CCLXXIV.—*The Evaluation and Interpretation of Parachors.*

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IN a recent paper dealing with surface-tension relations in the fatty acid series (Hunten and Maass, *J. Amer. Chem. Soc.*, 1929, **51**, 153), the observed parachors of the lower members of the series were found to be consistently greater than those calculated with the aid of Sugden's atomic and structural constants (J., 1924, **125**, 1177), whilst the reverse held with the higher members, and it was suggested that such deviations from the normal were to be attributed to the same obscure cause giving rise to a parallel variation in the value of the Ramsay–Shields–Eötvös coefficient. As, however, the observed parachors in the series in question increase by more or less regular increments of about 40 units per CH_2 group from 93·3 for formic acid to 778·0 for stearic acid, it seemed to the present authors that the anomaly, so far as concerns parachors, might be due, at least in part, to the use of too small a difference for CH_2, *viz.*, 39 units. The further fact that the observed parachors of *n*-hexacosane and *n*-hexacontane (Schenck and Kintzinger, *Rec. trav. chim.*, 1923, **42**, 759), *n*-dotriacontane (Hunten and Maass, *loc. cit.*), tripalmitin, and tristearin (Walden and Swinne, *Z. physikal. Chem.*, 1912, **79**, 700), and, in general, of all compounds of high molecular weight, are some 2% or more greater than the calculated values (see Table II), appeared to substantiate this conclusion, and the existing surface tension data were, therefore, systematically re-examined.

Now Sugden's constants were mainly evaluated from the earlier members of the various series of organic compounds irrespective of whether they had straight or branched chains, and his neglect of the influence of chain branching, which appears invariably to cause a slight, but definite, decrease in parachor, led to the adoption of 39 units as the value of a CH_2-increment. Of the isomeric heptanes (Edgar and Calingaert, *J. Amer. Chem. Soc.*, 1929, **51**, 1540) and octanes (Richards, Speyers, and Carver, *ibid.*, 1924, **46**, 1196), for example, the normal compounds have the highest parachors, whilst those of the branched isomerides decrease in proportion to the number of side chains present (compare Tables II and IV). Again, amongst the various isomeric aliphatic esters (Schiff, *Annalen*, 1884, **223**, 47 ; *Gazzetta*, 1884, **14**, 368), the parachors of the *iso*-compounds are lower than those of the normal esters (compare the table given by Sugden, *loc. cit.*); and in the same way, the parachor of pinacolin is smaller than that of methyl *n*-butyl ketone (Harkins, Clark, and Roberts, *J. Amer. Chem. Soc.*, 1920, **42**, 700), that of methylhexylcarbinol smaller than that of *n*-octyl alcohol (Harkins and Cheng, *ibid.*, 1921, **43**, 35), and so on. It is evident, therefore, that a more accurate estimate of the true value of a CH_2-increment would be obtained by taking into consideration series consisting of compounds of one type only, *e.g.*, all *iso*- or all normal. When this is done for a number of different series the mean difference for CH_2 is found to be 40 units, as indicated by the data for the fatty acid series, and thence, by estimating the other atomic and structural constants in the usual way, the values given in Table I are obtained.

TABLE I.

Recalculated Atomic and Structural Constants.

CH_2	40	O	20	Triple bond	+38
C	9·2	S	50	Double bond	+19
H	15·4	Se	63	Single bond (duplet) Semipolar double bond	± 0
—		—			
F	25·5	B	(21·5)		
Cl	55	Si	(31)	Singlet linkage	− 9·5
Br	69	Be	(42)	—	
I	90	Al	(55)	—	
—		Cr	(58)	3-Membered ring	+12·5
N	17·5	Tl	(62)	4-Membered ring	+ 6
P	40·5	Sn	(64·5)	5-Membered ring	+ 3
As	54	Hg	(69)	6-Membered ring	+ 0·8
Sb	68	Bi	(80)	7-Membered ring	− 4

The atomic constants are, for the most part, only slightly different from those deduced by Sugden, but the use of the larger CH_2-increment, and hence of modified carbon and hydrogen values, leads, in general, to greater accuracy of calculated parachors, especially in the case of compounds of high molecular weight (see Table II). By the use of these constants, moreover, the parachor loses its strictly additive character and becomes definitely constitutive, stresses due to spatial arrangement of, and electrostatic influences between, atoms and groups in a molecule being accompanied by well-defined parachor variations. In view of the comparative scantiness of the available data, and the consequent possibility that some of the values given in Table I may require further modification, it would be premature to attempt a strictly quantitative treatment of the subject, but some of its more important aspects are indicated below.

In particular, the interatomic stresses in substituted ring systems, in branched-chain derivatives, and in compounds containing accumulated negative groups are shown to have an effect on the parachor which can be accounted for by the systematic introduction of numerical positive or negative "strain constants," the physical significance of which is discussed.

Further, it is shown that, by using the recalculated values, the parachors of hydroxy-compounds and amines may be brought into line with those of non-associated substances on the assumption that the effective volume of the hydrogen atom decreases with increasing electron-affinity of the atom to which it is attached; and finally, that the apparent parachor anomaly of fused salts (Sugden and Wilkins, this vol., p. 1291) may be accounted for by assigning a higher parachor value to the ions than to the bound atoms of the halogens, a method of estimating such ionic parachors being indicated.

TABLE II.

Parachors of the n-*Paraffins.*

				[*P*] calc.	
Compound.	Formula.	Observers.	[*P*] obs.	M. & P.	S.
Ethane	C_2H_6	M. & W.	110·5	110·8	112·2
Propane	C_3H_8	M. & W.	150·8	150·8	151·2
n-Butane	C_4H_{10}	C. & M.	190·3	190·8	190·2
n-Hexane	C_6H_{14}	I. C. T.	270·4	270·8	268·2
n-Heptane	C_7H_{16}	E. & C.	310·8	310·8	307·2
n-Octane	C_8H_{18}	I. C. T.	350·3	350·8	346·2
n-Hexacosane	$C_{26}H_{54}$	S. & K.	1082	1070·8	1048·2
n-Dotriacontane	$C_{32}H_{66}$	H. & M.	1322	1310·8	1282·2
n-Hexacontane	$C_{60}H_{122}$	S. & K.	2480	2430·8	2374·2

M. & P. = Present authors. S. = Sugden.
M. & W. = Maass and Wright, *J. Amer. Chem. Soc.*, 1921, **43**, 1098.
C. & M. = Coffin and Maass, *ibid.*, 1928, **50**, 1427.
I. C. T. = International Critical Tables, Vol. 4, pp. 433 *et seq.* (Mean corrected surface tensions there given are used in conjunction with densities based, where possible, on concordant determinations of two independent workers.)
E. & C. = Edgar and Calingaert, *loc. cit.*
S. & K. = Schenck and Kintzinger, *loc. cit.*
H. & M. = Hunten and Maass, *loc. cit.*

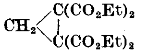
Effect of Ring Formation.—Justification for the interpretation of parachor variations on the basis of intramolecular strain is afforded by the parallelism between the constants for the various cyclic structures and the valency deflexion suffered by the atoms in the latter (compare Baeyer, *Ber.*, 1885, **18**, 2277; Ingold, J., 1921, **119**, 305), and further, by the variation of such constants in certain substituted rings.

The presence of a carbonyl group in a ring, for example, shifts the position of zero ring-constant from the six- to the seven-membered ring—an effect which would appear to be connected with the influence of potential semicyclic double bonds in hindering the formation of the smaller rings (compare Ingold, *loc. cit.*; Vogel, this vol., p. 721). Thus, the apparent ring constant in *cyclo*pentanone is + 6·0, in *cyclo*hexanone + 4·0, and in *cyclo*heptanone − 0·2 (see

Table III), whereas the mean values for the ring constants in the corresponding non-ketonic structures are + 3·0, + 0·8, and − 4·0 units respectively. For purposes of calculation, therefore, the introduction of a carbonyl group into a ring must be regarded as giving rise to a " positive " strain equivalent to about 3·0 units, the parachor of such a group being thus 48·2 (*i.e.*, C + O + double bond) plus this " strain constant " (σ in the tables), *i.e.*, 51·2 units.

TABLE III.

Ring Formation.

