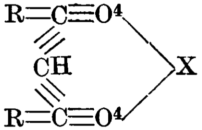
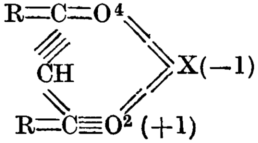
XLIX.—*The Parachor and Chemical Constitution. Part X. Singlet Linkages in Chelated Co-ordination Compounds.*

By SAMUEL SUGDEN.

IN Part V of this series (J., 1927, 1173), the author suggested that the metallic derivatives of the β-diketones possessed the structure shown by the electronic formula (I).* Here both the oxygen atoms of the diketone are attached to an equivalent of the metal X by singlet linkages. According to the general theory of Sidgwick ("The Electronic Theory of Valency," Oxford Univ. Press, 1927, 52 *et seq.*), these substances would have the structure (II), in which the bond between one oxygen atom and the metal is a "co-ordinate link," *i.e.*, a duplet link in which one atom (oxygen) supplies both electrons. There is now ample stereochemical evidence for assuming that the linkages to the metal in these substances are "directed" linkages (compare Burgess and Lowry, J., 1924, **125**, 2081; Mills and Gotts, J., 1926, 3121; Mann and Pope, *ibid.*, p. 2675), so that other formulæ involving polar bonds need not be considered.

(I.)





(II.)

The main object of this investigation was to ascertain whether the metallic derivatives of β-diketones exhibited the parachor anomaly which has been found in other compounds containing singlet linkages, *e.g.*, phosphorus and antimony pentachlorides (Sugden, *loc. cit.*). Compounds of uni-, bi-, and ter-valent metals with different chelate groups have been examined, and in each case the expected deficiency in the parachor has been found. Before considering the experimental results it is convenient to point out one difference between the implications of the singlet and the duplet formulæ for these substances which appears to be of considerable importance.

It was first suggested by Lowry (*Trans. Faraday Soc.*, 1923, **18**, 285) that the effective charges of each atom in the molecule could be calculated by reckoning each shared electron at half its value. Numerous recent investigations on the dipole moments of molecules calculated from dielectric constants have shown that this hypothesis, whilst not strictly accurate, is substantially correct. According to Lowry's hypothesis, all organic compounds except those containing

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* In these formulæ each link represents one shared electron, and the superscript numbers give the number of unshared electrons.

polar bonds (or semipolar double bonds) should have zero moment; it is found that ketones, alcohols, amines, etc., do exhibit a small moment of about 1—2 × 10^{-18} e.s.u., but this is much less than the moment corresponding to unit opposite charges on adjacent atoms separated by an atomic diameter (say 10^{-8} cm.), *viz.*, 4·8 × 10^{-18} e.s.u. Moments of this magnitude are only found with compounds, *e.g.*, nitrobenzene, which contain a semipolar double bond; hence the net atomic charges calculated on Lowry's hypothesis will probably be nearly correct. When this method is applied to formulæ (I) and (II), it is readily seen that (I) gives neutral atoms whilst (II) gives a *negative* metal atom attached to a *positive* oxygen atom. This, in the author's opinion, is highly improbable, not so much because the existence of a dipole is postulated, but because the charges ascribed to the atoms are directly opposed in sign to those which would be expected from their known electron affinity. Thus for the stable aluminium acetylacetonate, formula (II) gives an aluminium atom with three *negative* charges attached to three *positively* charged oxygen atoms; if such a structure were formed, it seems probable that the electronegative oxygen, with its high affinity for electrons, would abstract an electron from the electropositive aluminium atom, giving a rearrangement of linkages which would neutralise the atomic charges, *e.g.*, (I).

With the pentachlorides of phosphorus and antimony the polarity argument has not the same cogency. Here the duplet formula gives neutral atoms whilst the singlet formula gives a positive charge to the phosphorus or antimony, and a negative charge to two of the halogen atoms. These charges are, of course, compatible with the electrochemical character of the elements concerned.

(1) *Thallium Compounds.*

The work on thallium compounds has been greatly facilitated by the kindness of Dr. R. C. Menzies in lending specimens of thallous ethoxide, ethyl thalloacetoacetate, and dimethylthallium benzoylacetone. The parachors of these and other thallium compounds are collected in Table I and are used to determine the atomic parachor for thallium. The calculation of $\Sigma[P]$ for the co-ordinated compounds (omitting the constant for thallium) is illustrated by the case of ethyl thalloacetoacetate :

C_6 = 6 × 4·8 = 28·8
H_9 = 9 × 17·1 = 153·9
O_3 = 3 × 20·0 = 60·0
2 Non-polar double bonds = 46·4
6-Membered ring = 6·1
$\Sigma[P]$ (duplets) = 295·2.

For the singlet formula the contribution due to two singlet linkages, 2 × (−11·6), must be included. Hence

$\Sigma[P]$ (singlets) = 272·0.

It will be seen that the full value for the six-membered ring is

TABLE I.

