63. *Molecular Volume and Structure. Part IX.*

By T. W. Gibling.

The recent publication of new determinations of parachors of a number of paraffins affords an opportunity to review the method of calculation previously proposed. Visualisation of a molecular volume as consisting in general of the " spheres of influence " of the constituent atoms—these " spheres " always interpenetrating to some extent—confirms the idea that the method of derivation of "atomic and structural constants" was based on mistaken assumptions; it also gives a simple explanation of the reductions in parachor value observable in all homologous series, these reductions being produced by " interference " between non-linked atoms, *i.e.*, by the overlapping of their " envelope volumes " or " spheres of influence."

Quayle, Day, and Brown (*J. Amer. Chem. Soc.*, 1944, **66**, 938) state that " the parachors in *n*-saturated hydrocarbons have been found to be almost unique in being additive in nature," though they modify this in a footnote : " Even the values for the saturated hydrocarbons are not considered to be strictly additive by some observers. However, they are at least essentially so. If variations exist they appear to be of a distinctly lower order of magnitude for chains of short or moderate length." They add : " It is essential that the CH_2 increment in the saturated hydrocarbons be re-examined from time to time as compounds of higher purity become available and as the techniques of measurement are improved," and they determined the parachors of eight *n*-paraffins, pentane to duodecane, concluding that " there is no apparent change in the CH_2 increment as the chain is increased up to $C_{12}H_{26}$," their mean CH_2 values (over the temperature range 20—50°) varying from 39·5 to 40·5, with an over-all mean of 40·0.

These statements are in accord with the ideas expressed by the author in discussing the methods used in the calculation of parachors (J., **1941**, 299), in reference to which Quayle *et al.* quote him correctly as asserting " that the CH_2 value seems to show progressively higher values throughout any homologous series," but incorrectly as saying that this is " due to decreasing ' interference ' effects." No hypothesis was advanced by the author to account for the so-called " expansion " phenomenon (for the existence of which he adduced evidence from the parachors of more than 20 compounds of high molecular weight), but it was later suggested by him that among the lower members of any series other than the *n*-paraffins " interference " effects might be expected, which would produce irregularities in the progression in the case of the earlier CH_2 increments.

The formula proposed by the author to represent the parachors so far recorded for *n*-paraffins was $[2c + (n - 2)k]f^n$, where c, the value for CH_3–, was 55·2; k, the –CH_2– value, was 39·8; f **1·0004165**, and n the number of carbon atoms in the molecule. According to this, the CH_2 difference, starting at 39·9 for $n = 2$ or **3**, would become 40·2 for $n = 10$ or 11; for $n = 2$—12, the mean CH_2 difference would be rather more than 40·0; for $n = 59$ or 60, it would be 41·8, with a mean of rather less than 40·9 between $n = 2$ and 60. Inclusion of the newly determined parachors gives a slightly improved agreement between calculated and mean observed values as compared with that shown in the original table (*loc. cit.*, p. 301), as follows :

n-Paraffins, C_nH_{2n+2}.

n.	[*P*], calc.	[*P*], obs.†	Diff., %.	*n*.	[*P*], calc.	[*P*], obs.†	Diff., %.	*n*.	[*P*], calc.	[*P*], obs.†	Diff., %.
2	110·5	110·5	±0·0	7	310·3	310·1[3]	−0·1	12	510·9	510·6	−0·1
3	150·4	150·8	+0·3	8	350·4	350·8[3]	+0·1	26	1077	1082	+0·5
4	190·3	190·3	±0·0	9	390·5	391·1	+0·2	32	1322	1322	±0·0
5	230·3	231·0	+0·3	10	430·6	430·5[2]	−0·0	60	2480	2480	±0·0
6	270·3	270·6[4]*	+0·1	11	470·8	470·8	±0·0				

* Excluding one determination (273·3) which differs from the rest by 1%.

† The figure in brackets gives the number of independent observations upon which the mean [*P*] value is based.