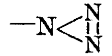
Compound.	Formula.	Σ At. *P*.*	σ.	[*P*] calc.	[*P*] obs.	Observers.
*cyclo*Pentanone	$(CH_2)_4>CO$	211·2	+ 3	214·2	214·2	V.
*cyclo*Hexanone	$(CH_2)_5>CO$	249·0	+ 3	252·0	252·2	V.; H. & B.
*cyclo*Heptanone	$(CH_2)_6>CO$	284·2	+ 3	287·2	288·0	V.
1 : 1-Dimethyl-*cyclo*hexane	$(CH_2)_5>CMe_2$	320·8	− 3	317·8	316·1	K.
β-*iso*Amylene	$CHMe{:}CMe_2$	219·0	− 3	216·0	216·9	I. C. T.
Ethyl *cyclo*propane-1 : 1-dicarboxylate	$(CH_2)_2>C(CO_2Et)_2$	422·9	− 6	416·9	417·1	S. & Wi.
Ethyl *cyclo*propane-1 : 1 : 2 : 2-tetra-carboxylate	 $CH_2\left\langle\begin{matrix}C(CO_2Et)_2\\ \vert\\ C(CO_2Et)_2\end{matrix}\right.$	713·3	−12	701·3	701·1	S. & Wi.
Ethyl *cyclo*butane-1 : 1-dicarboxylate	$(CH_2)_3>C(CO_2Et)_2$	456·4	− 6	450·4	454·1	S. & Wi.
Ethyl chloromaleate	$C_2HCl(CO_2Et)_2$	429·0	− 6	423·0	423·3	I. C. T.
Methyl α-bromo-cinnamate	$CHPh{:}CBr\cdot CO_2Me$	432·4	− 6	426·4	426·6	S. & Wh.
Benzene	C_6H_6	205·4	0	205·4	206·0	I. C. T.
*cyclo*Hexane	C_6H_{12}	240·8	0	240·8	239·3	I. C. T.
Pyridine	C_5H_5N	198·3	0	198·3	199·7	I. C. T.
Piperidine	$C_5H_{11}N$	230·8	0	230·8	232·5	I. C. T.
Methyl*cyclo*pentane	$C_5H_9\cdot Me$	243·0	0	243·0	242·8	K.
Thiophen	C_4H_4S	189·4	0	189·4	189·3	I. C. T.; P. & R.
Phenyl azide	$C_6H_5N_3$	274·0	− 6·5	267·5	267·3	L. & T.
p-Tolyl azide	$C_6H_4Me\cdot N_3$	314·0	− 6·5	307·5	307·0	L. & T.
Nitrous oxide	N_2O	86·5	− 6·5	80·0	80·5	G.; Ve.

* Σ At. *P* = sum of the atomic and structural constants, including " strain constants " (if any), other than that under consideration.

V. = Vogel, J., 1928, 2010.
H. & B. = Herz and Bloch, *Z. physikal. Chem.*, 1924, **110**, 23.
K. = Kistiakowski, *Ann. Inst. Polyt. Petrograd*, 1904, **1**, 450.
S. & Wi. = Sugden and Wilkins, J., 1927, 139.
S. & Wh. = Sugden and Whittaker, J., 1925, **127**, 1868.
P. & R. = Peel and Robinson, J., 1928, 2068.
L. & T. = Lindemann and Thiele, *Ber.*, 1928, **61**, *B*, 1529.
G. = Grunmach, *Ann. Physik*, 1901, **6**, 559; 1904, **15**, 401; 1907, **22**, 107.
Ve. = Verschaffelt, *Comm. Phys. Lab. Univ. Leiden*, Nos. 18, 28.
I.C.T. = International Critical Tables (see p. 2114).

gem-Dialkyl and -dicarbethoxyl groups, on the other hand, in harmony with their known influence in stabilising strained rings, appear to introduce a " negative " strain, the parachors of cyclic compounds containing such groupings being lower than those calculated additively (compare Sugden, J., 1927, 139; 1928, 410; Vogel, J., 1928, 2010). The diminution depends, to some extent, on the nature of the groups concerned, and the size of the ring, but as a first approximation, — 3·0 units may be taken as a representative mean value of the strain constant for *gem*-dialkyl groups, and — 6·0 units as that for *gem*-dicarbethoxyl and other similar negative groups. Ethylenic compounds, in this connexion, may be regarded as two-membered ring systems (see Table III).

By analogy, the differing strain in heterocyclic compounds might be expected to show in the deviation of their parachors from the normal, but lack of data precludes confirmation of this corollary. In harmony with their similar stability, the ring constants of benzene, *cyclo*hexane, pyridine, and piperidine, and, amongst five-membered rings, of methyl*cyclo*pentane and thiophen, are the same within the limits of experimental error.

An interesting point arises in connexion with the $\cdot\mathrm{N}\colon\mathrm{N}\cdot$ grouping, the presence of which in a cyclic structure is known to exert a stabilising influence (witness the remarkable stability of the triazoles and tetrazoles). Few such compounds have been examined, but from the available data for azides and for nitrous oxide (Table III), on the assumption of a ring structure in both cases (compare Sidgwick, this vol., p. 1108), the strain constant associated with the presence of the group in question may be tentatively assessed at $-$ 6·5 units. If, however, this contraction is taken as an indication that the double bond between the two nitrogen atoms has a lower parachor value (*viz.*, 19 $-$ 6·5 $=$ 12·5) than the corresponding carbon–carbon linkage, then the alternative linear constitution for azides is also possible, for on such a basis the calculated parachors of the $-\mathrm{N}{=}\mathrm{N}\overset{\rightarrow}{\equiv}\mathrm{N}$ and  $-\mathrm{N}{<}\begin{smallmatrix}\mathrm{N}\\ \| \\ \mathrm{N}\end{smallmatrix}$ groups would be identical, the structural constant for a three-membered ring being also 12·5 units.

Effect of Chain Branching.—Comparable with the effect produced by *gem*-dialkyl groups in cyclic structures, chain branching in aliphatic hydrocarbons and their derivatives is accompanied by a slight, but definite, diminution of parachor (see p. 2112). The decrement varies somewhat according to the position and length of the side chain, but within the limits of experimental error a mean value of $-$ 3·0 would appear to be applicable to all branched groups of the type $\mathrm{CHR_2}\cdot$, and double this value to $\mathrm{CR_3}\cdot$ radicals and doubly-branched compounds $\mathrm{CHR_2}\cdot$ . . . $\cdot\mathrm{CHR_2}$. For $\mathrm{CHMe_2}$ the decrement is slightly less, and for $\mathrm{CHEt_2}$ slightly greater, than this mean value, but the available data are not such as to justify differentiation between the two. The contraction also appears to be of the same order with $\mathrm{CHPh_2}\cdot$ groups.

The effect of accumulation of alkyl substituents round a benzene nucleus—a special case of chain branching—is more difficult to assess, but, by assuming that the resulting contraction is brought about by a stress transmitted from atom to atom *via* the orbits of the binding electrons, it may be approximately estimated in a

TABLE IV.

Chain Branching.

Compound.	Formula.	Σ At. *P*.	σ.	[*P*] calc.	[*P*] obs.	Observers.
γ-Methylhexane	$CHMeEt{\cdot}Pr$	310·8	− 3	307·8	306·6	E. & C.
ββ-Dimethylpentane	$CMe_3{\cdot}Pr$	310·8	− 6	304·8	305·3	E. & C.
ββγ-Trimethylbutane	$CMe_3{\cdot}CHMe_2$	310·8	− 9	301·8	301·4	E. & C.
βδ-Dimethylpentane	$CHMe_2{\cdot}CH_2{\cdot}CHMe_2$	310·8	− 6	304·8	305·5	E. & C.
β-Methylheptane	$CHMe_2{\cdot}[CH_2]_4{\cdot}Pr$	350·8	− 3	347·8	348·7	R. S. & C.
βε-Dimethylhexane	$CHMe_2{\cdot}[CH_2]_2{\cdot}CHMe_3$	350·8	− 6	344·8	345·5	I. C. T.
Mesitylene	$C_6H_3Me_3$ (1 : 3 : 5)	325·4	− 3·6	321·8	320·8	I. C. T.
Durene	$C_6H_2Me_4$ (1 : 2 : 4 : 5)	365·4	− 8·0	357·4	355·6	D. & Fr.
Pentamethylbenzene	C_6HMe_5	405·4	−13·8	391·6	390·0	D. & Fr.
Di*iso*amyl ether	$(CHMe_2{\cdot}CH_2{\cdot}CH_2)_2O$	450·8	− 6	444·8	445·7	K. & M.
Pinacolin	$CMe_3{\cdot}COMe$	279·0	− 6	273·0	273·4	I. C. T.
Phorone	$(CMe_2{:}CH)_2CO$	375·4	− 6	369·4	368·3	S.; D. & M.

