**27.** *Atom Polarisation.    Part II.    Relationships between Molecular Dimensions and Boiling Points for Branched-chain Paraffins.*

By ARNOLD AUDSLEY and FRANK R. GOSS.

Exaltations of molecular volume and of refraction for branched-chain paraffins are negative and directly related to the extent of the chain-branching when the exaltations are measured at the boiling point, or more strictly in the gaseous state. As, however, the boiling points themselves are not related to the molecular shape in the same simple manner, the molecular functions have, at 20°, values which, although their sequence is changed, fall on a series of characteristic curves.

Atom polarisation and dispersion are not noticeably affected by chain-branching, and consequently the exaltations of refraction and polarisation are identical within narrow limits and the polarisations fall on the same series of curves as the refractions.

Sensitive methods for the detection of impurities, particularly those of high dielectric constant, can be based on these properties of the hydrocarbons.

*Relationships between Molecular Volume and Boiling Point.*—In a comparison of the molecular volume of homologous series of similarly branched paraffins, Egloff and Kuder (*J. Physical Chem.*, 1941, **45**, 836) have shown that, at the boiling points, molecular volume can be expressed as a logarithmic function of boiling point. From their formula it may be deduced that the exaltation, or difference from the value for the straight-chain isomer, of the molecular volume for any branched-chain paraffin can be expressed as a function of the exaltation of the boiling point for that isomer. Now the molecular volumes for the normal paraffins, when plotted against molecular weight, lie on smooth curves, both at the boiling points as found by Egloff and Kuder, and also at 20° according to Deanesley and Carleton (*ibid.*, 1941, **45**, 1104; cf. Part I of this series, *J.*, 1950, 2989). It will be seen, however, from Fig. 1 that the exaltations of the boiling point for the branched-chain series, when plotted against molecular weight, undergo an abrupt change of direction at some point between $C_5$ and $C_9$, below which the data are discarded by Egloff and Kuder in the derivation of their expression. This change of direction occurs in each case where the chain length increases to five or more carbon atoms, and must be attributed to variations in the potentialities for curling of the carbon chain, because it is already known from our measurements of the solvent-effect constants of the alkyl iodides (*J.*, 1942, 358, Fig. 3) that a marked and definite change takes place in the increments of the solvent-effect constant and hence of the shape of the carbon chain between the fifth and the sixth member of the homologous series. The change of direction beyond a chain length of five carbon atoms will therefore occur between $C_5$ and $C_9$ according to the nature of the chain branching, and is not just an anomaly associated with the initial members of the various series. From these considerations it follows that the molecular-volume exaltations at the boiling point may be expected to change direction at the same position in the series, and it is owing to this circumstance that Egloff and Kuder discarded the lower members of the series.

It should also be found that the molecular-volume exaltations at a fixed temperature such as 20° should exhibit a similar change of direction, because the increase of molecular volume between 20° and the boiling point will be related to the (b. p. — 20°) temperature interval, which in passing up the series is subject to the same sharp discontinuity as the exaltations of the boiling point. This sharp change of direction in the molecular volume curves is, in fact, realised experimentally, and is shown in Fig. 2; the shapes of the curves although algebraically inverted are strikingly similar to those in Fig. 1. The change of direction in the various homologous series occurs at precisely the same points for the molecular volume at 20° as for the exaltations of the boiling points.

Egloff and Kuder (*loc. cit.*) found that, at the boiling point, the molecular-volume exalt-ations are all negative, and for isomeric paraffins fall into the same sequence as that for the change of shape of the molecules from an elongated to a compact structure. On the contrary, the exaltations of the boiling points, $\Delta$ b. p., although also negative, are not related to the shape of the structure in the same sequence as the molecular volume (see Table I). The molecular volumes ($M/d$) of the isomers at 20° fall into a different order from that at the boiling point, because the temperature coefficients of $M/d$ for the various isomers have to be multiplied by the varying number of degrees which depend on the values of $\Delta$ b. p. In the case of the seven $C_7$ isomers considered by Egloff and Kuder (*loc. cit.*) those isomers having relatively small exaltations



FIG. 1.

*Exaltation of the boiling points of the branched-chained paraffins.*

FIG. 2.

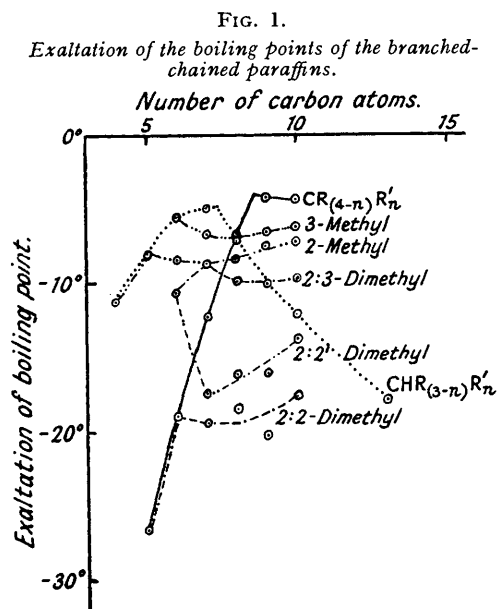*Exaltation of the molecular volumes of the branched-chain paraffins at 20°.*

FIG. 1.

