56. *Molecular Volume and Structure. Parts I and II.*

By T. W. Gibling.

Part I.

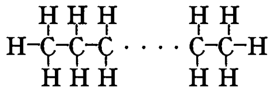
The bases of the method in general use for the calculation of parachors are discussed, and it is suggested that atomic and structural equivalents should be replaced by group values. The difference in parachor corresponding to addition of a CH_2 group appears to show regular progressive increase throughout any homologous series of compounds, except among the earlier members, in the volumes of which decreases due to " interference effects " are always found. The parachors of the normal paraffins, $CH_3\cdot[CH_2]_{n-2}\cdot CH_3$, can be expressed as $[2c + (n - 2)k]f^n$, where c, k, and f are constants; $2c + (n - 2)k$ is taken as the standard value for the parachor. Standard values are allotted to the different groups found in the molecules of paraffins and olefins, and certain " interference reductions " are assessed. The new method gives satisfactory agreement (of the order of 0·2%) between calculated and mean observed values, and also leads to the better elucidation of problems of structure, as will be shown in subsequent parts of this series.

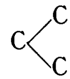
The application of molecular volumes to problems of structure must be limited to a large extent by the methods employed in the analysis of these quite complex functions, and undue simplification in treatment will tend to impair their usefulness.

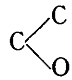
The most successful of the attempts to devise comparable conditions for the measurements of molecular volumes had a purely empirical origin. MacLeod (*Trans. Faraday Soc.*, 1923, **19**, 38) found that the surface tension (γ) of a normal liquid was proportional to the fourth power of the difference between its density (D) and that of its saturated vapour (d) at all temperatures from its freezing point to about 30° below its critical temperature; *i.e.*, $\gamma^{\frac{1}{4}}/(D-d) = C$ (a constant). Sugden (J., 1924, **125**, 1177) multiplied the above expression by the molecular weight (M) and called the product the " parachor " of the liquid: $[P] = M\gamma^{\frac{1}{4}}/(D - d)$. He showed that the parachor could be regarded, at any rate to a first approximation, as the molecular volume of a liquid under standard internal pressure, and that the function possessed the property of additivity to a remarkable degree. His method of analysis, based largely upon that of Kopp (*Annalen*, 1855, **95**, 153, 303) for molecular volumes of liquids at the boiling point, was attractively simple but had certain shortcomings, as was realised by Mumford and Phillips (J., 1928, 155; 1929, 2112; *Ber.*, 1930, **63**, 1818), whose proposed modifications, however, did not gain general acceptance.

In recent years improvement in technique has led to some advance in the accuracy of parachor determination; *e.g.*, Gillespie, Macbeth, and Mills (J., 1940, 280) estimate the normal maximum error in their parachor measurements to be less than 1 in 4000, as compared with Sugden's 1 in 200. Some workers (*e.g.*, Vogel, J., 1938, 1323; 1940, 1528) have been obliged to postpone comparison of experimental with calculated results until a more satisfactory method of evaluating the necessary constants can be evolved. The present paper is an attempt to derive such a method on the assumption that the parachor, possibly in a slightly modified form, may be regarded as a truly additive and constitutive function capable of affording considerably more information regarding the structure of molecules than has hitherto been realised.

In his calculation of " atomic constants," Sugden (" The Parachor and Valency," 1929, **35**) tacitly assumed that the contribution of any atom to the molecular volume is the same no matter to what other atoms it may be united by single bonds, *e.g.*, that in (I) the effective volumes of the carbon and hydrogen atoms are constants. It can be regarded as axiomatic

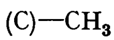

(I.)

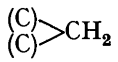

(II.)

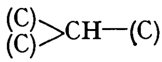

(III.)

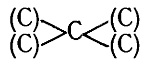
that the volume contribution of a given atom will vary with the nature of the atoms to which it is linked, and it is not legitimate to assume that the extent of such variation is negligible, especially in the case of carbon and hydrogen, the dimensions of which differ considerably. In the molecule (I) there are two types of carbon atom, the two end atoms differing from the others, and it is unlikely that the two types will contribute equally to the volume.

Sugden's method of calculation also made no allowance for the "interference" which is bound to occur when atoms, though not directly united, are nevertheless brought into fairly close conjunction, as in such groupings as (II) and (III), and it ignored the fact that the parachors recorded for compounds containing branched carbon chains are, in the majority of cases, substantially smaller than those of their so-called straight-chain isomers. Mumford and Phillips realised that a definite contraction, as measured by parachor value, is to be associated with a change in structure from (V) to (VI), and that a further contraction is observable in a change from (VI) to (VII), but they failed to appreciate the corollary that the change in structure from (IV) to (V) should also involve reduction of volume. They suggested the adoption of negative parachor equivalents, or " strain


(IV.)


(V.)


(VI.)


(VII.)

constants," to allow for diminution of volume " brought about either by the closer packing of atoms or groups within the molecule, or by a decrease in the effective size of one or other of the atoms concerned," and they also recognised the variability of effective atomic parachors, suggesting the use of different values for hydrogen according to the nature of the atom with which it is united. They did not, however, make full application of these principles to their fundamental calculation, the determination of constants for carbon and hydrogen in the paraffins.

No satisfactory method of measuring an " atomic volume " of any kind has yet been evolved, except, of course, for helium, neon, etc., and for certain elements in the solid state, and indeed, it is doubtful whether any precise significance can be attached to the term as applied to liquid compounds. In these circumstances it seems better to calculate " group values ", *i.e.*, the normal contributions of (IV), (V), etc., to the molecular volumes under consideration, and to attempt to assess any " interference corrections " which may be required owing to the proximity of other atoms or groups in the molecules.