The mean difference (col. 4) is just over ± 0·1%, and the better agreement between observed and calculated values for high molecular-weight compounds obtained by using the author's formula is illustrated, for the last three paraffins, by comparison of the observed values with those calculated from the constants proposed by various workers: Sugden (S), Mumford and Phillips (MP), Vogel (V), Desreux (D), Bayliss (B), Quayle *et al.* (Q). The last two columns in the following table contain the values calculated by the author (G) and the observed values.

Atom, group, etc.	(S).	(MP).	(V).	(D).*	(B).†	(Q).	(G).	Obs.
C	4·8	9·2	11·5	8·3	9·1	9·0	—	—
H	17·1	15·4	14·4	15·8	15·4	15·5	—	—
CH_3–	56·1	55·4	54·7	55·7	55·3	55·5	55·2 ‡	—
–CH_2–	39·0	40·0	40·3	39·9	39·9	40·0	39·8 ‡	—
n-$C_{26}H_{54}$	1048	1071	1077	1069	1068	1071	1077	1082
n-$C_{32}H_{66}$	1282	1311	1318	1308	1308	1311	1322	1322
n-$C_{60}H_{122}$	2374	2431	2447	2426	2425	2431	2480	2480
Mean diff., %	3·6	1·4	0·7	1·5	1·6	1·4	0·2	—

* *Bull. Soc. chim. Belg.*, 1935, **44**, 249. † *J. Amer. Chem. Soc.*, 1937, **59**, 444.

‡ " Reduced parachor " values—see later.

The percentage differences on which the above means are calculated are those between [*P*], obs. and [*P*], calc. For the whole 14 paraffins, the respective mean percentage differences are: ± 1·6, 0·3, 0·4, 0·5, 0·5, and 0·4, as compared with the author's ± 0·1, mentioned above.

The eight new values measured by Quayle *et al.* are on the average about 0·1% higher than those calculated by the author's formula, but before any change is made in the constants in that formula, it would appear advisable to determine afresh the parachors of the last three hydrocarbons in the above table and of others between, say, C_{20} and C_{60}.

In their calculations, most observers continue to use values, styled " atomic constants," like those quoted above for C and H. As previously explained (*loc. cit.*), the author regards the method by which such values have been obtained as inadmissible for two reasons: (1) the volume contribution of any atom, such as C, is not constant but varies according to the nature of the other atoms with which it is linked; (2) no allowance has been made for the " interference " between the non-linked atoms in the grouping $>C\cdot CH_2\cdot C<$. In each case the effective contribution of C in –CH_2– is reduced in comparison with that of C in –CH_3.

The above argument will become clearer if one considers the nature of a " molecular volume." That of neon at its b. p., *i.e.*, − 246·3°, is 16·8, giving $27{\cdot}7 \times 10^{-24}$ cm.^{3} as the mean volume of a neon atom at that temperature. This volume may be regarded ideally as a sphere of radius $1{\cdot}88 \times 10^{-8}$ cm., consisting of an " envelope volume " surrounding the much smaller sphere which may be considered to represent the normal confines of the atom (Fig. 1). The extent of this envelope will depend upon the conditions, increasing, *e.g.*, with rise in temperature. Now the parachor of a liquid is regarded as a " comparative volume " in such ideal conditions that the liquid is under standard internal pressure. Thus, the ideal volumes of an atom of, say, neon ([*P*], 25·0) and one of argon ([*P*], 54·0) may be visualised as spheres with volumes proportional to these numbers.

Pauling (" The Nature of the Chemical Bond," 1940, 164) lists the following covalent radii (in A.) for atoms of some of the earlier elements:

H.	He ([*P*], 20·5).	C.	N.	O.	F.	Ne ([*P*], 25·0).
0·30	—	0·77	0·70	0·66	0·64	—

If now one imagines the atoms C to F in their simple hydrides with the hydrogen atoms stripped off, but the atom still retaining all the outer electrons, one has the four negative ions each with the same electronic structure as $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Ne}}:$. The ideal volumes of this series of atoms should then be in descending order of magnitude, with the volume of C probably rather more than twice that of Ne. Consider now two similar atoms covalently linked by a single bond, as in F_2 or $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:$. The " envelope volumes " of the two atoms will interpenetrate to some extent, as illustrated, with rather extreme simplification, in Fig. 2, and thus the molecular volume of F_2 will be less than twice the ideal volume of $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:$. Similar diagrams would serve to illustrate the molecular volumes of H : H and $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}:$ (as in $CH_3\cdot CH_3$). If two atoms of different size are linked, *e.g.*, $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}:H$, the result will be as shown in Fig. 3, with the effective volumes of the C and H atoms (indicated by using a dotted line as the section of the circular internal boundary), respectively greater and less than they would be in C–C and H–H.