E. & C. = Edgar and Calingaert, *loc. cit.*
R. S. & C. = Richards, Speyers, and Carver, *loc. cit.*
D. & Fr. = Dutoit and Friderich, *Arch. Sci. phys. nat.*, 1900, **9**, 105.
K. & M. = Kremann and Meingast, *Monatsh.*, 1914, **35**, 1323.
S. = Sugden, J., 1928, 410.
D. & M. = Dutoit and Mojoiu, *J. Chim. physique*, 1909, **7**, 169.
I.C.T. = International Critical Tables (see p. 2114).

manner similar to that outlined by Højendahl (J., 1924, **125**, 1381). On this basis the stress between two substituents in the 1 : 2-, 1 : 3-, and 1 : 4-positions would be, respectively, 0·565, 0·408, and 0·36 times that of a corresponding *gem*-dialkyl group, and the parachors of the *o*-, *m*-, and *p*-disubstituted compounds would therefore be lower than those calculated additively by $0{\cdot}565 \times 3 = 1{\cdot}7$, $0{\cdot}408 \times 3 = 1{\cdot}2$, and $0{\cdot}36 \times 3 = 1{\cdot}1$ units, respectively. Individually, by reason of the comparatively large molecules involved, these contractions are experimentally imperceptible, though it is, perhaps, significant that three independent observers (Schiff, *loc. cit.*; Richards, Speyers, and Carver, *loc. cit.*; Morgan and Daghlien, *J. Amer. Chem. Soc.*, 1911, **33**, 672) agree in finding the parachor of *o*-xylene to be about a unit lower than those of the corresponding *m*- and *p*-isomerides. Their cumulative effect, however, makes them of considerable importance in the case of the polymethyl-benzenes. In 1 : 2 : 4 : 5-tetramethylbenzene, for instance, the parachor will be diminished owing to various stresses as follows: between the 1-methyl group and those in the 2-, 4-, and 5-positions, by $1{\cdot}7 + 1{\cdot}1 + 1{\cdot}2 = 4{\cdot}0$ units; between the 2-methyl group and those in the 4- and 5-positions, by $1{\cdot}2 + 1{\cdot}1 = 2{\cdot}3$ units; between the 4- and 5-methyl groups, by 1·7 units; total = 8·0 units. The calculated parachor will, therefore, be $365{\cdot}4 - 8{\cdot}0 = 357{\cdot}4$, in good agreement with the experimental value, 355·6.

Some further comparisons of calculated and observed parachors in the case of branched-chain compounds are given in Table IV.

Effect of Accumulation of Negative Groups.—Corresponding with the depressant effect of halogen accumulation on other physical properties (molecular refraction, magnetic rotation, molecular viscosity, heat of formation, etc.), the attachment of two or more halogen atoms or other negative groups to the same carbon atom is also attended by a well-defined decrease in parachor (compare Sugden, *loc. cit.*). The contraction is again rather variable, depending on the size and polarity of the atoms and groups concerned, but on an average, $^-CHX_2$ groups ($X = Cl$, CN, CO_2R, OR, etc.) have a parachor 3 units less, $^-CX_3$ groups 6 units less, and compounds of the type CX_4 9 units less than those calculated additively. With bromine, the contractive effect is apparently more marked, the strain constants being about 1·5 times these values (see Table V).

TABLE V.

Accumulation of Negative Atoms and Groups.

Compound.	Formula.	Σ At. *P*.	σ.	[*P*] calc.	[*P*] obs.	Observers.
Ethylidene chloride	$CHMeCl_2$	190·0	− 3	187·0	188·5	I. C. T.
Benzal chloride	$CHPh\cdot Cl_2$	324·6	− 3	321·6	320·6	Sch.
Ethyl chloroacetate	$CH_2Cl\cdot CO_2Et$	255·6	− 3	252·6	252·1	Sch.
Ethyl cyanoacetate	$CH_2(CN)\cdot CO_2Et$	265·3	− 3	262·3	262·1	W. & S.
Diethylacetal	$CHMe(OEt)_2$	310·8	− 3	307·8	306·9	Sch.
Chloroform	$CHCl_3$	189·6	− 6	183·6	183·4	I. C. T.
Dichlorobromomethane	$CHCl_2Br$	203·6	− 6	197·6	196·8	W. & S.
Ethyl dichloroacetate	$CHCl_2\cdot CO_2Et$	295·2	− 6	289·2	291·7	Sch.
Carbon tetrachloride	CCl_4	229·2	− 9	220·2	220·0	I. C. T.
Chloropicrin	$CCl_3\cdot NO_2$	247·7	− 9	238·7	236·8	Sch.
Ethyl trichloroacetate	$CCl_3\cdot CO_2Et$	334·8	− 9	325·8	327·6	I. C. T.
s-Tetrachloroethane	$CHCl_2\cdot CHCl_2$	269·2	−10·5	258·7	259·0	W. & S.
Perchloroethylene	$CCl_2{:}CCl_2$	257·4	−15	242·2	244·5	I. C. T.
Ethylene dibromide	$CH_2Br\cdot CH_2Br$	218·0	− 1·5	216·5	215·5	I. C. T.
s-Tetrabromoethane	$CHBr_2\cdot CHBr_2$	325·2	−15·7	309·5	310·4	I. C. T.
Bromoform	$CHBr_3$	231·6	− 9	222·6	221·9	I. C. T.
o-Chloronitrobenzene	$Cl\cdot C_6H_4\cdot NO_2$	303·1	− 3·4	299·7	299·9	S. & Wi.
o-Bromonitrobenzene	$Br\cdot C_6H_4\cdot NO_2$	317·1	− 3·4	313·7	312·9	S. & Wi.
m-Dichlorobenzene	$C_6H_4Cl_2$	284·6	− 2·4	282·2	281·0	J.
p-Chloroiodobenzene	$Cl\cdot C_6H_4\cdot I$	319·6	− 2·2	317·4	316·4	S.
o-Bromotoluene	$C_6H_4Me\cdot Br$	299·0	− 2·5	296·5	294·3	I. C. T.
o-Toluonitrile	$C_6H_4Me\cdot CN$	294·7	− 2·5	292·2	292·7	I. C. T.
m-Nitrotoluene	$C_6H_4Me\cdot NO_2$	303·5	− 1·8	301·7	300·6	I. C. T.
p-Chlorotoluene	$C_6H_4Me\cdot Cl$	285·0	− 1·6	283·4	283·6	I. C. T.
1-Chloro-2 : 4-dinitrobenzene	$C_6H_3Cl(NO_2)_2$	361·2	− 8·0	353·2	351·6	J.
1 : 4-Dichloro-2-nitrobenzene	$C_6H_3Cl_2\cdot NO_2$	342·7	− 8·0	334·7	335·4	J.

I. C. T. = International Critical Tables (see p. 2114). Sch. = Schiff, *loc. cit.*
W. & S. = Walden and Swinne, *loc. cit.*
S. & Wi. = Sugden and Wilkins, J., 1925, **127**, 2517.
S. = Sugden, J., 1924, **125**, 1167. J. = Jaeger, *Z. anorg. Chem.*, 1917, **101**, 1.

In the case of benzene derivatives the net effect of accumulation of negative groups may be estimated as in the preceding section, the diminution of parachor brought about by two negative substituents in the 1 : 2-, 1 : 3-, and 1 : 4-positions being 3·4, 2·4, and 2·2 units respectively, since the strain constant for *gem*-dicarbethoxyl and similar negative groups is double that for *gem*-dialkyl groups. (The accumulation of both alkyl and negative groups may be provisionally regarded as having an intermediate contractive effect.) The same method may also be used for the estimation of the contraction due to accumulated halogen atoms on adjacent carbon atoms, this case being of particular interest, for the juxtaposition of, say, two $CHCl_2$– groups produces a parachor diminution over and above that due to each individually. With *s*-tetrachloroethane, for instance, in addition to the decrease of 6 units due to the presence of the two dichloro-groups, the stress between the latter, which, on the basis of Højendahl's thesis is equivalent to half that existing between four chlorine atoms on the same carbon atom (the other half being transmitted to the hydrogen atoms), will give rise to a further contraction of $\frac{1}{2} \times 9 = 4{\cdot}5$ units, making a total diminution of 10·5 units. In perchloroethylene, on the other hand, where the whole of the stress is transmitted between the contiguous carbon atoms, the contraction will be $6 + 9 = 15$ units, both these values being in agreement with experiment (see Table V).