There is first, however, a further difficulty to be resolved. The abnormally large parachors recorded for substances of high molecular weight have not yet received a satisfactory explanation. They have been ascribed to experimental error, but careful examination of all homologous series in which members sufficiently far apart have been investigated indicates that the " expansion effect " is quite general, the CH_2 difference slowly but steadily increasing with increase in the parachor values. This " expansion " partly explains the difficulty of deciding upon a satisfactory value for the CH_2 equivalent. Sugden's original number, 39·0, was a mean derived from the parachors of members of several homologous series, including compounds whose molecules are "associated" in the liquid state and others with groups of strongly polar character which cause considerable reductions in the parachors of the earlier members in the series, as is shown in Part II. Moreover, no distinction was made between normal compounds and those having branched chains, and values recorded for the parachors of isomerides were averaged, all alkyl esters of fatty acids, for example, being treated as one series. Mumford and Phillips's value, 40·0, is more satisfactory, being approximately the mean derived from the observed parachors from ethane to decane; whereas that of Vogel (J., 1934, 1758), *viz.*, 40·3, takes into account the parachors of substances of higher molecular weight.

In "A List of Parachors" (*Brit. Assoc. Rep.*, 1932, 265), besides the eight values lying between 1000 and 2500 (all of which are treated in Parts I and II), some dozen values of between 500 and 1000 are given for compounds of fairly simple type (or at least 20 if the higher fatty acids are correctly treated as consisting mainly of dimeric molecules) and, in all cases where it is possible to make a comparison, the parachors recorded are appreciably greater than those calculated by using mean "group values" and applying the necessary "interference corrections." For the great majority of substances with parachors of less than 500 the differences to be expected lie within the limits of experimental error, but even here a comprehensive investigation shows that, the mean "group values" being used, the parachors calculated for the lower or higher members in the various series are respectively, on the whole, rather greater or less than the experimental values. The necessity for postulating this expansion effect is made especially clear in the series of esters, tricaprin to tristearin, with parachors (between 1400 and 2400) which agree almost perfectly with the calculated values (p. 308). If the expansion effect were ignored, the whole argument with regard to the structure of the molecules—an argument immediately confirmed by the parachors (about 200—830) of alkyl carbonates and malonates—would fall to the ground. It is perhaps of some significance that an exactly similar effect is apparent in molecular volumes of liquids at the boiling point, though in this case the rate of expansion is considerably greater. Whatever may be the physical cause of the expansion phenomenon, there can be little doubt of its existence. Assuming then the desirability of arriving at a function that shall be as nearly as possible perfectly additive (as well as, to some extent, constitutive), one must apply some slight correction to the parachor as at present defined.

The author suggests that examination of the parachors of any sufficiently extended homologous series will show that the CH_2 difference is not constant, but increases progressively (though very slowly at first) from member to member, *any definite irregularities observed in the progression being traceable to peculiarities in structure.*

Among the normal paraffins, $CH_3{\cdot}[CH_2]_{n-2}{\cdot}CH_3$, the increase occurs with perfect regularity from the *second* member onwards, and the parachors of these compounds may be represented with considerable accuracy by the formula $[2c + (n - 2)k]f^n$, in which c and k are the effective contributions by CH_3– and –CH_2–, respectively, and f is an "expansion factor" only slightly greater than unity. Using the following values for the constants: $c = 55{\cdot}2$, $k = 39{\cdot}8$, $f = 1{\cdot}0004165$, one finds that the percentage differences between the mean observed parachors and the calculated values for all the n-paraffins investigated lie between $-$ 0·2 and + 0·5.

Normal paraffins, C_nH_{2n+2}.

n.	[P]. calc.	[P], obs.	Mean diff., %.	n.	[P], calc.	[P], obs.	Mean diff., %.
2	110·5	110·5	±0·0	8	350·4	350·3, 351·0	+0·1
3	150·4	150·8	+0·3	10	430·6	429·7	−0·2
4	190·3	190·3	±0·0	26	1077	1082	+0·5
6	270·3	270·1, 270·4, 270·4, 273·3	+0·3	32	1322	1322	±0·0
				60	2480	2480	±0·0
7	310·3	309·3, 310·8	−0·2				

The agreement is usually within 0·2%, which is about the order of accuracy to be expected in parachor determinations, and this may be compared with that obtained by using the various "atomic constants" previously proposed and making no correction for expansion:

Sugden (S), C, 4·8, H, 17·1; Mumford and Phillips (MP), C, 9·2, H, 15·4; Vogel (V), C, 11·5, H, 14·4.

Mean difference, %, between [P] obs. and [P] calc.

n.	S.	MP.	V.	*n*.	S.	MP.	V.
2	−1·5	+0·3	+1·0	8	+1·3	+0·0	−0·2
3	−0·3	±0·0	+0·7	10	+1·3	−0·3	−0·5
4	−0·1	−0·3	+0·2	26	+3·2	+1·3	+0·5
6	+1·1	−0·2	+0·2	32	+3·1	+0·8	+0·3
7	+0·9	−0·2	−0·3	60	+4·5	+2·0	+1·4
					Mean 1·7	0·5	0·5

Investigation of other homologous series shows that expansion occurs at exactly the same rate as in the *n*-paraffins; *i.e.*, the magnitude of the CH_2 increment depends upon the magnitude of the parachors, but is independent of the type of compound. Thus the set of corrections which can readily be prepared for the *n*-paraffins (see Conversion Table, p. 304) may be graphed and used for correcting the observed parachors of other substances. The corrected values so obtained are found to be, within the limits of experimental error, truly additive (and constitutive) functions and may be styled "Standard Values" (S.V.). Conversely, using the effective group values previously determined and applying any interference corrections that may be necessary, one can convert the S.V. so calculated for any member in a series into the (calculated) parachor, and the value obtained may be compared with the experimental value. The S.V. of a *n*-paraffin from ethane onwards is $2c + (n-2)k$, and the parachor is this value multiplied by f^n; the difference between the two is, of course, the "expansion correction" (E.C.).