Now consider the linkage of three carbon atoms as in Fig. 4: a further decrease in volume would appear likely to be brought about by the overlap of the " envelope volumes," or " spheres of influence," of the non-linked atoms C_1 and C_3, as indicated in the darkened part of the figure. The evidence for such a decrease in volume is given by the values calculable for the groups existing in paraffins, *n*-, *iso*-, and *neo*-. On the author's scale of " reduced parachors " (R.P.)—a term preferable to " standard values " (*loc. cit.*, p. 302; J., 1943, 150)—the following R.P.'s form a series with the differences between adjacent members not constant, as might have been expected, but with a constant increase of 2·2 units: CH_4, 68·4; $CH_3\cdot(C)$, 55·2 (diff., 13·2); $(C)\cdot CH_2\cdot(C)$, 39·8 (diff., 15·4); $\genfrac{}{}{0pt}{}{(C)}{(C)}{>}CH\cdot(C)$, 22·2 (diff., 17·6); $\genfrac{}{}{0pt}{}{(C)}{(C)}{>}C{<}\genfrac{}{}{0pt}{}{(C)}{(C)}$, 2·4 (diff., 19·8). This constant increase is attributed by the author to " interference " between atoms attached to a common carbon atom. Thus, let the reductions in R.P. value due to the various groupings be as follows: $\mathrm{C}<\begin{matrix}\mathrm{C}\\ \mathrm{C}\end{matrix}\Big\}, a$; $\mathrm{C}<\begin{matrix}\mathrm{C}\\ \mathrm{H}\end{matrix}\Big\}, b$; $\mathrm{C}<\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\Big\}, c$. Then, we have the following scheme :

Group.	Reductions.	Diff.	Const. diff. of differences.
CH_4	$6c$	—	—
$CH_3{\cdot}(C)$	$3b + 3c$	$3b - 3c$	—
$(C){\cdot}CH_4{\cdot}(C)$	$a + 4b + c$	$a + b - 2c$	$a - 2b + c$
$\begin{matrix}(C)\\ (C)\end{matrix}\!>\!CH{\cdot}(C)$	$3a + 3b$	$2a - b - c$	$a - 2b + c$
$\begin{matrix}(C)\\ (C)\end{matrix}\!>\!C\!<\!\begin{matrix}(C)\\ (C)\end{matrix}$	$6a$	$3a - 3b$	$a - 2b + c$

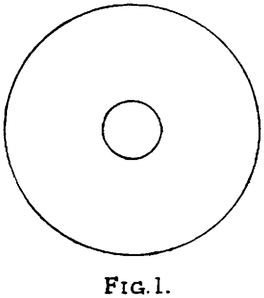

FIG. 1.

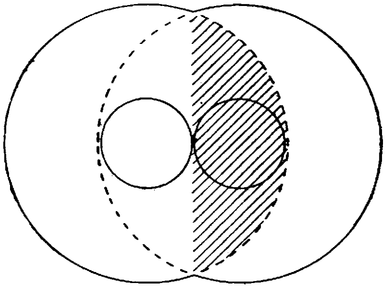

FIG. 2.

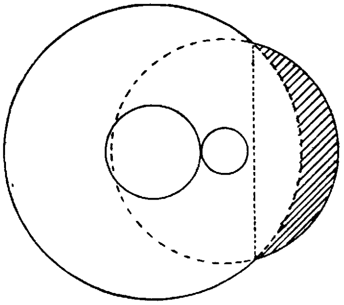

FIG. 3.