Carbonyl Compounds, etc.—As might be expected from the "positive" strain associated with cyclic carbonyl groups, the "negative" strain in tetra-substituted methanes, CX_4, is eased when doubly-bound oxygen replaces two of the negative groups (X), the strain constants for derivatives of the type COX_2 being smaller than those for the parent CX_4 compounds. Their actual values vary considerably and appear to depend on the electron-affinities of the X-groups present (as estimated, *e.g.*, from the ionisation constants of the *p*-substituted benzoic acids, $C_6H_4X{\cdot}CO_2H$; compare Lucas, *J. Amer. Chem. Soc.*, 1926, **48**, 1827), much in the same way as do the optical exaltation (Eisenlohr, *Ber.*, 1911, **44**, 3188; Karvonen, *Ann. Acad. Sci. Fennicæ*, 1916, *A*, **10**, No. 4, 1) and the additive power (Stewart, J., 1905, **87**, 186; Vorländer, *Annalen*, 1905, **341**, 9) of the carbonyl group in different environment. For purposes of calculation, how-

TABLE VI.

Carbonyl Compounds.

Compound.	Formula.	Σ At. *P*.	σ.	[*P*] calc.	[*P*] obs.	Observers.
Acetone	$COMe_2$	159·0	0	159·0	161·5	I. C. T.
Methyl ethyl ketone	$COMe{\cdot}Et$	199·0	0	199·0	198·8	I. C. T.
Acetophenone	$COPh{\cdot}Me$	293·6	0	293·6	293·8	I. C. T.
Distyryl ketone	$(CHPh{:}CH)_2CO$	564·6	0	564·6	564·5	S.
*iso*Valeraldehyde	$CHMe_2{\cdot}CH_2{\cdot}CHO$	236·0	0	236·0	237·5	Sch.
Benzaldehyde	$Ph{\cdot}CHO$	253·6	0	253·6	255·1	I. C. T.
Ethyl carbonate	$CO(OEt)_2$	279·0	−3	276·0	277·4	S. R. W.
Phenyl carbonate	$CO(OPh)_2$	468·2	−3	465·2	467·4	S. R. W.
Ethyl chlorocarbonate	$Cl{\cdot}CO_2Et$	218·6	−3	215·6	216·9	R. & S.
Benzoyl chloride	$COPh{\cdot}Cl$	293·2	−3	290·2	289·8	Sch.
Succinyl chloride	$(CH_2{\cdot}COCl)_2$	286·4	−6	280·4	282·6	G. & S.
Carbonyl chloride	$COCl_2$	158·2	−6	152·2	151·6	P. & M.
Ethyl acetate	$Me{\cdot}CO_2Et$	219·0	−3	216·0	216·9	I. C. T.
Propyl propionate	$Et{\cdot}CO_2Pr$	299·0	−3	296·0	295·3	Sch.
*iso*Butyl *iso*butyrate	$CHMe_2{\cdot}CO_2Bu^{\beta}$	373·0	−3	370·0	371·2	Sch.
Methyl benzoate	$Ph{\cdot}CO_2Me$	313·6	−3	310·6	310·4	I. C. T.
*iso*Propyl β-phenylpropionate	$CH_2Ph{\cdot}CH_2{\cdot}CO_2Pr^{\beta}$	470·6	−3	467·6	467·4	W. & S.
Di*iso*amyl sebacate	$C_8H_{16}(CO_2C_5H_{11})_2$	881·2	−6	875·2	877·0	W. & S.
Tristearin	$C_3H_5(C_{18}H_{35}O_2)_3$	2395·4	−9	2386·4	2380·0	W. & S.

I. C. T. = International Critical Tables (see p. 2114). S. = Sugden, J., 1928, 410.
Sch. = Schiff, *loc. cit.* S. R. W. = Sugden, Reed, and Wilkins, J., 1925, **127**, 1525.
R. & S. = Ramsay and Shields, J., 1893, **63**, 1089.
G. & S. = Garner and Sugden, J., 1927, 2877.
P. & M. = Paterno and Mazzucchelli, *Gazzetta*, 1920, **50**, i, 30.
W. & S. = Walden and Swinne, *loc. cit.*

ever, the COX_2 derivatives may conveniently be divided into three groups according as the strain constant is (i) zero (*e.g.*, in ketones, aldehydes); (ii) about 3·0 units (*e.g.*, in carbonates, chlorocarbonates, esters, acid chlorides), or (iii) about 6 units (*e.g.*, in carbonyl chloride). The contraction of 3·2 units which Sugden (*loc. cit.*) found it necessary to introduce in the case of esters would thus appear to be a special case of a more general principle.

The use of such strain constants is illustrated by the examples given in Table VI.

Oxygen Compounds of Other Elements.—From the general resemblance between sulphur and carbon dioxides, thionyl and carbonyl chlorides, sulphites and carbonates, etc., the strain constants for the oxy-compounds of carbon might reasonably be expected to apply to the analogous compounds of sulphur, notwithstanding the presence of a semipolar double bond in the latter in place of the non-polar double bond in the former. The parachor of thionyl chloride, therefore, should be 6 units less, and those of sulphinates and sulphites 3 units less, than those calculated additively. If the atomic parachor of sulphur be taken as 50 (its value in sulphides, mercaptans, thiocyanates, etc.), and if a semipolar double bond be regarded as equivalent to an ordinary single bond, these inferences are in complete accord with experiment (see Table VII).

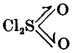
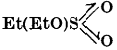
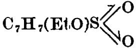
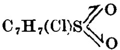
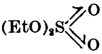
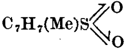
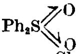
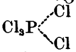
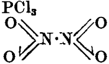
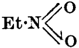
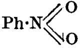
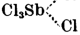
Similar ideas being extended to the derivatives of sexavalent sulphur, since the accumulation of n chlorine atoms round a central carbon atom depresses the parachor by $3(n - 1)$ units, the strain constant for sulphur hexachloride, the parent of such compounds, should by analogy be $5 \times (-3) = -15$ units. In sulphuryl chloride, therefore, in which two pairs of chlorine atoms are replaced by oxygen atoms, the strain constant would be $3 \times (-3) = -9$ units, and in sulphates, sulphonates, and sulphonyl chlorides, $2 \times (-3) = -6$ units.

In the same way, the five chlorine atoms in phosphorus pentachloride might be expected to produce a contraction of $4 \times 3 = 12$ units, which would be reduced to $3 \times 3 = 9$ units in phosphorus oxychloride, and to $2 \times 3 = 6$ units in phosphates; and, similarly, in nitro-compounds and nitrates, both of which are derived in three stages from a hypothetical nitrogen pentachloride, the strain constant should be -3 units, whilst nitrites, derived from nitrogen trichloride in two stages, should be normal. As will be seen from Table VII, parachors calculated in accordance with these principles are in all cases in good agreement with those obtained experimentally.

The strain constants, it must be emphasised, are additional to, and independent of, any structural features (rings, double bonds, etc.) which may be present in the molecules concerned, the calculated

TABLE VII.

Chloro- and Oxy-compounds of Elements other than Carbon.