The method of calculation, using normal group values (already corrected for interference effects), may be illustrated in the case of *n*-pentane:

$2CH_3\cdot(C)$ at 55·2 = 110·4 } S.V., calc. = 229·8; add E.C. = 0·5;
$3(C)\cdot CH_2\cdot(C)$ at 39·8 = 119·4 } then [*P*] = 230·3.

From the parachors recorded for *iso*- and *neo*-paraffins, S.V. for the groupings (VI) and (VII) have been determined, with the result that the values for groups occurring in paraffins are found to be as follows:

Group.	S.V.	Diff.	Group.	S.V.	Diff.
(IV)	55·2	—	(VI)	22·2	−17·6
(V)	39·8	−15·4	(VII)	2·4	−19·8

The constant increase in these differences must be due to interference between atoms attached to a common carbon atom. Assuming, as would appear most likely, that the hydrogen atoms are too small to produce an appreciable interference effect, one sees that the reduction in parachor value due to the grouping (II) is 2·2. Hence:

Group.	Ideal S.V. (without interference).	Constant diff.	Group.	Ideal S.V. (without interference).	Constant diff.
(IV)	55·2	—	(VI) *	28·8	−13·2
(V)	42·0	−13·2	(VII) †	15·6	−13·2

* This obviously involves three $C{<}^{C}_{C}$ groupings.

† In $^{C_1}_{C_2}{>}C{<}^{C_3}_{C_4}$ there are 6 interference effects to be considered: those between C_1, C_2; C_1, C_3; C_1, C_4; C_2, C_3; C_2, C_4; and C_3, C_4.

From the parachors of olefins the following values are obtained:

Group.	S.V.	Diff.	Group.	S.V.	Diff.
CH_2=(C)	49·7	—	$^{(C)}_{(C)}{>}C$=(C)	16·7	−17·6
(C)·CH=(C)	34·3	−15·4			

Thus the grouping $C{\lessdot}^{C}_{C}$ appears to involve the same reduction in parachor as $C{<}^{C}_{C}$, *viz.*, 2·2, and the following will therefore be the ideal values for the double-bonded groups found in olefins :

Group.	Ideal S.V. (without interference).	Constant diff.	Group.	Ideal S.V. (without interference).	Constant diff.
CH_2=(C)	49·7	—	(C)(C)>C=(C) *	23·3	−13·2
(C)·CH=(C)	36·5	−13·2			

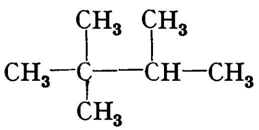
* This involves one C<(C)(C) and two C<(C)(C) groupings.

The following table gives the calculated and observed parachors for all paraffins and olefins included in the British Association list (see p. 301). The group values used in the calculations are as follows :

CH_3·(C), 55·2; (C)·CH_2·(C), 39·8; (C)(C)>CH·(C), 22·2; (C)(C)>C<(C)(C), 2·4; CH_2=(C), 49·7; (C)·CH=(C), 34·3; (C)(C)>C=(C), 16·7.

The method of calculation is shown in the following examples :

ββγ-Trimethylbutane



5CH_3·(C)	at 55·2	= 276·0	S.V., calc. = 300·6
(C)(C)>CH·(C)	at 22·2	= 22·0	E.C.* = +0·8
(C)(C)>C<(C)(C)	at 2·4	= 2·4	∴ [P], calc. = 301·4

* E.C. is derived from a table of corrections constructed for the *n*-paraffins (see p. 301) or from a graph made from that table.

β-*iso*Amylene

CH_3·CH=C<CH_3 CH_3

3CH_3·(C)	at 55·2	= 165·6	S.V., calc. = 216·6
(C)·CH=(C)	at 34·3	= 34·3	E.C. = +0·4
(C)=C<(C)(C)	at 16·7	= 16·7	∴ [P], calc. = 217·0

Hydrocarbon.	S.V., calc.	E.C.	[P], calc.	[P], obs.	Mean diff., %.
Ethane	110·4	+ 0·1	110·5	110·5	±0·0
Propane	150·2	+ 0·2	150·4	150·8	+0·3
Butane	190·0	+ 0·3	190·3	190·3	±0·0
*iso*Pentane	227·6	+ 0·5	228·1	230·0	+0·8
Hexane	269·6	+ 0·7	270·3	270·1, 270·4, 270·4, 273·3	+0·3
Heptane	309·4	+ 0·9	310·3	309·3, 310·8	−0·2
γ-Methylhexane	307·2	+ 0·9	308·1	306·6	−0·5
βδ-Dimethylpentane	305·0	+ 0·9	305·9	305·5	−0·1
ββ-Dimethylpentane	302·8	+ 0·9	303·7	305·3	+0·5
ββγ-Trimethylbutane	300·6	+ 0·8	301·4	301·4	±0·0
Octane	349·2	+ 1·2	350·4	350·3, 351·0	+0·1
β-Methylheptane	347·0	+ 1·2	348·2	348·7	+0·1
Di*iso*butyl	344·8	+ 1·1	345·9	345·0, 345·5	−0·2
Decane	428·8	+ 1·8	430·6	429·7	−0·2
Di*iso*amyl	424·4	+ 1·8	426·2	422·7, 425·7, 426·9, 427·8	−0·1
Hexacosane	1065·6	+11·6	1077	1082	+0·5
Dotriacontane	1304·4	+17·5	1322	1322	±0·0
Hexacontane	2418·8	+61·2	2480	2480	±0·0
Ethylene	99·4	+ 0·1	99·5	99·5	±0·0
Propylene	139·2	+ 0·2	139·4	139·7	+0·2
Amylene	218·8	+ 0·4	219·2	218·2	−0·5
β-*iso*Amylene	216·6	+ 0·4	217·0	216·9	−0·0
Diallyl	247·6	+ 0·6	248·2	248·2	±0·0