			Singlets.		Duplets.	
Substance.	Formula.	[*P*] obs.	$\Sigma[P]$.	Tl.	$\Sigma[P]$.	Tl.
Ethyl thalloaceto-acetate	$TlC_6H_9O_3$	332·2	272·0	60·2	295·2	37·0
Dimethylthallium benzoylacetone ...	$Me_2TlC_{10}H_9O_2$	523·7	459·1	64·6	482·3	41·4
			Mean	62·4	Mean	39·2

		[*P*] obs.	$\Sigma[P]$.	Tl.
Thallous ethoxide ...	TlOEt	177·3	115·1	62·2
Thallous formate ...	$TlCHO_2$	150·3	80·3	70·0
Thallous acetate ...	$TlC_2H_3O_2$	183·5	119·3	64·2
Thallous nitrate ...	$TlNO_3$	177·3	92·5	(84·8)
		Mean (excluding nitrate)		65·5

included in both cases, although in the singlet formula this ring contains two singlet linkages. This treatment gives satisfactory results with all the cyclic co-ordinated compounds discussed in the present paper, even when the ring contains a larger number of singlets. Another point which should be mentioned is that no correction is introduced for the variation in size of the shell of electrons around the metallic atom. It will appear later (p. 323) that the size of this shell has no effect upon the parachor.

The two co-ordinated thallium compounds give Tl = 62·4 for the singlet formula, and Tl = 39·2 for the duplet formula. The simpler compounds of known structure in the lower part of the table show clearly that the first of these figures is correct and that the lower value given by the duplet formula is inadmissible. Thallous nitrate gives an abnormally high value for which no explanation can be offered at present. A similar large positive anomaly has been found with other salts of strong acids and bases and with certain fused metals, and will be discussed in a later paper. From all the thallium compounds except the nitrate the mean parachor is Tl = 64.

Further evidence in favour of this value is furnished by the constants for the adjacent elements in the periodic table, *viz.*, mercury and lead. For metallic mercury $[P] = 69{\cdot}4$; for mercury diphenyl $[P]$ obs. $= 448{\cdot}7$, $\Sigma[P] = 380{\cdot}0$, whence Hg = 68·7. A carefully purified specimen of lead tetraethyl, for which the author is indebted to Dr. E. W. J. Mardles, gave $[P]$ obs. $= 456{\cdot}6$, $\Sigma[P] = 380{\cdot}4$, whence Pb = 76·2. The sequence Hg = 69, Tl = 64, Pb = 76 is reasonable, but the value Tl = 39 is inconsistent. It is evident that the co-ordinated thallium compounds exhibit the parachor anomalies predicted for the singlet linkages in formula (I).

(2) *Beryllium Compounds.*

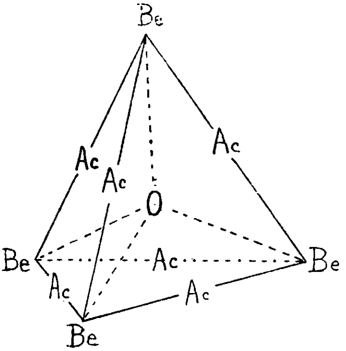
The parachors of three beryllium compounds are given in Table II; these substances were all prepared from a highly purified specimen of the oxide for which the author is indebted to Prof. J. F. Spencer.

TABLE II.

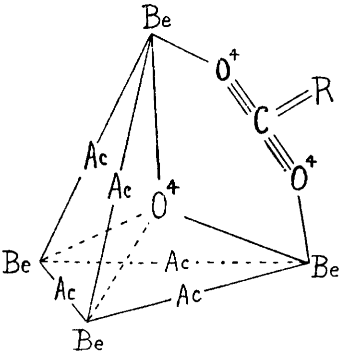
			Singlets.		Duplets.	
Substance.	Formula.	[P] obs.	Σ[P].	Be.	Σ[P].	Be.
Beryllium acetylacetonate	$Be(C_5H_7O_2)_2$	470·4	426·0	44·4	472·4	− 2·0
Beryllium propionylacetonate	$Be(C_6H_9O_2)_2$	539·0	504·0	35·0	550·4	−11·4
Basic beryllium propionate	$Be_4O(C_3H_5O_2)_6$	985·4	849·6	34·0	1035·2	−12·4
			Mean	37·8	Mean	− 8·6

For this element there are no suitable fusible compounds of known constitution which can be used to determine the atomic parachor independently, but a limit can be set by assuming that it must lie between the constants for the adjacent elements, lithium and boron. The data of Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1) for fused lithium salts give rather variable results but indicate that Li = *ca.* 50, whilst the constant for boron is 16·4 (Etridge and Sugden, J., 1928, 989). The value Be = 37·8 given by the singlet formula is compatible with these results, whereas the negative value given by the duplet formula is quite inadmissible.

The third compound in the table is one member of a series of beryllium compounds of a peculiar type. The disposition of the atoms in the molecule of the corresponding acetate has been established by *X*-ray analysis of the crystals (Bragg and Morgan, *Proc. Roy. Soc.*, 1923, *A*, **104**, 437; Morgan and Astbury, *ibid.*, 1926, *A*, **112**, 441). A unique oxygen atom occupies the centre of a tetrahedron at the corners of which the beryllium atoms are situated, and the six acyl groups span the six edges of the tetrahedron (III).