Compound.	Formula.	Σ At. *P*.	σ.	[*P*] calc.	[*P*] obs.	Observers.
Thionyl chloride	$Cl_2S \rightarrow O$	180·0	− 6	174·0	173·5	S.R.W.; R. & S.
Ethyl *p*-toluene-sulphinate	$C_7H_7{\cdot}S \rightarrow O(OEt)$	415·4	− 3	412·4	410·3	Ph.
s-Ethyl sulphite	$(EtO)_2S \rightarrow O$	300·8	− 3	297·8	299·7	W. & S.
Sulphur monochloride	$Cl_2S \rightarrow S$	210·0	− 6	204·0	204·3	R. & S.; H. & Sch.
Sulphuryl chloride	 $Cl_2S\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}$	200·0	− 9	191·0	190·1	S.R.W.; R. & S.
as-Ethyl sulphite	 $Et(EtO)S\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}$	300·8	− 6	294·8	295·8	W. & S.
Ethyl *p*-toluene-sulphonate	 $C_7H_7(EtO)S\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}$	435·4	− 6	429·4	431·8	F. & S.
p-Toluenesulphonyl chloride	 $C_7H_7(Cl)S\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}$	375·0	− 6	369·0	367·8	F. & S.
Ethyl sulphate	 $(EtO)_2S\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}$	320·8	− 6	314·8	313·8	S.R.W.
Benzylmethylsulphone	 $C_7H_7(Me)S\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}$	375·4	− 6	369·4	369·8	F. & S.
Diphenylsulphone	 $Ph_2S\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}$	470·0	− 6	464·0	465·7	F. & S.
Phosphorus pentachloride	 $Cl_3P\genfrac{}{}{0pt}{}{\cdot\cdot Cl}{\cdot\cdot Cl}$	296·5	−12	284·5	282·5	S.
Phosphorus oxychloride	$Cl_3P \rightarrow O$	225·5	− 9	216·5	217·6	S.R.W.; R. & S.
Ethyl phosphate	$(EtO)_3P \rightarrow O$	406·7	− 6	400·7	399·1	S.R.W.
Phenyl phosphate	$(PhO)_3P \rightarrow O$	690·5	− 6	684·5	686·5	S.R.W.
Phosphorus trichloride	PCl_3	205·5	− 6	199·5	200·0	I. C. T.
Nitrogen peroxide	 $\genfrac{}{}{0pt}{}{O\searrow}{O\nearrow}N{\cdot}N\genfrac{}{}{0pt}{}{/\!\!/O}{\searrow O}$	153·0	− 6	147·0	145·8	R. & S.
Nitroethane	 $Et{\cdot}N\genfrac{}{}{0pt}{}{/\!\!/O}{\searrow O}$	171·9	− 3	168·9	171·2	I. C. T.
Nitrobenzene	 $Ph{\cdot}N\genfrac{}{}{0pt}{}{/\!\!/O}{\searrow O}$	266·5	− 3	263·5	264·5	I. C. T.
Ethyl nitrate	 $EtO{\cdot}N\genfrac{}{}{0pt}{}{/\!\!/O}{\searrow O}$	191·9	− 3	188·9	189·8	I. C. T.
Nitrosyl chloride	$Cl{\cdot}N{=}O$	111·5	− 3	108·5	108·1	B. & P.
n-Butyl nitrite	$C_4H_9O{\cdot}N{=}O$	251·9	0	251·9	251·8	S.R.W.
Diphenyl selenoxide	$Ph_2Se \rightarrow O$	463·0	0	463·0	461·6	H. & S.
Selenium oxychloride	$Cl_2Se \rightarrow O$	193·0	− 6	187·0	181·1	H. & S.
Antimony pentachloride	 $Cl_3Sb\genfrac{}{}{0pt}{}{\cdot\cdot Cl}{\cdot\cdot Cl}$	324·0	−12	312·0	311·8	S.
Antimony trichloride	Cl_3Sb	233·0	− 6	227·0	227·4	S.
Arsenic trichloride	Cl_3As	219·0	− 6	213·0	212·3	H. & S.; J.
Phenyldichloroarsine	$Ph{\cdot}AsCl_2$	354·0	− 3	351·0	348·3	H. & S.
Boron trichloride	BCl_3	186·5	− 6	180·5	178·8	M. & R.
Ethyl borate	$B(OEt)_3$	367·7	− 6	361·7	363·1	E. & S.

S.R.W. = Sugden, Reed, and Wilkins, *loc. cit.* R. & S. = Ramsay and Shields, *loc. cit.*
Ph. = Phillips, J., 1925, **127**, 2570. W. & S. = Walden and Swinne, *loc. cit.*
H. & Sch. = Harvey and Schuette, *J. Amer. Chem. Soc.*, 1926, **48**, 2065.
F. & S. = Freiman and Sugden, J., 1928, 263. S. = Sugden, J., 1927, 1173.
E. & S. = Etridge and Sugden, J., 1928, 989.
I. C. T. = International Critical Tables (see p. 2114).
B. & P. = Briner and Pylkoff, *J. Chim. physique*, 1912, **10**, 640.
H. & S. = Henley and Sugden, this vol., p. 1058.
J. = Jaeger, *Z. anorg. Chem.*, 1917, **101**, 1.
M. & R. = Mills and Robinson, J., 1927, 1823.

parachor of phosphorus pentachloride, for instance, being the algebraic sum of those of one phosphorus atom (40·5), five chlorine atoms (55 each), two singlet linkages (— 9·5 each), and a strain constant of — 12 units. Their actual values may require modification when a more extensive range of compounds has been examined, but existing data for chloro- and oxy-compounds indicate that they may be taken as integral multiples of 3. This procedure not only has the merit of simplicity, but also makes it possible to classify analogous compounds into groups according to the numerical values of their strain constants (see Table VIII), thereby correlating and systematising the conceptions developed above.

The position of sulphones in such a scheme is of particular interest in connexion with the abnormally low parachors found by Freiman and Sugden (*loc. cit.*) for sulphonal and trional. Simple sulphones, according to the data of these authors (see Table VII), belong to Group 2 of the scheme, so that the strain constant associated with the two R·SO$_2$· groups present in sulphonal will be $2 \times (-6) = -12$ units. No compounds of the type R_2CX_2 ($R =$ alkyl; $X =$ negative group), other than those under consideration, appear to have been examined, but from the configurational resemblance which they bear to the sulphones, they also may be tentatively assigned to Group 2—a position which is consistent with their relationships to the CR_3X and CRX_3 compounds. The calculated parachor of sulphonal will thus be 18 less than the sum of the atomic constants, *i.e.*, $490{\cdot}8 - 18 = 472{\cdot}8$, which is only 1·5% higher than the experimental value (465·5). With trional ([*P*]obs., 493·8; calc., 512·8) the agreement is less good (the greater contractive value of the *gem*-methylethyl grouping being, perhaps, partly responsible for the discrepancy), but it would, nevertheless, seem probable that the apparent parachor anomaly of disulphones has its origin, at least in part, in intramolecular strain.

A further point of interest arises in connexion with the parachors of carbon and sulphur dioxides. If we regard the former as derived from carbon tetrachloride by successive replacement of the two pairs of chlorine atoms by oxygen atoms, it is evident, from a consideration of the valency deflexions involved, that the partial relief of strain which accrues from the first stage of the process will be more or less completely nullified by the second, so that the strain constants for carbon dioxide and tetrachloride should have approximately the same value, *viz.*, — 9 units; and similarly for sulphur dioxide, except that the compensating effect of the second replacement might be expected to be less marked on account of the presence of a semipolar double bond in the intermediate compound, thionyl chloride. These inferences appear to be substantiated by experiment, the

TABLE VIII.

Classification of Compounds according to Strain Constants.

Group	0.	1.	2.	3.	4.	5.
Strain constant ...	0	-3	-6	-9	-12	-15
Carbon compounds.	$R·CH_2·X$	$R·CHX_2$ $R_2CH·X$	$R·CX_3$ $R_3C·X$	CX_4 R_4C	—	—
	$R·CO·H$ $R·CO·R$ $R·CO·NH_2$	$R·CO·OH$ $RO·CO·NH_2$ $R·CO·OR$ $RO·CO·OR$ $R·CO·Cl$ $RO·CO·Cl$	$Cl·CO·Cl$	CCl_4	—	—
Sulphur compounds.	—	$R·SO·OR$ $RO·SO·OR$	$Cl·SO·Cl$	(SCl_4)	—	—
	—	—	$R·SO_2Cl$ $RO·SO_2·R$ $R·SO_2·R$ $RO·SO_2·OR$	SO_2Cl_2	$(SOCl_4)$	(SCl_6)
Nitrogen compounds.	$R·NH_2$	R_2NH	R_3N	—	—	—
	$NO·R$ $NO·OR$	NO Cl	(NCl_3)	—	—	—
	—	$NO_2·R$ $NO_2·OR$	(NO_2Cl)	$(NOCl_3)$	(NCl_5)	—
Phosphorus compounds.	—	—	PX_3 R_3P	—	—	—
	—	—	$PO(OR)_3$	$POCl_3$	PCl_5	—
Miscellaneous.	R_2SeO	$R·SeO·OH$	$Cl·SeO·Cl$	CrO_2Cl_2	$SbCl_5$	—
	—	—	BX_3; AsX_3; SbX_3	SiX_4 SnX_4	—	—

(R = Hydrocarbon radical; X = negative group.)

observed parachor of carbon dioxide (78·2; Quinn, *J. Amer. Chem. Soc.*, 1927, **49**, 2704; Verschaffelt, *loc. cit.*) being 9 units, and that of sulphur dioxide (101·5; Grunmach, *loc. cit.*; Stowe, *J. Amer. Chem. Soc.*, 1929, **51**, 410) 7·5 units, lower than those calculated additively (87·2 and 109·0 respectively). It must be pointed out, however, that for the latter compound the observed parachor is not incompatible with the alternative cyclic structure (Rankine and Smith, *Proc. Physical Soc.*, 1922, **35**, 33), for which the calculated parachor is 102·5.

It is not possible to derive a strain constant for carbon disulphide in this way until data for thiocarbonyl chloride and other thiocarbonyl derivatives are available, but since the distortion of electron orbits in such compounds will, presumably, be less than that in the corresponding oxy-compounds, by reason of the greater size of the sulphur atom, their strain constants might be expected to be proportionately smaller. The fact that the observed parachor of carbon disulphide (143·7; " International Critical Tables ") is only 3·5 units lower than the calculated value (147·2) is, therefore, not inconsistent with the views developed above.