Conversion Table.

Normal paraffins, C_nH_{2n+2}: S.V. $= 2c + (n - 2)k$, where $c = 55{\cdot}2$ and $k = 39{\cdot}8$; $[P] =$ S.V. $\times f^n$, where $f = 1{\cdot}0004165$; E.C. = difference between S.V. and $[P]$.

n.	S.V.	[*P*].	E.C.	*n*.	S.V.	[*P*].	E.C.	*n*.	S.V.	[*P*].	E.C.
				21	866·60	874·21	7·61	41	1662·6	1691·2	28·6
2	110·40	110·49	0·09	22	906·40	914·74	8·34	42	1702·4	1732·4	30·0
3	150·20	150·39	0·19	23	946·20	955·31	9·11	43	1742·2	1773·7	31·5
4	190·00	190·32	0·32	24	986·00	995·90	9·90	44	1782·0	1815·0	33·0
5	229·80	230·28	0·48	25	1025·8	1036·5	10·7	45	1821·8	1856·3	34·5
6	269·60	270·27	0·67	26	1065·6	1077·2	11·6	46	1861·6	1897·6	36·0
7	309·40	310·30	0·90	27	1105·4	1117·9	12·5	47	1901·4	1939·0	37·6
8	349·20	350·37	1·17	28	1145·2	1158·6	13·4	48	1941·2	1980·4	39·2
9	389·00	390·46	1·46	29	1185·0	1199·4	14·4	49	1981·0	2021·8	40·8
10	428·80	430·59	1·79	30	1224·8	1240·2	15·4	50	2020·8	2063·3	42·5
11	468·60	470·75+	2·15+	31	1264·6	1281·0	16·4	51	2060·6	2104·8	44·2
12	508·40	510·95−	2·55−	32	1304·4	1321·9	17·5	52	2100·4	2146·4	46·0
13	548·20	551·18	2·98	33	1344·2	1362·8	18·6	53	2140·2	2188·0	47·8
14	588·00	591·44	3·44	34	1384·0	1403·7	19·7	54	2180·0	2229·6	49·6
15	627·80	631·73	3·93	35	1423·8	1444·7	20·9	55	2219·8	2271·2	51·4
16	667·60	672·06	4·46	36	1463·6	1485·7	22·1	56	2259·6	2312·9	53·3
17	707·40	712·43	5·03	37	1503·4	1526·7	23·3	57	2299·4	2354·6	55·2
18	747·20	752·82	5·62	38	1543·2	1567·8	24·6	58	2339·2	2396·4	57·2
19	787·00	793·45+	6·25+	39	1583·0	1608·9	25·9	59	2379·0	2438·2	59·2
20	826·80	833·72	6·92	40	1622·8	1650·1	27·3	60	2418·8	2480·0	61·2

Part II.

Reductions in parachor produced by bent chains of atoms occurring in aliphatic hydrocarbons, alkyl ethers and esters are discussed, and the problem of apportioning suitable values to groups involving linkage of heterogeneous atoms is considered in relation to the parachors of alkyl ethers and esters. In compounds containing a carbonyl group further definite reductions in parachor are found, which appear to be brought about by interaction between the atoms of this group and of neighbouring groups, and the effects are attributed to the polarity of the molecules of these compounds. Among triacyl esters of glycerol and alkyl malonates, and also among alkyl carbonates from propyl onwards, additional interference appears to occur, causing diminution of parachor value to an extent that points to the existence of closely-packed parallel chains of carbon atoms in the molecules.

Reductions in Parachor produced by Bent Chains.—In Part I it was estimated that, on the scale on which the parachor standard value (S.V.) for the group CH_3– is 55·2, the ideal S.V. of a $-CH_2-$ group should be 42·0. When the latter group is attached to two other alkyl groups, however, its effective contribution becomes 39·8, *i.e.*, the grouping (V) (p. 300) involves a diminution in parachor value of 2·2. The whole of this reduction has been assumed to be due to the mutual interference of the two carbon atoms linked to a common carbon atom, the hydrogen atoms being supposed to be too small to produce an appreciable effect. From the parachors for the methyl and ethyl esters of the fatty acids, formic to valeric (see table, p. 307), it appears that S.V., $(C){\cdot}CH_2{\cdot}(O)$, is 39·4, *i.e.*, $C\left<\begin{smallmatrix}C\\O\end{smallmatrix}\right\} = -2{\cdot}6$ To this interference among the atoms in the chains of the molecules of all except the first one or two members of homologous series must be attributed the apparently " singular properties of the methyl group " referred to by Lewis (J., 1940, 36).