(III.)



(IV.)

This formula is readily interpreted in terms of singlet linkages as shown in (IV); it consists of six interlocked six-membered rings of which only one is shown in detail in the formula. Here, as in the singlet formulæ for the acetylacetonates, etc., all the atoms in the molecule are neutral, and the acyl groups are disposed in such a manner as to give the symmetrical arrangement of the oxygen atoms required by the *X*-ray evidence. If the singlet linkages are replaced by duplets, unlikely polarities are produced : the beryllium atoms become negative and the central oxygen atom is assigned a charge of + 2, which is highly improbable.

An attempt was made to determine the parachor of the acetate, but its high vapour pressure at its melting point causes such rapid evaporation that trustworthy surface tension data have not yet been obtained. The next homologue has a much lower melting point and could be more easily handled ; its parachor quoted in Table II is in good agreement with formula (IV), but is incompatible with the similar formula in which the singlet linkages are replaced by duplets. In computing [*P*] calc. for this substance the constant for the ring system is taken as that of 6 six-membered rings.

(3) *Aluminium Compounds.*

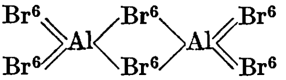
Table III shows the parachors of three aluminium compounds, of which the first two contain three β-diketone residues so that the difference between the values of Σ[*P*] calculated for the singlet and duplet formulæ is large. Here again the singlet formula gives a reasonable atomic parachor, Al = 38·6, whereas the duplet formula gives a negative constant. The value given by the singlet formula lies satisfactorily between the constants for sodium (*ca.* 80, from Jaeger's data on fused salts) and silicon (*ca.* 25) ; it is also between the constants for boron (16·4) and gallium (50·0), the last value being calculated from the observations of Richards and Boyer (*J. Amer. Chem. Soc.*, 1921, **43**, 274) on molten gallium.

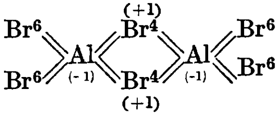
The third substance in Table III, aluminium bromide, presents some features of special interest. Its molecular weight as vapour, and in most solvents, corresponds to Al_2Br_6, and the fused substance has practically no electrical conductivity for 100° above its melting point. The polar formula $Al^{\cdots}[AlBr_6]'''$ is therefore excluded and the substance must be regarded as a covalent compound. The simplest symmetrical formula which can be written for the double

TABLE III.

Substance.	Formula.	[*P*] obs.	Singlets. Σ[*P*].	Singlets. Al.	Duplets. Σ[*P*].	Duplets. Al.
Aluminium acetylacetonate	$Al(C_5H_7O_2)_3$	680·5	639·0	41·5	708·6	−28·1
Aluminium propionylacetonate	$Al(C_6H_9O_2)_3$	788·0	756·0	32·0	825·6	−37·6
Aluminium bromide ...	Al_2Br_6	457·6	373·2	42·2	419·6	+19·0
			Mean	38·6		

molecule is shown with singlet linkages in (V) and with duplet linkages in (VI). It will be seen from Table III that (V) gives a parachor for aluminium which agrees with that found from the β-diketone derivatives, whereas (VI) gives a result which differs from the parachor given by these substances with either singlet or duplet formulæ. Moreover, (VI) is open to objection on the grounds of polarity, for it postulates negative aluminium atoms and positive bridging bromine atoms.


(V.)


(VI.)

(4) *Unco-ordinated Derivatives of β-Diketones.*

In the course of this work several substances have been found which behave as if they possess an open-chain structure and do not contain the characteristic chelate ring: their parachors are collected in Table IV, which includes the free diketones as well as certain derivatives. It has frequently been assumed that a hydrogen atom can be linked to two other atoms, as in the anion of dimeric hydrofluoric acid, F·H·F′, and can complete a chelate ring, thus giving a cyclic structure to the enol form of the free β-diketones. On theoretical grounds this structure is possible if the two links are singlets, but the hypothesis of two duplet links proceeding from a hydrogen atom appears to be incompatible with Pauli's exclusion principle (*Z. Physik*, 1925, **31**, 765), which plays such an important part in modern theories of spectra and atomic structure. The number of electrons which can occupy the *K*-level in any atom is limited strictly by Pauli's rule to two, and in the modern wave-mechanics theory of covalent linkages this restriction holds for shared electrons

TABLE IV.

Substance.	Formula.	[*P*] obs.	[*P*] calc. (open chain).	[*P*] calc. (co-ordinated; singlets).
Acetylacetone	$C_5H_8O_2$	245·4	247·2	230·1
Propionylacetone ...	$C_6H_{10}O_2$	279·7	286·2	269·1
Benzoylacetone	$C_{10}H_{10}O_2$	382·4	381·1	364·0
Boron acetylacetone difluoride	$(C_5H_7O_2)BF_2$	300·6	297·5	280·4
Stannic bisacetylacetone dichloride	$(C_5H_7O_2)_2SnCl_2$	617·2	627·5*	591·3*

* Sn = 56·5. This value is based on the parachors of stannic chloride and bromide, the determination of which will be described in a later communication.

also (compare Heitler and London, *ibid.*, 1927, **44**, 455; London, *ibid.*, 1928, **46**, 455). Hence the singlet structure —H— is possible, but not the duplet structure =H=.