The Significance of Strain Constants.—Since the parachor is virtually a measure of molecular volume under comparable conditions as regards internal pressure, and is, therefore, more or less independent of the cohesion between the molecules (compare Sugden, this vol., p. 1055), the contractions referred to above as strain constants would appear to connote a real diminution of molecular volume, brought about either by the closer packing of atoms and groups within the molecule, or by a decrease in the effective size of one or other of the atoms concerned. In the case of the branched chain hydrocarbons and their derivatives the former is a possible cause, but the contractive effect of accumulation of negative groups cannot reasonably be accounted for on this basis in view of the electrostatic forces of repulsion which will operate between the charged groups.

On the basis of modern theories of atomic structure, the " bond " between an atom of high electron-affinity, such as chlorine, and an atom of smaller electron-affinity, such as carbon, must be regarded as being partially polarised, the shared-electron orbits round the latter having contracted in accordance with the frequency and symmetry conditions of Fowler and Sidgwick (*Trans. Faraday Soc.*, 1923, **19**, 459, 469; compare Højendahl, *loc. cit.*). The accumulation of chlorine atoms round a carbon atom will, therefore, result in a considerable diminution of the effective volume of the latter. A similar conclusion also follows from the point of view of wave mechanics (London, *Z. Physik.*, 1928, **46**, 455), the contraction resulting from a decrease in the electron density in the vicinity of the carbon nucleus (compare also Goldschmidt's work, summarised in *Trans. Faraday Soc.*, 1929, **25**, 253, on the influence of co-ordination number and electron-affinity on the distance between atomic centres in crystals).

The negative strain constants associated with the presence of $^-CHCl_2$ and $^-CCl_3$ groups would thus appear to correspond with a real diminution in the effective size of the central carbon atom, and to be, in fact, a measure of such diminution. The circumstance that the observed parachor of carbon tetrachloride (220·0) is equal to four times the atomic constant of chlorine lends support to this view, for on the above basis, this compound consists essentially of four bound chlorine atoms clustered round a central carbon atom which is, for the greater part of the time, stripped of its outer electrons, and is thus of comparatively negligible dimensions.

With compounds of sulphur, nitrogen, phosphorus, and other elements of variable valency, the use of strain constants may, to a certain extent, be avoided by assigning different parachor values to the elements in their various states of valency, as has been done, *e.g.*, in the case of molecular refraction, by Strecker and Spitaler (*Ber.*, 1926, **59**, *B*, 1754) for sulphur and phosphorus, and by v. Auwers and Heimke (*Ber.*, 1928, **61**, *B*, 1041) for nitrogen. Such procedure, however, does not lead to very concordant results, and in view of its inapplicability to carbon compounds, it was thought preferable to retain a constant atomic parachor for each such element, and to account for all anomalies by the systematic introduction of strain constants.

A somewhat similar method of computation has recently been applied to molecular refraction (Samuel, *Naturwiss.*, 1929, **17**, 13; *Z. Physik*, 1929, **53**, 380), numerical positive or negative "group refractions" being assigned to the various organic groups, corresponding in sign and magnitude with their polarising properties (see also Swarts, *Bull. Soc. chim. Belg.*, 1925, **34**, 161; Fajans, *Ber.*, 1926, **59**, *B*, 249; *Z. Elektrochem.*, 1928, **34**, 502; Nekrasov, *Z. physikal. Chem.*, 1929, **140**, 342).

Hydroxy-compounds and Amines.—For associated substances, as noted by Sugden (J., 1924, **125**, 32, 1177), the observed parachor is less than the calculated value, but increases slowly with temperature, approaching it in the neighbourhood of the critical temperature. As will be seen from Sugden's data (*ibid.*, p. 32), however, for a given liquid the quotient $\gamma^{\frac{1}{4}}/(D - d)$, γ being the surface tension and D and d the orthobaric densities of liquid and vapour at the same temperature, is comparatively constant for temperatures up to the boiling point, and for this temperature range, therefore, the substance may be regarded as having a definite parachor.

It is not, of course, possible to evaluate such parachors from the constants given above, but examination of a series of alcohols, acids, amines, and amides shows that they may be brought into line with other compounds by assuming that the volume of a hydrogen atom in combination with nitrogen is smaller (12·5) than when united to carbon (15·4), and still smaller (10·0) when combined with oxygen. This assumption—a logical consequence of the views advanced above, the effective volume of the hydrogen atom decreasing with increasing electron-affinity of the atom to which it is attached—forms the basis of Lowry's theory of acidity (*Phil. Mag.*, 1924, **47**, 1021), and in addition to Rankine's work on the viscosity of the gaseous hydrides (*Trans. Faraday Soc.*, 1922, **17**, 719; *Proc. Physical Soc.*, 1922, **34**, 181; compare Smith, *Trans. Faraday Soc.*, 1923, **18**, 302), which led to the formulation of this theory, a considerable amount of evidence can be advanced in support of its fundamental postulate. Huggins (*Physical Rev.*, 1923, **21**, 205; 1926, **28**, 1086), for example, has pointed out that the diameter of the hydrogen atom, as deduced from the *X*-ray analysis of crystals, varies from compound to compound, being 1·02 Å. in potassium hydrogen fluoride, 1·46 Å. in ice, and 1·65 Å. in ammonium chloride; and to this list may be added the more recent value of 1·70 Å. in tetramethylammonium compounds (Vegard and Sollesnes, *Phil. Mag.*, 1927, **4**, 985). Again, Traubenberg and Philipp (*Physikal. Z.*, 1921, **22**, 587) have shown that the stopping-power of compounds for α-rays—a function of electronic frequencies, and hence of orbital dimensions—is not strictly additive, that of the hydrogen atom changing from 0·187 (air = 1) in methane and ethane to 0·173 in ammonia and 0·16 in hydrogen chloride.

Moles (*Anal. Fís. Quím.*, 1927, **25**, 204), from an examination of the molecular volumes at absolute zero of the hydrides of the elements of Groups 4—7 of the periodic classification, was led to the further conclusion that in each group the volume occupied by hydrogen increases with the atomic volume of the element forming the hydride, and in this connexion the subjoined table, giving the apparent atomic parachor of hydrogen in combination with different elements, is of interest :

Group 4.	Group 5.	Group 6.	Group 7.
Carbon 15·4	Nitrogen 12·5	Oxygen 10·0	—
—	—	Sulphur 15·4	Chlorine 12·8
—	—	—	Bromine 16·4

(The values in Group 7 are derived from the data of Steele, McIntosh, and Archibald, *Z. physikal. Chem.*, 1906, **55**, 145; those in the other groups are mean values obtained from series of hydrocarbons, amines, alcohols, and mercaptans.)

Whether the hydrogen atoms in such combinations retain their individuality, or whether their nuclei are buried to a greater or less depth beneath the expanded outer electron shells of the central atom, as suggested by Paneth (*Ber.*, 1925, **58**, *B*, 1138) from the physical resemblance of the gaseous hydrides to the rare gases (see also, Bell, *Phil. Mag.*, 1924, **47**, 549), is immaterial from the present point of view, the assumption being that the apparent effective volume of hydrogen varies in the manner described.

If these values for hydrogen in combination with nitrogen and oxygen be accepted, the parachors and strain constants of amino- and hydroxy-compounds may be predicted according to the principles developed above. Thus, whilst the parachor of a primary amine is that calculated additively, with secondary amines, as with compounds containing an R_2CH^- group, a strain constant of $-3{\cdot}0$ units must be introduced, and with tertiary amines, one of $-6{\cdot}0$ units (compare R_3C^- groups). Again, acids, like esters, belong to Group 1 in Table VIII (strain constant, $-3{\cdot}0$), whereas amides, consonant with the lesser electron-affinity of the amino-group, are normal. In the same way, α-hydroxy-esters, $CHR(OH){\cdot}CO_2R$, and α-halogenated acids, $CHRX{\cdot}CO_2H$, in common with other compounds of the type $RCHX_2$, appear to require a strain constant of approximately -3 units over and above that associated with the carboxyl group itself (see Table IX).