The apportioning of a parachor value to a group which involves linkage of heterogeneous atoms cannot be effected by using available data. In, *e.g.*, dimethyl ether, the ideal volume contributions of the methyl groups will not be the same as in propane, in which they are united to an atom of larger size, nor will the interference effect between the two groups be identical in the different molecules since they are not the same distance apart in each. For purposes of calculation it will be satisfactory to allot to CH_3–(O) the same value as for CH_3–(C) and then to obtain a value for (C)·O·(C) by difference.

The parachor of diethyl ether may be taken as 211·1, the mean of the values recorded in " A List of Parachors " (see p. 301); whence

[*P*], $CH_3{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_3$	211·1
Expansion correction (see Part I)	− 0·4
S.V., $CH_3{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_3$	210·7
Deduct 2(C)·CH_2·(O) at 39·4	− 78·8
S.V., $CH_3{\cdot}O{\cdot}CH_3$	131·9
Deduct 2CH_3– at 55·2	−110·4
S.V., (C)·O·(C)	21·5

A value so obtained, however, is quite arbitrary and is not strictly comparable with group contributions already determined.

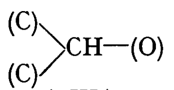
For later use it is necessary to evaluate the groups (VIII) and (IX). The interference corrections in the former are those for $2C{<}^{C}_{O}$ and $C{<}^{C}_{C}$, *i.e.*, − (2 × 2·6 + 2·2) = − 7·4, and since the ideal value for the group is 28·8 (see Part I), S.V. for (VIII) = *21·4*; similarly, S.V. for (IX) = 15·6 − (3 × 2·6 + 3 × 2·2) = *1·2*.

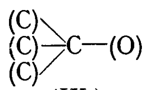
Using standard values for (C)·O·(C), 21·5, and (C)·CH_2·(O), 39·4, together with those for alkyl groups (obtained in Part I and listed on p. 303), one can compare the calculated and observed parachors of alkyl ethers :

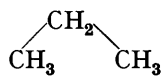
Ethers, $C_nH_{2n+1}{\cdot}O{\cdot}C_mH_{2m+1}$.

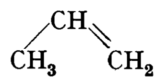
Ether.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.
Diethyl	210·7	+0·4	211·1	211·1	±0·0
Ethyl propyl	250·5	+0·6	251·1	252·0	+0·4
Dipropyl	290·3	+0·8	291·1	290·9	−0·1
Dibutyl	369·9	+1·3	371·2	369·9	−0·4
Diamyl	449·5	+1·9	451·4	449·9	−0·3
Di*iso*amyl	445·1	+1·9	447·0	445·7	−0·3

(Each of these parachors is the result of a single determination, except that the value for diethyl ether is the mean of four.)


(VIII.)


(IX.)


(X.)


(XI.)

The molecules of paraffins and olefins give little or no evidence of polarity. Consequently, once one has arrived at the bent carbon-chain structure, as in (X) and (XI), no further alteration in the type of structure is to be anticipated as one continues to ascend a series, and molecular volumes, as measured by the parachor, as well as many other physical constants, are found to change with perfect regularity from member to member (although, see p. 300, the CH_2 parachor increments increase as the parachor increases). Also, from the fact that a mean CH_2 S.V. increment of about 39·8 is found in all series of carboxy-esters (formates, acetates, etc.) from the ethyl ester onwards, and from examination of the parachors of alkyl ethers recorded above, it appears that the introduction of an oxygen atom into a carbon chain does not appreciably affect the normal course taken by that chain. With compounds containing a group of marked polarity, such as Cl–(C), Br–(C), I–(C), R·CO·(C), C_6H_5·(C), however, this regularity in the CH_2 increment is only attained after the first few (generally five) members in a series.

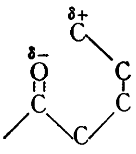
Corrections for Compounds containing a Carbonyl Group.—In order to bring his calculated values for the parachors of carboxy-esters into reasonable agreement with the observed values, Sugden (" The Parachor and Valency," 1929, 42) applied an *ad hoc* correction of − 3·2. By employing group values instead of atomic and structural equivalents, one obtains diminutions in parachor value in *all* classes of compounds which contain the carbonyl group—aldehydes, ketones, and carboxy-acids, as well as their anhydrides and esters. Using standard values (S.V.) for the groups, one discovers that, among the lower members of any one such series, Δ_{CH_2} (the difference in S.V. due to a change in constitution by $-CH_2-$) is less than 39·8, the constant value found among paraffins and olefins. For instance:

Carbonyl Compounds, $C_nH_{2n+1}\cdot CO\cdot R$.

Δ_{CH_2} between S.V. of adjacent members in a series:

Change in group C_nH_{2n+1}.	Δ.	Change in group C_nH_{2n+1}.	Δ.
H– to CH_3–	38·8	C_3H_7– to C_4H_9–	38·1
CH_3– ,, C_2H_5–	37·8	C_4H_9– ,, C_5H_{11}– and onwards ...	39·8 (normal Δ)
C_2H_5– ,, C_3H_7–	39·0		

The reductions in normal value extend as far as the sixth atom in the chain, the oxygen atom being counted as the first. For ketones the reductions apply to both the carbon chains attached to the carbonyl group. No extra reductions are produced by further extension, or by branching, of the carbon chain. It would appear that these contractions in volume are due to the proximity of the doubly-linked oxygen atom to the carbon atoms referred to above, and that therefore there is a bending back of the carbon chain towards the oxygen atom, so as to form a partly-closed ring, the change from the normal direction being presumably a consequence of the polarity of the molecule; the effect ceases just at the point where this imagined ring would be potentially completed (see inset).