The experimental results show, however, that the free β-diketones have but little tendency to form the chelate ring. Propionylacetone gives a parachor a little smaller than the value calculated for the open-chain formula, and this may be due to the presence of some 30% (±10%) of the cyclic isomeride. In making this estimate, the influence of the change from the keto to the enol (or dienol) structure, which might cause a small decrement due to the pressure of a free hydroxyl group, has been ignored for the following reasons. (1) The decrement is only 4—5 units in the lower alcohols and diminishes rapidly as the homologous series is ascended, so it would not be expected appreciably to affect the parachor in question. (2) By his bromine titration method, K. H. Meyer (*Ber.*, 1912, **45**, 2843) finds that pure acetylacetone is 76% and benzoylacetone 98% monoenolic; their parachors agree well with the values calculated for the diketone formula (Table IV), so the effect of enolisation is negligibly small.

The parachors found for the last two substances in the table are unexpected, but show quite definitely that these compounds are mainly open-chain derivatives of acetylacetone, *e.g.*,

$$CH_3{\cdot}CO{\cdot}CH{:}C(OBF_2){\cdot}CH_3.$$

This boron compound, examined by Morgan and Tunstall (J., 1924, **125**, 1965), differs markedly in its properties from the well-known bisacetylacetone boronium chloride. The fluoride is definitely a covalent compound, whilst the chloride gives rise to a series of salts in which the ionised chlorine atom is replaced by a number of other anions. In the tin series (Morgan and Drew, *ibid.*, p. 375) the bromide possesses properties somewhat different from those of the chloride and may have a different structure.

It is clear from the data in Table IV that a derivative of a β-diketone or any similar compound which contains chelate groups is not necessarily co-ordinated, and that the formation of the characteristic chelate ring can be detected by means of the parachor. An interesting field of investigation presents itself in the study of the conditions which favour or inhibit the formation of the ring; from the few results at present available it is clear that the nature of the metallic atom, the other groups attached to this atom, and the substituents attached to the β-diketone molecule may all play a part. In particular, the somewhat large variation in the atomic constants for beryllium and aluminium (see Tables II and III) may be due to incomplete co-ordination of the acetylacetonates at their melting point, whilst the other derivatives with lower melting points are more completely co-ordinated. To settle this point, an investigation of the parachors of a number of beryllium compounds with different types of chelate groups is now in progress.

Discussion.

It is evident from the results described in sections (1), (2), and (3) that the parachor anomaly detected in the higher halides is reproduced in the co-ordinated compounds of uni-, bi-, and ter-valent metals, and that the parachors of all these compounds are accounted for simply and consistently by the hypothesis of singlet linkages. The higher valencies in these compounds must therefore be due to the operation of some common mechanism, and any alternative explanation in which duplet links are retained must also be capable of predicting the parachor anomaly in both series of compounds.

A little consideration of the formulæ will show that such an explanation cannot be found in the size of the electronic shell about the central atom. Thus, on the assumption of duplet linkages, the thallium atom in the co-ordination compounds studied has a shell of 6 or 8, the beryllium atom 8, the aluminium atom 12, and, in the pentachlorides, the phosphorus and antimony atoms have a shell of 10. There is no simple relation between these numbers and the observed parachor anomalies.

It is possible, however, to formulate an alternative explanation in which the duplet linkages are retained and most of the parachor anomalies accounted for. This consists in the simple hypothesis that the sharing of an electron brings about a contraction of about 12 units in the parachor.

It is convenient here to distinguish between the normal and the higher valencies of an element. The former may be defined in the following manner. If an element possesses n valency electrons, then its normal valency is n or $8-n$, whichever is the smaller. The value of this definition lies in the fact that for all substances in which the elements exert their normal valencies the chemical formulæ can be translated into electronic formulæ by replacing each chemical bond by a shared pair of electrons. Higher valencies may then be ascribed to (*a*) the transference of electrons from one atom to another as in polar bonds and semipolar double bonds, (*b*) the sharing of more than the normal number of electrons, and (*c*) the formation of singlet linkages.

The values at present adopted for the atomic parachors are in nearly every case deduced from compounds in which the constituent elements exert their normal valencies. The one assumption made in deducing these constants is that the contribution of a single chemical bond is zero. It is readily shown that this hypothesis really means that the effect of sharing an electron is neglected. So long, however, as these constants are used to predict the parachors of other normal compounds, any error due to this omission is automatically allowed for, since each atom in the molecule is again sharing its normal number of electrons. The same compensation is found for compounds containing semipolar double bonds; thus in phosphorus oxychloride, the phosphorus atom shares 5 of its electrons with other atoms,or two more than the normal number, but this is balanced by the fact that the oxygen atom, which normally shares 2 of its 6 electrons, now shares none.