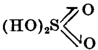
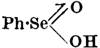
Further, by reason of the diminished value of hydrogen in hydroxy-compounds, the parachor of the $\cdot C(OH){:}CH\cdot$ group is 5·4 units smaller than that of a $\cdot CO{\cdot}CH_2\cdot$ group, and it should therefore be possible, in cases of keto-enol tautomerism, to arrive at an approximate estimate of the relative proportions of the two forms present. Few such instances have been accurately examined, but the data (see " International Critical Tables ") for ethyl acetoacetate ([*P*] obs., 303·3. Calc., enol, 298·8; keto, 304·2), and for acetylacetone ([*P*] obs., 242·0. Calc., enol, 241·8; keto, 247·2), at ordinary temperatures, are in harmony with Meyer's conclusion (*Annalen*, 1911, **380**, 212; *Ber.*, 1912, **45**, 2543) that the former is mainly ketonic (8% enol), and the latter mainly enolic (80% enol). Sugden's more recent value (this vol., p. 316) for benzoylacetone ([*P*] obs., 382·4; calc., enol, 376·4; keto, 381·8) does not, however, accord well with its 98% monoenolic constitution.

Elements.—The variability of effective volume with atomic environment makes it improbable that atomic parachors derived from organic compounds will apply with any degree of accuracy to the free elements, for van der Waals (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 880), van Laar (*ibid.*, 1916, **18**, 1220; *J. Chim. physique*, 1916, **14**, 3), Ephraim (*Helv. Chim. Acta*, 1924, **7**, 474),

Table IX.

Hydroxy- and Amino-compounds.

(H attached to O = 10; H attached to N = 12·5.)

Compound.	Formula.	Σ At. *P*.	σ.	[*P*] calc.	[*P*] obs.	Observers.
Ethyl alcohol	C_2H_5OH	125·4	0	125·4	126·8	I. C. T.
Propyl alcohol	C_3H_7OH	165·4	0	165·4	165·4	I. C. T.
*iso*Butyl alcohol	C_4H_9OH	202·4	0	202·4	202·1	I. C. T.
tert.-Amyl alcohol	$C_5H_{11}OH$	239·4	0	239·4	241·1	I. C. T.
sec.-Octyl alcohol	$C_8H_{17}OH$	362·4	0	362·4	360·4	I. C. T.
Benzyl alcohol	$Ph\cdot CH_2OH$	260·0	0	260·0	259·6	I. C. T.
Phenol	$Ph\cdot OH$	220·0	0	220·0	221·3	I. C. T.
*cyclo*Hexanol	$C_6H_{11}OH$	255·4	0	255·4	254·9	H.; W.S.&S.
Ethyl malate	$CH_2\cdot CO_2Et$ | $CH(OH)\cdot CO_2Et$	415·8	− 3	412·8	412·4	M. & K.
Ethyl lactate	CH_3 | $CH(OH)\cdot CO_2Et$	270·6	− 3	267·6	268·5	I. C. T.
Ethyl tartrate	$CH(OH)\cdot CO_2Et$ | $CH(OH)\cdot CO_2Et$	430·4	− 6	424·4	428·1	J.
Methyl salicylate	$C_6H_4(OH)\cdot CO_2Me$	325·2	− 3·4	321·8	323·7	J.
Acetic acid	$CH_3\cdot CO_2H$	133·6	− 3	130·6	131·2	I. C. T.
Propionic acid	$C_2H_5\cdot CO_2H$	173·6	− 3	170·6	169·0	I. C. T.
*iso*Butyric acid	$C_3H_7\cdot CO_2H$	210·6	− 3	207·6	207·8	I. C. T.
Capric acid	$C_9H_{19}\cdot CO_2H$	453·6	− 3	450·6	447·7	H. & M.
Stearic acid	$C_{17}H_{35}\cdot CO_2H$	773·6	− 3	770·6	778·0	H. & M.
Undecylenic acid	$C_{10}H_{19}\cdot CO_2H$	481·8	− 3	478·8	478·2	H. C. & R.
Lævulic acid	$CH_3\cdot CO\cdot [CH_2]_2\cdot CO_2H$	261·8	− 3	258·8	258·6	J.
Chloroacetic acid	$CH_2Cl\cdot CO_2H$	173·2	− 6	167·2	168·3	J.
Dichloroacetic acid	$CHCl_2\cdot CO_2H$	212·8	− 9	203·8	203·8	J.
Trichloroacetic acid	$CCl_3\cdot CO_2H$	252·4	−12	240·4	241·3	J.
Nitric acid		106·5	− 3	103·5	105·4	A. & R.
Sulphuric acid		150·0	− 6	144·0	143·7	P.
Phenylseleninic acid		303·0	− 3	300·0	299·5	H. & S.
Acetaldoxime	$CH_3\cdot CH{:}NOH$	146·5	0	146·5	145·4	I. C. T.
Heptaldoxime	$C_6H_{13}\cdot CH{:}NOH$	346·5	0	346·5	343·7	D. & F.
Ethylamine	$C_2H_5\cdot NH_2$	137·9	0	137·9	137·4	J.
n-Propylamine	$C_3H_7\cdot NH_2$	177·9	0	177·9	178·5	J.; I. C. T.
*iso*Butylamine	$C_4H_9\cdot NH_2$	214·9	0	214·9	216·1	Sch.
tert.-Amylamine	$C_5H_{11}\cdot NH_2$	251·9	0	251·9	252·3	J.
Aniline	$Ph\cdot NH_2$	232·5	0	232·5	234·4	I. C. T.
p-Toluidine	$C_6H_4Me\cdot NH_2$	272·5	− 1·1	271·4	272·1	I. C. T.
Dimethylamine	Me_2NH	140·8	− 3	137·8	136·6	J.
Di-*n*-propylamine	Pr_2NH	300·8	− 3	297·8	297·2	I. C. T.
Di*iso*butylamine	$(C_4H_9)_2NH$	374·8	− 3	371·8	372·1	I. C. T.
Ethylaniline	$Ph\cdot NHEt$	315·4	− 3	312·4	310·4	I. C. T.
Dibenzylamine	$(Ph\cdot CH_2)_2NH$	490·0	− 3	487·0	485·6	T. & M.
Acetanilide	$Ph\cdot NHAc$	323·6	− 3	320·6	321·8	T. & M.
Trimethylamine	Me_3N	183·7	− 6	177·7	177·6	J.
Tri-*n*-propylamine	Pr_3N	423·7	− 6	417·7	414·6	J.; T. & M.
Dimethylaniline	$Ph\cdot NMe_2$	318·3	− 6	312·3	311·7	I. C. T.
Urethane	$NH_2\cdot CO_2Et$	206·1	− 3	203·1	202·2	T. & M.
Acetamide	$CH_3\cdot CO\cdot NH_2$	146·1	0	146·1	148·0	T. & M.
Benzamide	$Ph\cdot CO\cdot NH_2$	280·7	0	280·7	279·9	T. & M.

I. C. T. = International Critical Tables. H. = Hardy, *Proc. Roy. Soc.*, 1913, *A*, **88**, 303.
W. S. & S. = Weissenberger, Schuster, and Schuler, *Monatsh.*, 1924, **45**, 413.
M. & K. = Morgan and Kramer, *J. Amer. Chem. Soc.*, 1913, **35**, 1834. J. = Jaeger, *loc. cit.*
H. & M. = Hunten and Maass, *loc. cit.* H. C. & R. = Harkins, Clark, and Roberts, *loc. cit.*
A. & R. = Aston and Ramsay, J., 1894, **65**, 167. P. = Pound, J., 1911, **99**, 698.
H. & S. = Henley and Sugden, *loc. cit.*
D. & F. = Dutoit and Fath, *J. Chim. physique*, 1903, **1**, 358.
Sch. = Schiff, *loc. cit.* T. & M. = Turner and Merry, J., 1910, **97**, 2069.

Biltz (*Annalen*, 1927, **453**, 259), and others have shown that combination is attended by volume alterations.

In the case of the halogens, however, some agreement between calculated and observed values might be expected, for an atom of these elements will probably occupy much the same volume when united to another of its own kind as when combined with carbon. In the latter union it will be the shared-electron orbits round the less electronegative and more flexible carbon atom that will undergo adjustment, the halogen atom in both types of combination approximating in size to the rare gas which follows it in the periodic classification. This expectation is realised in the case of chlorine, the atomic parachor of the element being 54·5 (Marchand, *J. Chim. physique*, 1913, **11**, 573; Grunmach, *loc. cit.*; Johnson and McIntosh, *J. Amer. Chem. Soc.*, 1909, **31**, 1139), as compared with 55·0 in organic chlorides, whilst that of argon is 53·8 (Baly and Donnan, J., 1902, **81**, 907; compare Rudorf, *Ann. Physik*, 1909, **29**, 751). The approximate identity of the atomic parachors of fluorine in organic compounds (25·5) and of neon (25·1; van Urk, Keesom, and Nijhoff, *Proc. K. Acad. Wetensch. Amsterdam*, 1926, **29**, 914) may also be mentioned. The greater discrepancy in the case of bromine, the atomic parachor of which is 65·8 in the element ("International Critical Tables") and 69·0 in organic bromides, is in accord with the smaller electron-affinity and greater size and flexibility of its atoms.