With the method of calculation described above (for dimethyl ether), the value to be obtained for the carboxy-group, (C)·CO·O·(C), may be based upon the parachors recorded for ethyl acetate, *viz.*, 215·6, 215·7, 216·9, 217·1, 217·9; mean 216·6.

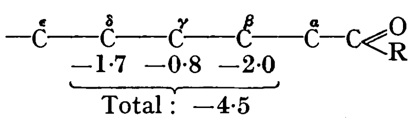
[*P*], $CH_3\cdot CO\cdot O\cdot CH_2\cdot CH_3$	216·6
E.C.	– 0·4
S.V., $CH_3\cdot CO\cdot O\cdot CH_2\cdot CH_3$	216·2
Deduct $(C)\cdot CH_2\cdot (O)$ at 39·4	– 39·4
S.V., $CH_3\cdot CO\cdot O\cdot CH_3$	176·8
Deduct $2CH_3$– at 55·2	–110·4
S.V., (C)·CO·O·(C)	66·4

It is useful also to have a group value for H·CO·O·(C):

S.V., $CH_3\cdot CO\cdot O\cdot CH_3$	176·8
$\Delta CH_3\cdot CO\cdot R/H\cdot CO\cdot R$	– 38·8
S.V., $H\cdot CO\cdot O\cdot CH_3$	138·0
Deduct CH_3– at 55·2	– 55·2
S.V., H·CO·O·(C)	82·8

It must be emphasised again that the values of such groups, which involve linkage of carbon and oxygen, are recorded only for purposes of calculation and are not to be regarded as expressing the volume contributions of these groups on any scale previously employed.

In performing calculations on carbonyl compounds one may give the alkyl groups in the carbon chain attached directly to carbonyl their normal effective values and then apply the necessary "carbonyl corrections":



The correction for the β, γ, or δ carbon atom in the chain is the difference between the Δ value recorded in the table above and the normal Δ (39·8). As pointed out before, in the case of alkyl groups containing branched carbon chains, the carbonyl corrections are found to apply to only one branch of the chain.

The following table contains all the alkyl esters of fatty acids for which parachors are given in the list mentioned on p. 301.

Esters of Fatty Acids, $C_nH_{2n+1}\cdot CO\cdot O\cdot C_mH_{2m+1}$.

Ester.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs. (mean).*	Diff., %.	Corrections applied.
Methyl formate	138·0	+0·1	138·1	138·15 [2]	+0·0	—
Methyl acetate	176·8	+0·3	177·1	176·95 [2]	−0·1	—
Ethyl formate	177·4	+0·3	177·7	177·7 [2]	±0·0	—
Methyl propionate	214·6	+0·4	215·0	215·0 [2]	±0·0	−2·0 : β
Ethyl acetate	216·2	+0·4	216·6	216·6 [5]	±0·0	—
Propyl formate	217·2	+0·4	217·6	216·1	−0·7	—
Methyl butyrate	253·6	+0·6	254·2	254·2 [2]	±0·0	−2·8 : β, γ
Ethyl propionate	254·0	+0·6	254·6	254·5 [3]	−0·0	−2·0 : β
*iso*Butyl formate	254·8	+0·6	255·4	262·4	+2·7	—
Propyl acetate	256·0	+0·6	256·6	256·05 [2]	−0·2	—
Ethyl *iso*butyrate	291·6	+0·8	292·4	292·9	+0·2	−2·0 : β
Methyl valerate	291·7	+0·8	292·5	292·5	±0·0	−4·5 : β, γ, δ
Ethyl butyrate	293·0	+0·8	293·8	293·7 [3]	−0·0	−2·8 : β, γ
*iso*Butyl acetate	293·6	+0·8	294·4	295·1	+0·2	—
Propyl propionate	293·8	+0·8	294·6	295·3	+0·2	−2·0 : β
*iso*Amyl formate	294·6	+0·8	295·4	293·65 [2]	−0·6	—
Ethyl *iso*valerate	330·6	+1·0	331·6	331·9	+0·1	−2·8 : β, γ
Ethyl valerate	331·1	+1·0	332·1	332·1	±0·0	−4·5 : β, γ, δ
*iso*Butyl propionate ...	331·4	+1·0	332·4	331·8	−0·2	−2·0 : β
Propyl *iso*butyrate ...	331·4	+1·0	332·4	332·6	+0·1	−2·0 : β
Propyl butyrate	332·8	+1·0	333·8	333·8	±0·0	−2·8 : β, γ
*iso*Amyl acetate	333·4	+1·0	334·4	334·35 [2]	−0·0	—
*iso*Butyl *iso*butyrate ...	369·0	+1·3	370·3	371·8	+0·4	−2·0 : β
*iso*Butyl butyrate	370·4	+1·3	371·7	370·5	−0·3	−2·8 : β, γ
Propyl valerate	370·9	+1·3	372·2	371·9	−0·1	−4·5 : β, γ, δ
*iso*Amyl propionate ...	371·2	+1·3	372·5	372·1	−0·1	−2·0 : β
*iso*Amyl butyrate	410·2	+1·6	411·8	409·7 [2]	−0·5	−2·8 : β, γ
Ethyl heptoate	410·7	+1·6	412·3	413·3	+0·2	−4·5 : β, γ, δ
Ethyl octoate	450·5	+2·0	452·5	452·7	+0·0	−4·5 : β, γ, δ
Ethyl pelargonate	490·3	+2·4	492·7	493·6	+0·2	−4·5 : β, γ, δ
*iso*Amyl stearate	965·7	+9·5	975·2	974·2	−0·1	−4·5 : β, γ, δ

* The numbers in brackets show the numbers of determinations upon which the means are based.