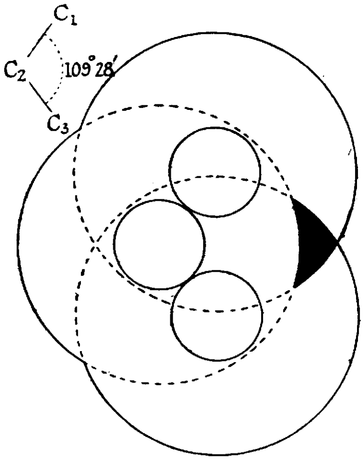

FIG. 4.

It has been assumed, apparently with justification, that b and c are negligible, whence $a = 2{\cdot}2$; but if this is not so, then most probably a is rather greater (*e.g.*, if, say, $b = 0{\cdot}3$ and $c = 0{\cdot}1$, then $a = 2{\cdot}7$).

The method, adopted by Sugden (" The Parachor and Valency," 1929, 35) and followed by later investigators, for the calculation of " atomic constants " consists essentially in subtracting the CH_2 value from the CH_3 value to give the value of H. If we also followed this method, using the CH_3 and CH_2 values given above, we should obtain H, 15·4; C, 9·0. According to the preceding argument, however, the CH_2 value has been decreased by 2·2, owing to " interference," and should therefore be reckoned as 42·0, whence H, 13·2; C, 15·6. These values would, of course, give satisfactory results in calculations, providing that the necessary corrections for interference occurring in carbon chains were made; but what exactly do these values so calculated for H and C stand for? The answer to this question can be found from a consideration of Figs. 2 and 3. The value for H (13·2), which may conveniently be abbreviated as [H], is equal to $\left[\mathrm{H}\!-\!\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\!-\!(\mathrm{C}) - (\mathrm{C})\!-\!\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\!-\!(\mathrm{C})\right]^{*} = 55{\cdot}2 - 42{\cdot}0$. Now, $\left[\mathrm{H}\!-\!\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\!-\!(\mathrm{C})\right] = \left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}}: + 3h - c/2\right]$, where h is $\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}}:\mathrm{H} - :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}}:\right]$, as in the shaded portion of Fig. 3, and $c/2$ is half the loss in volume due to the linkage of two carbon atoms, as in the shaded part of

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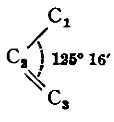
* Both these groups are assumed to be free from interference—see Part I, *loc. cit.*, p. 302.

Fig. 2; while $\left[(\mathrm{C})-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-(\mathrm{C})\right] = \left[:\overset{..}{\underset{..}{\mathrm{C}}}: + 2h - c\right]$. Thus $[\mathrm{H}] = [h + c/2]$; *i.e.*, the value allotted to H depends to a great extent upon the volume reduction produced by a C—C linkage. By similar argument one derives the value for C (15·6) as $\left[\begin{smallmatrix}(\mathrm{C})\\(\mathrm{C})\end{smallmatrix}\!>\!\mathrm{C}\!<\!\begin{smallmatrix}(\mathrm{C})\\(\mathrm{C})\end{smallmatrix}\right]^{*}$, *i.e.*, $\left[:\overset{..}{\underset{..}{\mathrm{C}}}: - 2c\right]$.

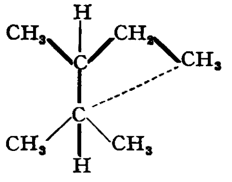
Using Sugden's method for calculating " structural constants," we should obtain + 15·4 as the value for a double bond (R.P., C_2H_4, 99·4; *loc. cit.*), and by reasoning similar to the above, this value can be shown to represent [2 volume reductions for a C—C linkage]—[the volume reduction due to a C=C linkage]. Since the carbon atoms in C=C are more closely associated than those in C—C, the reduction in volume for the former linkage will presumably be rather greater than that for the latter, but this is more than compensated for by the smaller number of carbon-to-carbon linkages in the molecule in the former case; which accounts for the *positive* value of the " double-bond constant." The double-bond group values derived from the R.P. of olefins, *viz.*, $CH_2{=}(C)$, 49·7; $(C){\cdot}CH{=}(C)$, 34·3; $\begin{smallmatrix}(\mathrm{C})\\(\mathrm{C})\end{smallmatrix}\!>\!\mathrm{C}{=}(\mathrm{C})$, 16·7, form a series with differences 15·4 and 17·6, *i.e.*, increasing by 2·2. Hence interference between C_1 and C_3 in the grouping (I) appears to be about the same as that between the corresponding atoms in Fig. 4, involving a correction of − 2·2 in each case. This seems reasonable from a calculation of the distance between C_1 and C_3 in each: the distances C–C and C=C being taken as $1{\cdot}54_3$ and 1·33 A., respectively, those between C_1 and C_3 in Fig. 4 and (I) are 2·52 and 2·55 A., respectively.