With the elements of Groups 5 and 6, the difference between the two "volumes" will be more marked. In the case of nitrogen, the six shared electrons in the molecule, N⋮N, will be symmetrically distributed between the two atoms, but in cyano-groups, by reason of the greater electron-affinity of the nitrogen atom, the distribution will be statistically unequal, with the result that the effective volume of the nitrogen atom will be increased at the expense of that of the carbon atom. Empirically, this effect may be ascribed to a variation in the "constant" for the triple bond, and as on this basis the double bond in −N:N− groups has a parachor value of 12·5 units (see above), the triple bond in molecular nitrogen, by analogy with the corresponding carbon linkages, would be $2 \times 12{\cdot}5 = 25$ units. The calculated parachor for elementary nitrogen would thus be $(2 \times 17{\cdot}5) + 25 = 60$, in good agreement with the observed value (60·4; Baly and Donnan, *loc. cit.*). It is not, of course, possible to make a similar forecast for oxygen.

In the case of hydrogen, whose atoms are more flexible than those of carbon but, at the same time, have a smaller electron-affinity, a reverse effect will obtain, for in C–H unions it will be the shared-electron orbits round the more electronegative carbon atom which will expand at the expense of those round the hydrogen nucleus. The fact that the atomic constant for hydrogen in hydrocarbons according to the present recalculation (15·4) is smaller than the observed atomic parachor of elementary hydrogen (17·4; Onnes and Kuypers, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 528), whereas according to Sugden's original evaluation (17·1) the two are practically identical, may, therefore, be advanced as an argument in support of the new value.

General.—The use of the recalculated atomic and structural constants does not, it must be emphasised, invalidate the general conclusions drawn by Sugden and his co-workers, with the exception of that correlating ring constants with " degree of unsaturation " (Sugden and Wilkins, J., 1927, 139), and possibly also that attributing the apparent anomaly of disulphones to the presence of singlet linkages (Freiman and Sugden, *loc. cit.*); that author's views on other cases of singlet linkages and on the two types of double bond remain unaffected.

The new method of computation is, admittedly, less convenient for ordinary purposes than the simple summation of Sugden's " mean " constants, but this disadvantage is largely counterbalanced by the resulting general improvement in the agreement between observed and calculated parachors, and by the insight obtained into intramolecular relationships.

It is necessary to add, in view of the recent appearance of a paper dealing with the parachors of fused salts (Sugden and Wilkins, this vol., p. 1291), that the use of one and the same atomic constant for the combined atom and for the ion of an element is difficult to reconcile with modern atomic theories, which imply that positive ions occupy a smaller and negative ions a larger " volume " than the corresponding atoms in covalent combination (compare Born, *Z. Physik*, 1920, **1**, 45). Although the parachors so calculated are in agreement with the observed values in the case of certain salts of organic bases, the fact that large positive or negative anomalies are found with other similarly constituted salts strongly suggests that the agreement is fortuitous, and due to counterbalancing variations in the volumes of the two ions.

If, in accordance with the views developed above, the volume measured by the parachor is regarded as being directly and simply related to the actual dimensions of the molecule or atom concerned (compare the proportionality between parachors, critical volumes, and molecular volumes deduced from viscosity measurements; Sugden, this vol., p. 1055), then the parachor values of the ions of the halogens may be approximately estimated from the atomic parachors of the rare gases which follow them in the periodic classification, on the assumption that the radius of similarly constituted atoms and ions is determined by the distribution of the outermost electrons, and is inversely proportional to the effective nuclear charge. Calculation on this basis, either according to the older Bohr theory or according to the newer wave mechanics (see, *e.g.*, Pauling, *J. Amer. Chem. Soc.*, 1927, **49**, 765), indicates that the parachor values of the halide ions should, on an average, be 1·46 times those of the atoms of the corresponding rare gases, and hence, from the values given in the preceding section, about 1·44 times those of the halogen atoms in non-polar combination.

The approximate ionic parachors obtained by the use of this factor (F′ 36; Cl′ 79; Br′ 99; I′ 130), when subtracted from the observed parachors of the fused alkali-metal salts, give sensibly constant values for the parachors of the different alkali-metal ions (Li˙ 21; Na˙ 45; K˙ 76; Rb˙ 95; Cs˙ 109), and from these, in turn, the constants for the nitrate, metaphosphate, and sulphate ions (NO_3' 109; PO_3' 132; SO_4'' 172) may be obtained; the values calculated for the latter on the analogous assumption that each charged oxygen atom in such ions is equivalent to a combined fluorine atom with a net nuclear charge of 6 instead of 7, are 111, 134, and 162 respectively. By using these empirical ionic constants, the parachors of 20 out of the 30 alkali-metal salts examined by Jaeger (*loc. cit.*) can be predicted to within 2 units, and of 25 to within 4 units of the mean observed values (see Table X).

TABLE X.

*Salts of the Alkali Metals.**

Ionic parachors.		Li˙ 21	Na˙ 45	K˙ 76	Rb˙ 95	Cs˙ 109
F′	36	57 (58·5)	81 (82·7)	112 (109·0)	131 (123·1)	145 (136·9)
Cl′	79	100 (98·4)	124 (124·8)	155 (156·6)	174 (182·8)	188 (188·7)
Br′	99	— (—)	144 (143·8)	175 (174·3)	194 (192·7)	208 (207·5)
I′	130	— (—)	175 (170·8)	206 (205·2)	225 (226·8)	239 (242·4)
NO_3'	109	130 (131·5)	154 (152·9)	185 (189)	204 (197·9)	218 (218·0)
PO_3'	132	— (—)	177 (178·1)	208 (204·4)	— (—)	— (—)
SO_4''	172	214 (216·0)	262 (261·1)	324 (328·0)	362 (361·8)	390 (388·8)

* The observed parachors (in parentheses) are taken from Sugden and Wilkins (*loc. cit.*).

The extension of similar ideas to the salts of organic bases is difficult, since the contraction of the nitrogen atom as a result of the electron transfer will be accompanied by a simultaneous diminution in the effective volume of the hydrogen and other flexible atoms in the ion, by reason of the increased electron-affinity of the central atom. Assuming, however, that the volume change is confined to the nitrogen and hydrogen atoms, and that the nuclei of the latter are buried beneath the outer electron shell of the former, then the $NH_n^{\cdot}$ portion of the ion may be regarded as equivalent to a corresponding CH_n group with a net nuclear charge of $(5 + n)$ instead of $(4 + n)$. Very approximately, therefore, the parachor value of the $^{-}NH_3^{\cdot}$ group will be $55{\cdot}4 \times 7^3/8^3 = 37$, that of the $>NH_2^{\cdot}$ group $40 \times 6^3/7^3 = 25$, and that of the $\geqslant NH^{\cdot}$ group $24{\cdot}6 \times 5^3/6^3 =$ 14 units, which values give predicted parachors within a few units of those obtained experimentally by Sugden and Wilkins (*loc. cit.*) for the salts of the simpler organic bases (see Table XI).

TABLE XI.

Salts of Organic Bases.

Salt.	Ionic parachors. Kation.	Ionic parachors. Anion.	[*P*] calc.	[*P*] obs.
Ethylammonium nitrate	132·4	109	241·4	239·2
Methylaniline hydrochloride	270·4	79	349·4	348·6
Ethylaniline hydrochloride	310·4	79	389·4	381·9
Dimethylammonium nitrate	135·8	109	244·8	249·7
Diethylammonium nitrate	215·8	109	324·8	324·8
Dimethylaniline hydrobromide	311·8	99	410·8	412·8

In view of the simplifying assumptions involved, the agreement in both cases is probably largely fortuitous, but it would, nevertheless, seem to indicate that the explanation of the apparent parachor anomaly of fused salts must be sought on these lines.

Summary.

1. Re-examination of the existing surface tension data having indicated that the mean parachor increment for CH_2 adopted by Sugden is too small, the various atomic and structural constants have been re-evaluated by means of the corrected increment.

2. The recalculated values lead to better agreement between observed and calculated parachors, especially in compounds of high molecular weight.

3. Further, they are shown to afford information as to (i) the effects of intramolecular and interatomic stresses, for which allowance is made by the introduction of a "strain constant," (ii) the effective volume of the hydrogen atom in amino- and hydroxy-compounds, and (iii) the parachors of the ions in fused salts.

4. The general conclusions drawn by Sugden and his co-workers, in particular those relating to the existence of two types of double bond, non-polar and semipolar, and of singlet linkages, are not invalidated by the recalculation.

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