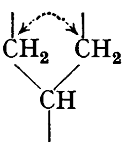
The standard values for the carbonyl group, as contained in ketones, and for the aldehyde group may be derived satisfactorily from the mean of the six independent determinations of the parachor of acetone, *viz.*, 160·9, 161·5, 161·5, 161·6, 161·7, 162·0, with the results: S.V. (C)·CO·(C) = *50·9*; S.V. (C)—CHO = *67·3*.

Aldehydes and Ketones, $C_nH_{2n+1}\cdot CO\cdot C_mH_{2m+1}$.

Compound.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs. (mean).	Diff., %.	Corrections applied.
Acetone	161·3	+0·2	161·5	161·5 [6]	±0·0	—
Methyl ethyl ketone ...	199·1	+0·3	199·4	198·8 [3]	−0·3	−2·0 : β
*iso*Valeraldehyde	236·9	+0·5	237·4	237·5	+0·0	−4·5 : β, γ, δ
Diethyl ketone	236·9	+0·5	237·4	236·8 [2]	−0·3	−4·0 : 2β
Methyl propyl ketone	238·1	+0·5	238·6	238·0 [2]	−0·3	−2·8 : β, γ
Pinacolin	272·1	+0·7	272·8	273·4	+0·2	−2·0 : β
Methyl *iso*butyl ketone	275·7	+0·7	276·4	276·5	+0·0	−2·8 : β, γ
Ethyl propyl ketone ...	275·9	+0·7	276·6	277·3	+0·2	−4·8 : 2β, γ
Methyl butyl ketone ...	276·2	+0·7	276·9	276·6 [2]	−0·1	−4·5 : β, γ, δ
Dipropyl ketone	314·9	+0·9	315·8	314·6 [2]	−0·4	−5·6 : 2β, 2γ
Methyl amyl ketone ...	316·0	+0·9	316·9	319·1	+0·7	−4·5 : β, γ, δ
Heptaldehyde	317·0	+1·0	318·0	318·0	±0·0	−4·5 : β, γ, δ
Methyl hexyl ketone ...	355·8	+1·2	357·0	356·1 [3]	−0·3	−4·5 : β, γ, δ
Di*iso*butyl ketone	390·1	+1·5	391·6	391·6	±0·0	−5·6 : 2β, 2γ
Methyl heptyl ketone	395·6	+1·5	397·1	396·8	−0·1	−4·5 : β, γ, δ

The above table includes determinations by Cowan, Jeffery, and Vogel (J., 1940, 171), who record parachors for 11 ketones, 7 of which have been previously investigated: in only one case is their result further from the calculated value than that of any earlier observer; for 5 of the 11 ketones their results are within 0·1% of the calculated parachor, and in 3 more cases within 0·2%.

Interference from Parallel Chains.—The parachors recorded for alternate members of the series of glycerol esters, tricaprin to tristearin, are considerably (some 1·6%) smaller than the calculated values. Examination of the individual differences between observed S.V. and those calculated by using the group values and carbonyl corrections given before shows that these differences can all be represented as $-2{\cdot}2(n+2)$, *i.e.*, the deficit in the S.V. expected amounts to 2·2 units per carbon atom in any one of the three acyl chains. Thus the reduction per trio of carbon atoms in these chains is the same as that produced by the mutual interference of the two outer carbon atoms attached to the central carbon atom in the glycerol nucleus (see inset). This must mean that the two outer chains do not splay, but continue along parallel paths, so that any two corresponding carbon atoms in these chains will be at such a distance from each other as to produce the interference measured by 2·2 parachor units. The molecules will then have a tuning-fork-like configuration, as has indeed been suggested by other physical evidence, *e.g.*, that adduced by Clarkson and Malkin (J., 1934, 666):



$$CH_3{\cdot}[CH_2]_n{\cdot}CO{\cdot}O{\cdot}CH{<}\begin{matrix}CH_2{\cdot}O{\cdot}CO{\cdot}[CH_2]_n{\cdot}CH_3\\ CH_2{\cdot}O{\cdot}CO{\cdot}[CH_2]_n{\cdot}CH_3\end{matrix}$$

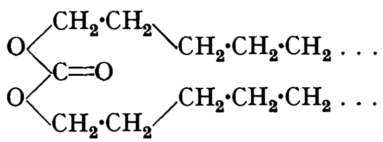
It must be noted, however, that the prongs and stem of the fork are not in the same plane and that each develops a coil in the portion of the chain near the crotch. Calculations based on these assumptions give the following values.

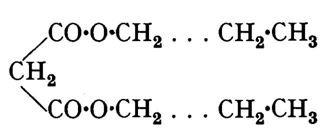
Ester.	S.V., calc. normally.	Extra corrn.: $-2{\cdot}2(n+2)$.	Resultant S.V.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.
Tricaprin	1406·7	−22·0	1384·7	+19·7	1404	1404	±0·0
Trilaurin	1645·5	−26·4	1619·1	+27·2	1646	1648	+0·1
Trimyristin	1884·3	−30·8	1853·5	+35·7	1889	1892	+0·2
Tripalmitin	2123·1	−35·2	2087·9	+45·4	2133	2127 *	−0·3
Tristearin	2361·9	−39·6	2322·3	+56·4	2379	2378 †	−0·0

* Mean of 2120 and 2134. † Mean of 2376 and 2380.