Quayle *et al.* (*loc. cit.*) also record the parachors of 18 *iso*-paraffins, 5 from their own measurements, and they conclude that the effect of branching of the carbon chain is not uniform, but that decreases in volume become greater as the branch moves towards the centre of the chain and as the length of the branch is increased. Except for those having one or other of two special types of structure, *iso*- and *neo*-paraffins so far investigated continue to show reasonable agreement between mean observed parachors and those calculated from the group values recorded above. In the following table, expansion corrections (E.C.) are taken from the table in Part I (*loc. cit.*, p. 304), in which lists of values for R.P. (or S.V.), [*P*], and E.C. (as the difference between the preceding two values) are given for all *n*-paraffins from ethane to hexacontane—the rate of expansion appears to be the same in all series, depending only upon the magnitude of the parachors. The reduced parachors are found to be truly additive and constitutive functions within the limits of experimental error.

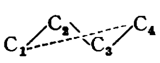
Paraffin.	R.P., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.
2-Methylbutane	227·6	+0·5	228·1	230·0	+0·8
3-Methylpentane	267·4	+0·7	268·1	267·9	−0·1
2 : 2 : 3-Trimethylbutane	300·6	+0·8	301·4	301·4	±0·0
2 : 2-Dimethylpentane	302·8	+0·9	303·7	305·3	+0·5
2 : 4-Dimethylpentane	305·0	+0·9	305·9	306·5[2]	+0·2
2-Methylhexane	307·2	+0·9	308·1	309·1	+0·3
3-Methylhexane	307·2	+0·9	308·1	306·85[2]	−0·4
2 : 4-Dimethylhexane	344·8	+1·1	345·9	344·9	−0·3
2 : 5-Dimethylhexane	344·8	+1·1	345·9	345·9[3]	±0·0
2-Methylheptane	347·0	+1·2	348·2	349·05[2]	+0·2
3-Methylheptane	347·0	+1·2	348·2	347·7	−0·1
4-Methylheptane	347·0	+1·2	348·2	347·6	−0·2
2 : 4-Dimethylheptane	384·6	+1·4	386·0	381·1	−1·3
2 : 5-Dimethylheptane	384·6	+1·4	386·0	384·9	−0·3
2 : 7-Dimethyloctane	424·4	+1·8	426·2	425·9[5]	−0·1



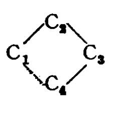
(I.)



(II.)

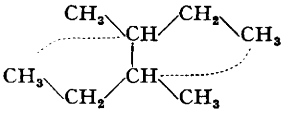


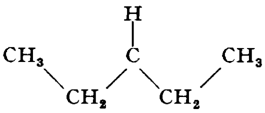
(III.)

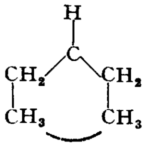


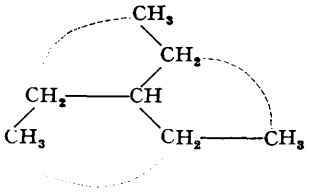
(IV.)