In the higher halides the singlet formula again gives the normal number shared, but the duplet formula does not Thus in phosphorus pentachloride, if all the chlorine atoms are held by duplets the total number of shared electrons is 10. In compounds in which these elements exert normal valencies the number shared is 3 for phosphorus, and 1 for each chlorine atom, giving a total of 8. In this pentachloride two extra electrons are shared, and if sharing gives a contraction of 12 units per electron, a parachor anomaly of —24 would be expected. Similarly, in the metallic derivatives of β-diketones, the formation of each of Sidgwick's " co-ordinate links " corresponds to the sharing of two extra electrons; parachor anomalies of — 24, — 48, and — 72 are therefore predicted for substances containing 1, 2, and 3 β-diketone residues, respectively. For the higher halides and the co-ordinated compounds the parachor results can therefore be accounted for by either the duplet or singlet structures.

A direct test which distinguishes between these two hypotheses is, however, provided by the data for mercury and thallium compounds (p. **318**). Elementary mercury is monatomic in the vapour state and probably also as liquid; if this is the case, the mercury atom has two unshared electrons. In mercury diphenyl these electrons are shared, so that, if sharing produces a contraction, the parachor for mercury deduced from the latter compound should be smaller than that found for metallic mercury; but the experimental data give almost identical values for the mercury parachor from these two substances. A still better example is provided by the first two thallium compounds in Table I. The thallous compound possesses two unshared electrons which are shared in the dimethylthallium derivative; both substances give very nearly the same value for the parachor of thallium, thus showing that sharing an electron has little or no effect upon its contribution to the parachor.

The author has not been able to find any other simple hypothesis which will allow the duplet formulæ to be retained and will also account for the parachor anomalies. The duplet formula is in any case open to criticism because of the improbable intramolecular polarities which it postulates. The theory of singlet, or more generally, odd-electron linkages is therefore at present the only hypothesis which gives a simple and consistent explanation of the experimental data.

One feature of the results of this investigation is the stability of valency shells of 4 electrons in the beryllium compounds and of 6 electrons in the aluminium compounds. In the light of these results it seems probable that other compounds of co-ordination number 6, *e.g.*, the cobaltammines, may also possess a stable group of 6 electrons, so that the six co-ordinated groups are held by singlet linkages. This view removes the stereochemical objections which can be raised against the arrangement suggested in an earlier paper (Sugden, *loc. cit.*, p. 1180) in which it was supposed that an octet was attained and two of the groups were held by duplets.

EXPERIMENTAL.

Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27) except for aluminium bromide, for which the method of capillary rise was employed (Sugden, J., 1921, **119**, 1483). Densities were in most cases determined by means of the U-shaped pyknometer described previously (J., 1924, **125**, 1171), which proved satisfactory even with substances melting above 200°. The parachor is calculated by the formula $P = M\gamma^{\frac{1}{4}}/(D - d)$, where M is the molecular weight, γ the surface tension in dynes/cm., and D and d are the densities of the liquid and the vapour. For all the substances studied, d is very small and has been neglected.

Ethyl thalloacetoacetate, $Tl(C_6H_9O_3)$, $M = 333{\cdot}1$. The specimen from Dr. R. C. Menzies melted sharply at 92° (corr.), but began to decompose above 100°. Measurements were therefore made at one temperature only: $D_{4^\circ}^{94\cdot5^\circ} = 2{\cdot}365$, γ at $94{\cdot}5^\circ = 30{\cdot}94$, whence $[P] = 332{\cdot}2$.

Dimethylthallium benzoylacetonate, $(CH_3)_2Tl(C_{10}H_9O_2)$, $M = 395{\cdot}2$. Dr. Menzies's specimen melted at 128—129° (corr.) and was stable up to 170°. Densities determined: $D_{4^\circ}^{131\cdot5^\circ}$ 1·797, $D_{4^\circ}^{140^\circ}$ 1·786, $D_{4^\circ}^{148^\circ}$ 1·776, $D_{4^\circ}^{156^\circ}$ 1·763; whence $D_{4^\circ}^{t^\circ} = 1{\cdot}975 - 0{\cdot}00135t$.

t	133°	142·5°	149°	157°	
γ	32·08	31·1	30·52	29·85	
D	1·795	1·783	1·773	1·763	
Parachor ...	524·0	523·4	523·7	523·8	Mean = 523·7.

Thallous ethoxide, $TlOC_2H_5$, $M = 249{\cdot}0$. Dr. Menzies supplied a pure specimen of this liquid (Found: Tl, 81·4. Calc., 81·95%).

Densities determined: $D_{4°}^{20°}$ 3·493, $D_{4°}^{38·5°}$ 3·455, $D_{4°}^{55·5°}$ 3·408; whence $D_{4°}^{t°} = 3·543 - 0·00241t$.

t	16·5°	28·5°	44·5°	
γ	38·7	37·3	36·2	
D	3·503	3·475	3·436	
Parachor	177·2	177·1	177·7	Mean = 177·3.