*The groups represented by R are as nearly identical as possible (R' is next higher alkyl group to R) : $CHR_{(3-n)}R'_n$ includes isobutane, 2-methylbutane, 3-methylpentane, 3-ethylpentane, etc. $CR_{(4-n)}R'_n$ includes neopentane, 2:2-dimethylbutane, 3:3-dimethylpentane, 3-ethyl-3-methylpentane, 3:3-diethylpentane, etc.*

of the boiling point move down whilst those with large values of $\Delta$ b. p. move up the series of isomers, as indicated by arrows in Table I, to give the molecular volume sequence at 20° with its apparent anomaly that certain isomers have, at 20°, lower densities than the normal paraffin.

TABLE I.

*Sequence of molecular volumes and boiling points compared with the molecular shape of $C_7$ paraffins.*

| Sequence for $M/d$ at b. p. | Molecular shape. | $\Delta$ b. p. | Change of sequence. | Sequence for $M/d$ at 20°. |
|---|---|---|---|---|
| n-Heptane | +++++++ | 0° | ↘ | 2 : 4-Dimethylpentane |
| 2-Methylhexane | +‡+++++ | −8·7 | ↘ | 2 : 2-Dimethylpentane |
| 3-Methylhexane | ++‡+++ | −6·6 | ↘ | 2-Methylhexane |
| 2 : 2-Dimethylpentane | +‡+++ | −19·5 | ↗ | n-Heptane |
| 2 : 4-Dimethylpentane | +‡+‡+ | −17·6 | ↗ | 3-Methylhexane |
| 3 : 3-Dimethylpentane | ++‡++ | −12·4 | ↘ | 2 : 2 : 3-Trimethylbutane |
| 2 : 2 : 3-Trimethylbutane | +‡++ | −17·6 | ↗ | 3 : 3-Dimethylpentane |

*Relationships between Refraction, Total Polarisation, and Boiling Point.*—In Part I of this series (*loc. cit.*) it was found that the values of the molecular refraction and total polarisation for the liquid n-paraffins can be derived by combining the gas values with the effect of the field
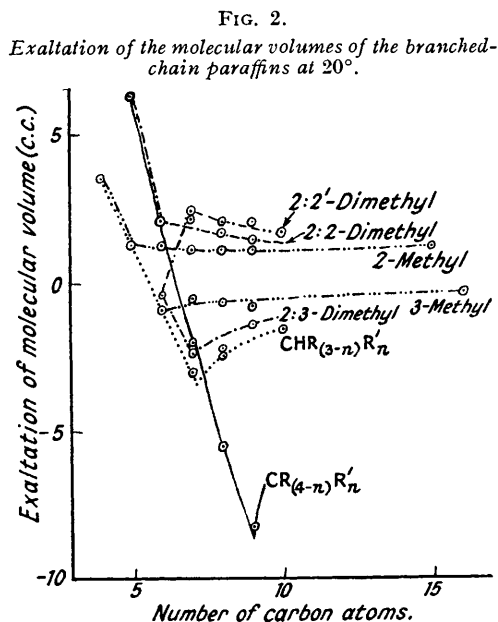
anisotropy, and that all the experimental values can be built up from electron polarisation terms for each kind of bond together with atom polarisation terms for each kind of atom, with in every case a parameter $x'$ corresponding to the contribution of each bond and atom to the shape of the molecule. The observed total polarisation $P_S$ for these compounds is thus made up essentially of three parts :

$$P_S = P_E + P_A + x' \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

In a set of isomeric paraffins the same atoms are present in each isomer and consequently $P_A$ should be constant, but as the electron orbits are differently arranged, the mobilities of the electrons will vary, giving different values of $P_E$. These can be expressed in terms of exaltations $\Delta P_E$ which are the amounts by which the electron polarisations of the isomers differ from those of the normal paraffin. Wibaut and Langedijk's data *(Rec. Trav. chim.,* 1940, **59**, 1220) show that the dispersions of isomeric paraffins are identical, so that for any given isomer $\Delta[R]$ for any wave-length is the same as $\Delta P_E$. The exaltation $\Delta P_{E+A}$ of the elastic polarisation must

Fig. 3.