One type of *iso*-paraffin for which the parachor, as calculated by the above method, is consistently higher than the observed value is that containing two adjacent $\geqslant$CH groups to one or both of which is attached an ethyl, or higher, radical, *e.g.*, 2 : 3-dimethylpentane (II). It seems likely that the most stable configuration of the groups in this molecule will be as shown here, the top and the bottom portion occupying *cis-trans*-positions. Then the $-CH_3$ of the ethyl group, tending to be repelled by the other CH_3 groups, will probably take up a position in which there is mutual interference between it and the further $\geqslant$CH group. Now the distance between C_1 and C_4 in (III) is 3·89 A. and in (IV) 2·57 A., all four atoms lying in the same plane in each case. For the distance 2·52 A. between two non-linked carbon atoms, the parachor " interference correction " is − 2·2 (see above), whereas for the distance 3·89 A. the correction must be negligible (otherwise the R.P. increment between C_2H_6 and C_3H_8 would be greater than that for successive pairs of *n*-paraffins). For the distance 2·57 A., then, one might expect a negative correction rather less than 2·2; actually it is — *1·7*. [It does not necessarily follow, of course, that all the four carbon atoms, as shown in this molecule (II), are in exactly the same plane.]


(V.)


(VI.)


(VII.)


(VIII.)

The full method of calculation for the parachor of a substance is illustrated in the case of 3 : 4-dimethylhexane (V), in which the upper and the lower half of the molecule are regarded as being in *cis-trans*-positions. From the sum of the group values (which themselves usually involve corrections for interference) is taken the sum of any extra corrections; this gives the " reduced parachor " (R.P.) (see p. 237). To this is then added the " expansion correction " (E.C.) and the result is the theoretical parachor, which in most cases is found to be approximately equal to that determined by experiment. Thus :

4 $CH_3\cdot$(C) at 55·2	220·8	2 corrns. at —1·7 (see above)	—3·4
2(C)·$CH_2\cdot$(C) at 39·8	79·6	Reduced parachor (R.P.)	341·4
2 ${(C) \atop (C)}{>}CH\cdot$(C) at 22·2	44·4	Expansion correction (E.C.)	+1·1
Σ group values	344·8	Parachor calculated	342·5

Paraffin.	R.P., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Extra corrns. (as above).
2 : 3-Dimethylpentane	303·3	+0·9	304·2	304·3	+0·0	—1·7
3 : 4-Dimethylhexane	341·4	+1·1	342·5	342·6	+0·0	—3·4
2 : 3-Dimethylhexane	343·1	+1·1	344·2	344·1	—0·0	—1·7
2 : 3-Dimethylheptane	382·9	+1·4	384·3	373·1	—2·9	—1·7

It will be observed that in the above two tables two *iso*-paraffins, *viz.*, 2 : 3- and 2 : 4-dimethylheptane, show very poor agreement between calculated and observed parachors.

3-Ethyl-pentane and -hexane each appear to require extra corrections of about — 3·6. These hydrocarbons may be regarded as symmetrically trisubstituted derivatives of trimethylmethane, the structure of which is obvious. In triethylmethane (3-ethylpentane) it would appear that each of the additional carbon atoms produces inteference necessitating a correction of — *1·2*, this interference occurring between all the three CH_3 groups or between each of them and the nearer of the other CH_2 groups in each case. It is clear that in 3-ethylpentane the CH_3 groups cannot be in either of the extreme positions shown in (VI) and (VII), in which they are imagined as being in a plane respectively above and below that of the CH_2 groups. In the former case the carbon-to-carbon distance would obviously be too great for interference; in the latter, the distances between the CH_3 groups would be 2·52 A., and the interference correction for each pair would be — 2·2, making a total correction of — 6·6. The CH_3 groups therefore appear to take up some intermediate position, such as that in (VIII), in which all the six carbon atoms of the CH_2 and CH_3 groups are shown as approximately in the same plane. If they are actually coplanar, the distance between the carbon of each CH_3 group and the carbon of the nearer (unlinked) CH_2 group will be 2·73 A. In (VIII) the molecule is shown as viewed from above; in (VI) and (VII), a side view of part of the molecule is given.

Paraffin..	R.P., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Extra corrns. (as above).
3-Ethylpentane	303·6	+0·9	304·5	304·2	—0·1	—3·6
3-Ethylhexane	343·4	+1·1	344·5	345·0	+0·1	—3·6

THE GRAMMAR SCHOOAL OF QUEEN ELIZABETH, WAKEFIELD.

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