Thallous formate, $TlHCO_2$, $M = 249·0$, was recrystallised from methyl alcohol and melted sharply at 101° (corr.). Densities determined: $D_{4°}^{104°}$ 4·967, $D_{4°}^{115·5°}$ 4·932, $D_{4°}^{125°}$ 4·908; whence $D_{4°}^{t°} = 4·977 - 0·0028\,(t - 100)$.

t	109°	118°	124°	
γ	81·3	78·8	75·3	
D	4·952	4·927	4·912	
Parachor	151·0	150·6	149·3	Mean = 150·3.

This liquid has a high surface tension and some difficulty was experienced in getting a regular formation of bubbles. The surface tensions quoted may be slightly too high.

Thallous acetate, $TlC_2H_3O_2$, $M = 263·0$, was recrystallised from ethyl alcohol and melted sharply at 131° (corr.). Densities determined: $D_{4°}^{137°}$ 3·765, $D_{4°}^{150°}$ 3·745, $D_{4°}^{166°}$ 3·717, $D_{4°}^{181°}$ 3·691; whence $D_{4°}^{t°} = 3·999 - 0·00170t$.

t	139°	159°	173°	204°	
γ	45·4	45·0	44·9	44·5	
D	3·763	3·729	3·705	3·652	
Parachor ...	181·5	182·7	183·7	186·0	Mean = 183·5.

This substance is remarkable in showing a very small rate of fall of surface tension with temperature.

Thallous nitrate, $TlNO_3$, $M = 266·$ From the measurements of Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1), $D_{4°}^{t°} = 4·923 - 0·00195t$.

t	211°	223°	231·5°	243°	
γ	112·3	111·7	110·4	109·6	
D	4·897	4·877	4·862	4·843	
Parachor ...	176·9	177·3	177·4	177·7	Mean = 177·3.

Jaeger finds rather higher surface tensions, giving $[P] = 180·7$.

Mercury, Hg, $M = 200$. The values found by different observers for the surface tension of mercury show slight variations, but these have only a small effect upon the parachor. Two modern series of measurements covering a range of temperatures up to the boiling point are those of Hogness (*J. Amer. Chem. Soc.*, 1921, **43**, 1621) and of Brown (*Phil. Mag.*, 1928, [7], **6**, 1044); the parachors calculated from these observations are given below, and since the mean values are identical, this value is adopted as the most probable.

Hogness:	t	20°	110°	200°	300°	354°	
	$[P]$	68·6	69·0	69·7	69·7	69·8	Mean = 69·4.
Brown:	t	18°	178°	218°	272°	326°	
	$[P]$	68·8	69·4	69·6	69·5	69·6	Mean = 69·4.

Both series of measurements were made with a modified form of the bubble-pressure method, which was also used by Sauerwald and Drath (*Z. anorg. Chem.*, 1926, **154**, 79), who found $\gamma_{20°} = 469—478$, whence the mean $[P] = 68{\cdot}7$, and by Bircumshaw (*Phil. Mag.*, 1928, [7], **6**, 510), who found $\gamma_{20°} = 500$, whence $[P] = 69{\cdot}8$. The measurements of Harkins and Ewing (*J. Amer. Chem. Soc.*, 1920, **42**, 2539) by the drop-weight method cover the range 0—60° and give a mean parachor of 69·0.

Mercury diphenyl, $Hg(C_6H_5)_2$, $M = 354{\cdot}1$, was recrystallised from alcohol and melted at 119° (corr.). Densities determined: $D_{4°}^{130{\cdot}5°}$ 1·935, $D_{4°}^{143{\cdot}5°}$ 1·918, $D_{4°}^{153°}$ 1·904, $D_{4°}^{166°}$ 1·882; whence $D_{4°}^{t°} = 2{\cdot}143 - 0{\cdot}00158t$.

t	129°	144°	156°	168·5°	
γ	35·97	34·63	33·42	32·75	
D	1·940	1·916	1·897	1·879	
Parachor ...	447·0	448·4	448·7	450·8	Mean = 448·7.

The author is indebted to Mr. H. J. Cavell for the observations on this substance.

Lead tetraethyl, $Pb(C_2H_5)_4$, $M = 323{\cdot}3$. Dr. E. W. J. Mardles kindly supplied a highly purified specimen of this substance, showing 99·7% purity. Densities determined; $D_{4°}^{18{\cdot}5°}$ 1·641, $D_{4°}^{28{\cdot}5°}$ 1·627, $D_{4°}^{40{\cdot}5°}$ 1·607, $D_{4°}^{43°}$ 1·595; whence $D_{4°}^{t°} = 1{\cdot}673 - 0{\cdot}00163t$.

t	20°	32·5°	45°	53·5°	
γ	28·48	27·40	26·39	25·10	
D	1·640	1·620	1·600	1·586	
Parachor ...	455·6	456·5	458·0	456·1	Mean = 456·6.