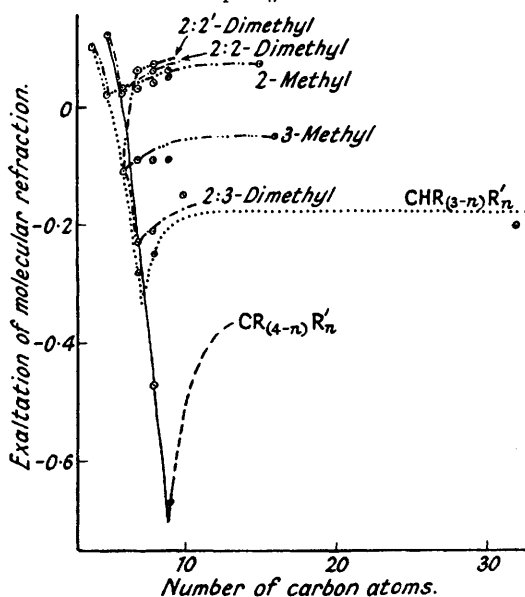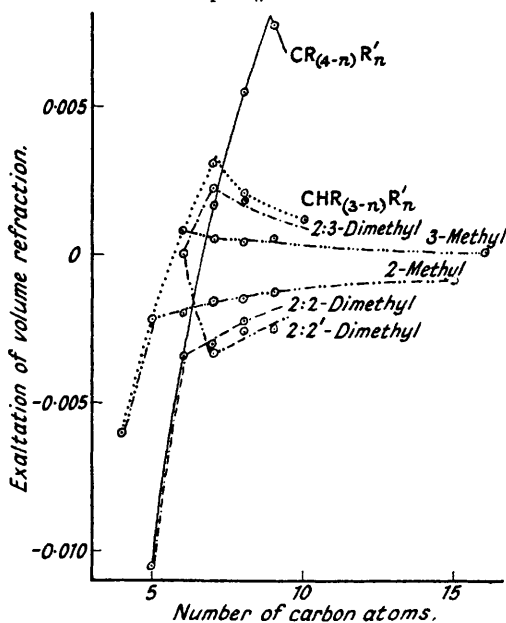*Exaltation of the molecular refraction of the branched-chain paraffins at 20°.*

Fig. 4.

*Exaltation of the volume refraction of the branched-chain paraffins at 20°.*



include $\Delta P_E$, but as $P_A$ should be constant for all the isomers, then for any given paraffin it should be found that

$$\Delta[R] = \Delta P_E = \Delta P_{E+A} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

As these small exaltations depend on the nature of the chain branching it is to be expected that for a *given homologous series* of similarly branched paraffins at the boiling point, $\Delta[R]^{b.p.}$ should be a constant because the value of $[R]^{b.p.}$ would be, as with the normal isomers, a linear function of molecular weight. At 20°, on the other hand, the values of $[R]^{20}$ for the branched-chain paraffins will, just as with the normal isomers, by a suitable modification of formula (1) and as explained in Part I *(loc. cit.),* differ from $[R]^{b.p.}$ by a value for the parameter $x'$ which is dependent on the (b. p. − 20°) intervals. The values of $x'$ for the branched-chain paraffins will be different from those of the corresponding normal isomers owing to their smaller (b. p. −20°) intervals, and this difference between the values of $x'$ must be added to the presumed constant exaltation for the particular homologous series of isomers at the boiling point. The values of $\Delta[R]^{20}$ so obtained, like those of $\Delta(M/d_4^{20})$, when plotted against molecular weight, give curves of similar shape (Fig. 3) to the curves for the exaltation of the boiling point, but tending towards a series of constant values for the higher members. A comparable parallelism between the exaltations of the molecular refraction and of the molecular volume for the liquid

TABLE II.

