrix} \overset{-1/2}{\diagup Cl^7} \\ \diagup Cl^6\text{—}Zr({=}Cl^6)_3 \\ \diagdown Cl^6\text{—}Zr({=}Cl^6)_3 \\ \underset{-1/2}{\diagdown Cl^7}\end{matrix}$$

(XV.)

of the chlorine atoms originally linked by singlets shares an electron with a zirconium atom (XV). A similar structure can be written for the corresponding compound with phosphorus oxychloride.

Finally, the singlet linkage gives a concrete picture of the vague term " residual affinity " used to explain so many chemical changes, *e.g.*, the Wagner–Meerwein transformation, the *trans* Beckmann change, etc.; in many of the theories of these reactions, in which a residual affinity becomes a complete covalency after a series of changes, the use of singlet linkages gives a clearer picture of the mechanism of the reaction. Another interesting aspect of the singlet, when it forms a semipolar single bond, is that it is a definite half-way stage between a covalency and a polar valency.

Sufficient has been said to show that the theory of odd-electron linkages here put forward is capable of simplifying and correlating a large body of chemical knowledge. Furthermore, it leads to conclusions (*e.g.*, the magnitude of the parachor) which can be subjected to an experimental test, and therefore fulfils all the requirements of a sound working hypothesis. In succeeding papers of this series it is hoped to apply this and other tests to a number of the substances formulated above; many of them are fusible without decomposition and can therefore be dealt with by the experimental methods described in this and other papers on the parachor.

EXPERIMENTAL.

In the course of this investigation measurements have been made of the surface tension and density of phosphorus pentachloride, antimony trichloride, and antimony pentachloride. From these, the parachors were calculated by the relation $P = \gamma^{1/4}/(D - d)$, where γ is the surface tension, and D and d are the densities of the liquid and saturated vapour, respectively.

Phosphorus pentachloride was purified by sublimation and stored in sealed tubes. It melted in a closed tube at 163—164° (corr.), which is much higher than the value, *viz.*, 148°, given by Casselmann (*Annalen*, 1852, **83**, 247). A small infusible residue remained when a quantity of the substance was melted; this appeared to be insoluble in the liquid and since its amount was small it is believed not to have any serious effect upon the surface-tension or density measurements.

Since the pentachloride has a large vapour pressure at its melting point, all the measurements had to be carried out in sealed vessels. The density of the liquid was therefore determined by the method of flotation. Small glass floats about 5 × 1 × 1 mm. were prepared and the temperature was determined (to the nearest 0·5°) at which they were in equilibrium with a suitable mixture of bromoform and benzene. The density of the liquid at this temperature was then determined by means of a pyknometer.

Each float was placed in a marked piece of quill tubing sealed at one end. One of the storage tubes was then broken and the open end of the quill tube forced into the mass of pentachloride until a sufficient quantity of the substance had been picked up; the pentachloride was rapidly tapped down to the closed end, and the tube sealed off. In this way exposure to the atmosphere for more than a few seconds was avoided and only a negligible quantity of moisture could have been absorbed.

Tubes filled in this manner were supported in a glycerol-bath provided with a thermometer and stirrer, and the temperatures of flotation were determined. Molten phosphorus pentachloride proved to be a mobile liquid and no difficulty was experienced in fixing the flotation temperatures to within ± 0·5°. The following results were obtained.

Float	1	5	6
Density	1·482	1·520	1·559
Flotation temp. (corr.)	218°	200·5°	181°

$$\text{whence } D\,\dot{\bullet} = 1{\cdot}624 - 0{\cdot}00208\,(t - 150).$$

A rough determination of the vapour pressure (dissociation pressure) was next made to ascertain the order of magnitude of the pressure within the tubes. This proved to be unexpectedly small, so that the density of the vapour could be calculated with sufficient accuracy from the vapour-pressure observations.

A quantity of the pentachloride was confined in a bulb of about 5 c.c. capacity connected to a capillary tube bent at right angles to give a long capillary limb. An index of mercury separated the gas in the bulb from a fixed quantity of air in the long limb of the apparatus; the distant end of the capillary tube was sealed whilst the whole apparatus was at a known temperature and at atmospheric pressure. The bulb was then heated in a glycerol-bath, and the volume of the air in the long limb measured by means of a millimetre scale. From this volume, the total pressure in the apparatus was calculated; by subtracting the pressure of the air present initially in the bulb, the vapour pressure (in atm.) of the pentachloride was obtained.

t (corr.).	Reading.	p_{total}.	p_{air}.	p_{PCl_5}.
13°	24·3	1·00	1·00	—
142·5	14·1	1·72	1·45	0·27
163	11·1	2·41	1·52	0·67
182	8·1	3·00	1·59	1·41
195·5	6·6	3·68	1·64	2·03

These figures can only be regarded as a rough approximation, but they indicate that below 200° no great pressure is developed. From the results, the density of the vapour at the three temperatures used for the measurement of the surface tension was calculated as follows. If the gas laws can be assumed to hold for the vapour, the density is given by $d = Mp/RT$, where M is the molecular weight and p the pressure. For phosphorus pentachloride a correction must be applied for the degree of dissociation, α, so that the formula becomes, putting $M = 208{\cdot}3$ and expressing R in c.c.-atm., $d = 2{\cdot}54\ p/(1 - \alpha)T$. The pressure p was interpolated from the figures given above, whilst the dissociation constant K was obtained from the observations of Cahours (*Annalen*, 1867, **141**, 42). Incidentally, it may be noted that, since the degree of dissociation in the vapour is less than 50%, the dissociation of the liquid must be very small. The calculation of d is set out below; as the values found are small compared with the liquid density, they need not be known with great accuracy, since it is the quantity $(D - d)$ which is used in calculating the parachor.