Beryllium acetylacetonate, $Be(C_5H_7O_2)_2$, $M = 207{\cdot}3$, was recrystallised from alcohol and melted at 109° (corr.). Densities determined: $D_{4°}^{111°}$ 1·017, $D_{4°}^{125°}$ 1·003, $D_{4°}^{132{\cdot}5°}$ 0·998, $D_{4°}^{146°}$ 0·985, $D_{4°}^{153{\cdot}5°}$ 0·979, $D_{4°}^{17\ °}$ 0·957; whence $D_{4°}^{t°} = 1{\cdot}119 - 0{\cdot}00092t$.

t	119°	129°	142°	151°	158°	169°
γ	27·6	26·6	25·3	24·6	23·8	22·9
D	1·010	1·001	0·989	0·980	0·974	0·964
Parachor	470·4	470·3	470·1	471·1	470·0	470·3
					Mean =	470·4.

Beryllium propionylacetonate, $Be(C_6H_9O_2)_2$, $M = 235{\cdot}3$, was prepared by boiling propionylacetone (purified by recrystallisation of the copper salt) in alcoholic solution with basic beryllium carbonate, and after recrystallisation from ligroin had m. p. 52·5—53·5° (corr.). Densities determined: $D_{4°}^{64°}$ 1·035, $D_{4°}^{75°}$ 1·024, $D_{4°}^{85{\cdot}5°}$ 1·014, $D_{4°}^{94{\cdot}5°}$ 1·005; whence $D_{4°}^{t°} = 1{\cdot}096 - 0{\cdot}000964t$.

t	60°	71·5°	84°	93°	
γ	31·78	30·60	29·20	28·35	
D	1·038	1·026	1·015	1·007	
Parachor ...	538·4	539·5	538·9	539·2	Mean = 539·0.

Basic beryllium propionate, $Be_4O(C_3H_5O_2)_6$, $M = 490·7$, was recrystallised from ligroin and melted at 137° (corr.). Densities determined: $D_{4°}^{142°}$ 1·056, $D_{4°}^{152°}$ 1·046, $D_{4°}^{169°}$ 1·028, $D_{4°}^{174°}$ 1·021; whence $D_{4°}^{t°} = 1·209 - 0·00108t$.

t	144°	150°	162°	173°	186°	
γ	20·30	19·59	18·64	17·61	16·62	
D	1·054	1·047	1·034	1·022	1·008	
Parachor	988·2	986·0	986·2	983·7	983·0	Mean = 985·4.

Aluminium acetylacetonate, $Al(C_5H_7O_2)_3$, $M = 324·3$, was recrystallised from acetone and melted at 198° (corr.). Densities determined: $D_{4°}^{204°}$ 0·992, $D_{4°}^{215°}$ 0·978, $D_{4°}^{224°}$ 0·969, $D_{4°}^{231°}$ 0·966, $D_{4°}^{260°}$ 0·935, $D_{4°}^{279°}$ 0·914; whence $D_{4°}^{t°} = 0·994 - 0·00100 (t - 200)$.

t	214°	216°	223°	232°	245·5°	278·5°
γ	18·20	17·81	17·28	16·85	15·72	13·21
D	0·980	0·979	0·971	0·962	0·949	0·915
Parachor	683·4	680·5	681·1	682·7	680·3	675·3
					Mean =	680·5.

Aluminium propionylacetonate, $Al(C_6H_9O_2)_3$, $M = 366·4$. This substance was obtained in good yield by shaking a concentrated aqueous solution of aluminium nitrate (1 mol.) and sodium acetate (4 mols.) with purified propionylacetone (3 mols.). The product was extracted with ligroin, and solvent and unchanged diketone were removed by heating to 100° under diminished pressure. The crude substance was a yellow oil which solidified on cooling to − 80° and then melted at 46—48°. It is very soluble in all organic solvents and was purified by dissolving in twice its volume of ligroin and cooling the solution to −15°. The crystals were filtered off on a funnel cooled by a freezing mixture, and the crystallisation was repeated. The substance was thus obtained as pale yellow crystals, m. p. 49° (corr.). Aluminium was determined by decomposing the substance in the crucible with nitric acid and igniting to oxide (Found: Al, 7·39. Calc.: Al, 7·40%). Densities determined: $D_{4°}^{53°}$ 1·087, $D_{4°}^{68°}$ 1·072, $D_{4°}^{81°}$ 1·060, $D_{4°}^{89°}$ 1·052; whence $D_{4°}^{t°} = 1·137 - 0·00096t$.

t	59°	65°	75°	92°	105°	
γ	29·3	28·4	27·6	25·6	24·4	
D	1·080	1·074	1·065	1·049	1·036	
Parachor	789·4	787·6	788·6	786·0	788·2	Mean = 788·0.

Aluminium bromide, Al_2Br_6, $M = 534$, purified by distillation, had m. p. 92° (corr.), b. p. 260°/754 mm. Densities determined: $D_{4°}^{104°}$ 2·628, $D_{4°}^{122°}$ 2·590, $D_{4°}^{144·5°}$ 2·538, $D_{4°}^{161°}$ 2·497; whence $D_{4°}^{t°} = 2·861 - 0·00225t$. These densities are in good agreement with those of Biltz and Voigt (*Z. anorg. Chem.*, 1922, **126**, 39). Since aluminium bromide is very hygroscopic, the surface tensions were determined in a sealed tube by the method of capillary rise, the apparatus and microscope fittings being as previously described (Sugden, J., 1921, **119**, 1483).

t	102°	120°	130°	147°	154°	
γ	25·5	24·2	23·5	22·5	21·7	
D	2·632	2·591	2·569	2·531	2·515	
Parachor	455·8	457·8	457·6	459·4	458·1	Mean = 457·6.