As pointed out in Part I, provided that one accepts the ideas put forward regarding the structure of these compounds, the above results afford very strong evidence for the existence of the "expansion effect" in the parachor, since the theoretical parachors were calculated by using group values and interference corrections derived from the experimental parachors of simple compounds of quite low molecular weight.

Moreover, other series in which similar reductions in parachor are susceptible of similar explanation are those of the alkyl carbonates and malonates, in which, of course, there are two alkyl chains. Among the former, the difference between the mean standard values of the methyl and ethyl esters is 79·0, or almost exactly 2 × 39·4; but thereafter the mean difference for successive numbers in the series is 77·4 instead of 79·6 [twice the normal $(C){\cdot}CH_2{\cdot}(C)$ value], *i.e.*, there is a reduction of 2·2 for each pair of corresponding carbon

(XII.) 

 (XIII.)

atoms in the alkyl chains, starting with the third pair. Thus, close packing of the two chains must begin after the second number of the series, as in (XII). This type of structure is in agreement with Thomson's conclusions (J., 1939, 1118) from dipole-moment measurement of the methyl and ethyl esters.

All the parachors except two were determined by Bowden and Butler (*ibid.*, p. 75). Omitting from consideration the parachor they give for the butyl ester,† one finds that S.V. $\begin{matrix}(C){\cdot}O\\(C){\cdot}O\end{matrix}{>}C{=}O$ is *85·5*.

Alkyl Carbonates, R_2CO_3.

R.	Σ group values.	Corrn.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.
CH_3	195·9	0	195·9	+0·3	196·2	196·2	±0·0
C_2H_5	274·7	0	274·7	+0·7	275·4	275·6 *	+0·1
C_3H_7	354·3	−2·2	352·1	+1·2	353·3	352·3	−0·3
C_4H_9	433·9	−4·4	429·5	+1·8	431·3	423·4 †	−1·8
iso-C_4H_9	429·5	−4·4	425·1	+1·8	426·9	428·1	+0·3
C_5H_{11}	513·5	−6·6	506·9	+2·5	509·4	508·2	−0·2
iso-C_5H_{11}	509·1	−6·6	502·5	+2·5	505·0	505·0	±0·0
C_6H_{13}	593·1	−8·8	584·3	+3·4	587·7	587·8	+0·0

* Mean of three values.

† Comparison of the physical constants recorded for the members of the series suggests that the specimen of *n*-butyl carbonate used was not pure.

Assuming that the alkyl chains in malonic esters also are closely packed, one arrives at the general structure (XIII), in which the interference between each pair of corresponding carbon atoms gives rise to a parachor correction of — 2·2 units.

Alkyl Malonates, $CH_2(CO·OR)_2$.

R.	Σ group values.	Corrn.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.*	Diff., %.
CH_3	283·0	− 2·2	280·8	+0·7	281·5	282·5	+0·3
C_2H_5	361·8	− 4·4	357·4	+1·2	358·6	360·4	+0·5
C_3H_7	441·4	− 6·6	434·8	+1·8	436·6	438·2	+0·4
isoC_3H_7	437·0	− 6·6	430·4	+1·8	432·2	437·1	+1·1
C_4H_9	521·0	− 8·8	512·2	+2·6	514·8	513·8	−0·2
isoC_4H_9	516·6	− 8·8	507·8	+2·5	510·3	511·8	+0·3
isoC_5H_{11}	596·2	−11·0	585·2	+3·4	588·6	586·9	−0·3
C_8H_{17}	839·4	−17·6	821·8	+6·8	828·6	828·7	+0·0

* Beck, Macbeth, and Pennycuick (J., 1932, 2258). Other determinations are: CH_3– 283·1; C_2H_5– 360·3, 362·0 (see list mentioned on p. 301).

Of the 145 parachors so far recorded in this paper (for 96 different compounds—aliphatic hydrocarbons, ethers, carboxy-esters, aldehydes, and ketones), 84 are within 0·2% of the calculated values and another 41 are within 0·5%. Four results which are included differ by more than 1% and are probably unreliable: *iso*butyl formate (+ 2·7%), butyl carbonate (— 1·8%), *iso*propyl malonate (+ 1·1%), and one of the values for hexane (+ 1·1%). The average difference is under 0·3%, and this is reduced to 0·2% if the 96 mean values are considered.

The standard group values derived from the parachors of substances considered in Part II are as follows:

(C)·O·(C), 21·5; (C)·CH_2·(O), 39·4; $\genfrac{}{}{0pt}{}{(C)}{(C)}$>CH·(O), 21·4; $\genfrac{}{}{0pt}{}{(C)}{\genfrac{}{}{0pt}{}{(C)}{(C)}}$>C—(O), 1·2; H·CO·(C), 67·3; (C)·CO·(C), 50·9; H·CO·O·(C), 82·8; (C)·CO·O·(C), 66·4; $\genfrac{}{}{0pt}{}{(C)·O}{(C)·O}$>CO, 85·5.

The following interference correction is involved: C<$\genfrac{}{}{0pt}{}{C}{O}$} — 2·6; and corrections for β, γ, and δ C atoms in alkyl chains attached to >C=O : β — 2·0, γ — 0·8, δ — 1·7.

The author thanks Dr. J. Colvin, University of Leeds, and Dr. K. G. Denbigh, University College, Southampton, for the interest they have taken in his work, and for valuable suggestions and advice given during the preparation of this paper.

The Grammar School of Queen Elizabeth, Wakefield. [*Received, January* 21*st*, 1941.]