t (corr.).	p (atm.).	K.	α.	d.	D.	$D - d$.
169·5°	0·78	0·175	0·43	0·0031	1·583	1·580
181	1·02	0·205	0·41	0·0041	1·560	1·556
192	1·81	0·255	0·35	0·0073	1·537	1·530

The surface tension was measured by the method of capillary rise, the apparatus and microscope fittings already described by the author (J., 1921, **119**, 1483) being used. Apparatus 3 was employed for which $r_1 = 0{\cdot}005495$ cm. and $r_2 = 0{\cdot}1310$ cm. The method of calculating a^2 from the capillary rise, H, was described in the above paper. The following results were obtained :

t (corr.).	H (mm.).	a^2 (mm.^{2}).	$D-d$ (g./c.c.).	γ (dynes/cm.).	Parachor.
169·5°	3·027	2·690	1·580	20·9	281·8
181	2·918	2·592	1·556	19·8	282·5
192	2·815	2·496	1·530	18·7	283·1
					Mean 282·5

[With Adolph Freiman.]

The surface tensions of antimony tri- and penta-chlorides were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27). The tables are set out in the manner described in earlier papers of this series. The bubbler used was No. 16a, and had the following constants : $r_2 = 0{\cdot}179$ cm., $A = 0{\cdot}008271$.

Antimony trichloride, $M = 228{\cdot}2$, was purified by distillation and had b. p. 219° (corr.). Densities determined : $D_{4^\circ}^{95\cdot5^\circ}$ 2·632, $D_{4^\circ}^{123\cdot5^\circ}$ 2·565, $D_{4^\circ}^{149\cdot5^\circ}$ 2·510-; whence $D_{4^\circ}^{t^\circ} = 2{\cdot}844 - 0{\cdot}00224t$. These densities are in good agreement with those found by Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1).

App.	*t*.	*P*.	*D*.	*φ*.	*γ*.	Parachor.
16a	109·5°	5067	2·599	1·0621	44·51	226·7
,,	127·5	4748	2·558	1·0653	41·84	226·9
,,	148·5	4462	2·511	1·0682	39·43	227·6
,,	166·5	4219	2·471	1·0710	37·38	228·3
					Mean	227·4

Antimony pentachloride, $M = 298{\cdot}1$, was distilled under diminished pressure; the fraction used boiled at 85° (corr.)/55 mm. Owing to the hygroscopic nature of this substance the densities were measured by using a sealed dilatometer. Densities determined : $D_{4^\circ}^{11\cdot5^\circ}$ 2·370, $D_{4^\circ}^{16^\circ}$ 2·358, $D_{4^\circ}^{36^\circ}$ 2·319, $D_{4^\circ}^{52^\circ}$ 2·289, $D_{4^\circ}^{78^\circ}$ 2·231; whence $D_{4^\circ}^{t^\circ} = 2{\cdot}392 - 0{\cdot}00204t$.

App.	*t*.	*P*.	*D*.	*φ*.	*γ*.	Parachor.
16a	15·5	4130	2·360	1·0692	36·53	311·5
,,	36	3938	2·318	1·0713	34·90	312·5
,,	56	3605	2·278	1·0765	32·11	311·4
,,	68	3447	2·253	1·0792	30·78	311·6
					Mean	311·8

Triphenylstibine, $M = 353{\cdot}0$. The following data are taken from the work of Walden and Swinne (*Z. physikal. Chem.*, 1912, **79**, 700). Since these investigators used Ramsay and Shields's value for benzene in standardising their apparatus, the surface tensions are corrected by multiplying by 1·0335 (Sugden, J., 1924, **125**, 34).

t.	*γ*.	*γ* (corr.).	*D*.	Parachor.
35·1	41·63	43·01	1·4200	636·6
47·0	40·58	41·93	1·4105	637·0
63·1	39·08	40·38	1·3952	637·7
77·3	37·60	38·85	1·3820	637·9
91·2	36·12	37·32	1·3683	637·7
103·0	34·92	36·08	1·3568	637·7
			Mean	637·4

Summary.

(1) The parachors of phosphorus and antimony pentachlorides have been determined and are 26 units below the sum of the atomic constants.

(2) Three formulæ for the structure of these substances from the standpoint of electronic valency theory have been discussed, and

the effect of each upon the parachor has been deduced by the aid of the relation between the parachor and the number of electrons in a linkage.

(3) The formula of Prideaux, in which two singlet linkages are present, is considered to give the best and simplest explanation of the observed anomaly. The parachor can therefore be used to detect the presence of such linkages, since each singlet linkage contributes — 12·4 units to this molecular constant.

(4) The electronic theory has been extended to include linkages composed of odd numbers of shared electrons. The modified theory has been applied to deduce formulæ for the higher halides of Groups V, VI, VII, and VIII, for borethane, nitric oxide, chelate groups, co-ordination compounds, and for a number of "molecular compounds."

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