Acetylacetone, $C_5H_8O_2$, $M = 100{\cdot}1$, purified by repeated fractionation under diminished pressure, had b. p. 60° (corr.)/20 mm. Densities determined: $D_{4^\circ}^{11{\cdot}5^\circ}$ 0·972, $D_{4^\circ}^{36{\cdot}5^\circ}$ 0·947, $D_{4^\circ}^{54^\circ}$ 0·929, $D_{4^\circ}^{68{\cdot}5^\circ}$ 0·914; whence $D_{4^\circ}^{t^\circ} = 0{\cdot}984 - 0{\cdot}00101t$.

t	11°	39·5°	66°	81°	
γ	32·18	28·50	25·70	24·14	
D	0·973	0·944	0·917	0·902	
Parachor	245·0	244·9	245·7	245·9	Mean = 245·4.

The author is indebted to Mr. H. Wilkins for the measurements on this substance.

Propionylacetone, $C_6H_{10}O_2$, $M = 114{\cdot}1$, purified by recrystallising the copper derivative from benzene and distilling the regenerated diketone, had b. p. 162·5° (corr.)/759 mm. Densities determined: $D_{4^\circ}^{15{\cdot}5^\circ}$ 0·962, $D_{4^\circ}^{25{\cdot}5^\circ}$ 0·952, $D_{4^\circ}^{39{\cdot}5^\circ}$ 0·939, $D_{4^\circ}^{50^\circ}$ 0·930; whence $D_{4^\circ}^{t^\circ} = 0{\cdot}976 - 0{\cdot}00093t$.

t	18·5°	29·5°	41°	50°	
γ	30·38	29·24	28·10	27·22	
D	0·959	0·949	0·937	0·930	
Parachor	279·1	279·5	280·0	280·0	Mean = 279·7.

Benzoylacetone, $C_{10}H_{10}O_2$, $M = 162{\cdot}1$, was recrystallised from ligroin and melted at 59° (corr.). Densities determined: $D_{4^\circ}^{69^\circ}$ 1·062, $D_{4^\circ}^{81^\circ}$ 1·052, $D_{4^\circ}^{90{\cdot}5^\circ}$ 1·044; whence $D_{4^\circ}^{t} = 1{\cdot}120 - 0{\cdot}000804t$.

t	69°	78·5°	89°	100°	
γ	39·1	38·3	37·1	35·8	
D	1·062	1·054	1·045	1·036	
Parachor	381·7	382·2	382·8	382·8	Mean = 382·4.

Boron acetylacetone difluoride, $(C_5H_7O_2)BF_2$, $M = 148{\cdot}0$, prepared as described by Morgan and Tunstall (*loc. cit.*), melted at 46° (corr.). Densities determined: $D_{4^\circ}^{52{\cdot}5^\circ}$ 1·220, $D_{4^\circ}^{72^\circ}$ 1·199, $D_{4^\circ}^{91^\circ}$ 1·179, $D_{4^\circ}^{109^\circ}$ 1·161; whence $D_{4^\circ}^{t^\circ} = 1{\cdot}275 - 0{\cdot}00105t$.

t	60°	74°	92·5°	109°	
γ	36·18	34·55	32·89	31·29	
D	1·212	1·197	1·177	1·160	
Parachor	299·5	300·0	301·1	301·7	Mean = 300·6.

Stannic bisacetylacetone dichloride, $(C_5H_7O_2)_2SnCl_2$, $M = 387{\cdot}8$, was prepared as described by Morgan and Drew (*loc. cit.*) and melted at 204° (corr.). Densities determined: $D_{4^\circ}^{207^\circ}$ 1·451, $D_{4^\circ}^{210^\circ}$ 1·448,

$D_{4^\circ}^{216^\circ}$ 1·440; whence $D_{4^\circ}^{t^\circ} = 1{\cdot}460 - 0{\cdot}00122(t - 200)$. This substance decomposed rapidly when heated above 225°.

t	208°	213°	221°	
γ	28·40	27·88	27·12	
D	1·450	1·444	1·434	
Parachor	617·5	617·0	617·1	Mean = 617·2.

Summary.

(1) The parachors of a number of thallium, beryllium, and aluminium derivatives of β-diketones have been determined and found to exhibit precisely the negative anomalies predicted by the author (J., 1927, 1179). Basic beryllium propionate and aluminium bromide are also found to contain singlet linkages in the molecule, and structures are suggested for these compounds.

(2) An alternative hypothesis to account for these negative anomalies has been examined and is shown to be incompatible with the available data for mercury and thallium compounds.

(3) The free β-diketones and certain derivatives are found to possess an open-chain structure and are not co-ordinated.

(4) The following atomic parachors have been determined: Hg = 69, Tl = 64, Pb = 76, Be = 38, Al = 39.

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