*Physical constants related to the refraction of branched-chain paraffins.*

| | Ref. no. | Hydrocarbon | B.p. | Δ b.p. | $d_4^{20}$ | M/d | Δ (M/d) | $n_D^{20}$ | $r_D$ | $\Delta r_D \times 10^5$ | $[R]_D$ | $\Delta[R]_D$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_5$ | 1. | 2-Methylbutane | 28·0° | — 8·1° | 0·6197 | 116·42 | 1·23 | 1·3539 | 0·21734 | —214 | 25·30 | 0·02 |
| | 2. | n-Pentane | 36·1 | — | 0·6263 | 115·19 | — | 1·3578 | 0·21948 | — | 25·28 | — |
| $C_6$ | 3. | 2 : 2-Dimethylbutane | 49·7 | —19·0 | 0·6492 | 132·74 | 2·06 | 1·3688 | 0·22553 | —340 | 29·94 | 0·02 |
| | 4. | 2-Methylpentane | 60·2 | — 8·5 | 0·6532 | 131·92 | 1·24 | 1·3715 | 0·22701 | —192 | 29·95 | 0·03 |
| | 5. | n-Hexane | 68·7 | — | 0·6594 | 130·68 | — | 1·3750 | 0·22893 | — | 29·92 | — |
| | 6. | 2 : 3-Dimethylbutane | 58·0 | —10·7 | 0·6617 | 130·23 | —0·45 | 1·3766 | 0·22893 | 000 | 29·81 | —0·11 |
| | 7. | 3-Methylpentane | 63·2 | — 5·5 | 0·6643 | 129·72 | —0·96 | 1·3766 | 0·22979 | 086 | 29·81 | —0·11 |
| $C_7$ | 8. | 2 : 4-Dimethylpentane | 80·8 | —17·6 | 0·6728 | 148·93 | 2·39 | 1·3815 | 0·23245 | —337 | 34·62 | 0·06 |
| | 9. | 2 : 2-Dimethylpentane | 78·9 | —19·5 | 0·6739 | 148·68 | 2·14 | 1·3822 | 0·23283 | —299 | 34·62 | 0·06 |
| | 10. | 2-Methylhexane | 89·7 | — 8·7 | 0·6787 | 147·63 | 1·09 | 1·3849 | 0·23429 | —153 | 34·59 | 0·03 |
| | 11. | n-Heptane | 98·4 | — | 0·6837 | 146·54 | — | 1·3877 | 0·23582 | — | 34·56 | — |
| | 12. | 3-Methylhexane | 91·8 | — 6·6 | 0·6970 | 145·85 | —0·69 | 1·3887 | 0·23635 | 053 | 34·47 | —0·09 |
| | 13. | 3 : 3-Dimethylpentane | 86·0 | —12·4 | 0·6933 | 144·52 | —2·02 | 1·3909 | 0·23753 | 171 | 34·33 | —0·23 |
| | 14. | 2 : 3-Dimethylpentane | 89·7 | — 8·7 | 0·6951 | 144·15 | —2·39 | 1·3920 | 0·23813 | 231 | 34·33 | —0·23 |
| | 15. | 3-Ethylpentane | 93·3 | — 5·1 | 0·6984 | 143·47 | —3·07 | 1·3935 | 0·23893 | 311 | 34·28 | —0·28 |
| $C_8$ | 16. | 2 : 5-Dimethylhexane | 109·3 | —16·3 | 0·6941 | 164·56 | 2·00 | 1·3928 | 0·23856 | —255 | 39·26 | 0·07 |
| | 17. | 2 : 2-Dimethylhexane | 107·0 | —18·6 | 0·6953 | 164·28 | 1·72 | 1·3935 | 0·23893 | —218 | 39·25 | 0·06 |
| | 18. | 2-Methylheptane | 117·2 | — 8·4 | 0·6979 | 163·67 | 1·11 | 1·3949 | 0·23969 | —142 | 39·23 | 0·04 |
| | 19. | n-Octane | 125·6 | — | 0·7026 | 162·56 | — | 1·3975 | 0·24111 | — | 39·19 | — |
| | 20. | 3-Methylheptane | 119 | — 7 | 0·7058 | 161·84 | —0·72 | 1·3985 | 0·24162 | 051 | 39·10 | —0·09 |
| | 21. | 2 : 3-Dimethylhexane | 115·7 | — 9·9 | 0·7123 | 160·36 | —2·20 | 1·4012 | 0·24307 | 196 | 38·98 | —0·21 |
| | 22. | 3-Ethylhexane | 118·9 | — 6·7 | 0·7136 | 160·07 | —2·49 | 1·4016 | 0·24328 | 217 | 38·94 | —0·25 |
| | 23. | 3-Methyl-3-ethylpentane | 118·4 | — 7·2 | 0·7274 | 157·03 | —5·53 | 1·4078 | 0·24659 | 548 | 38·72 | —0·47 |
| $C_9$ | 24. | 2 : 6-Dimethylheptane | 134·5 | —16·2 | 0·7098 | 180·68 | 1·99 | 1·3908 | 0·24285 | —246 | 43·88 | 0·05 |
| | 25. | 2-Methyloctane | 143·2 | — 7·5 | 0·7134 | 179·77 | 1·08 | 1·4032 | 0·22413 | —118 | 43·89 | 0·06 |
| | 26. | n-Nonane | 150·7 | — | 0·7177 | 178·69 | — | 1·4054 | 0·24531 | — | 43·83 | — |
| | 27. | 3-Methyloctane | 144·2 | — 6·5 | 0·7210 | 177·88 | —0·81 | 1·4065 | 0·24590 | 059 | 43·74 | —0·09 |
| | 28. | 3 : 3-Diethylpentane | 146·4 | — 4·3 | 0·7524 | 170·45 | —8·24 | 1·4200 | 0·25306 | 775 | 43·16 | —0·67 |
| $C_{10}$ | 29. | n-Decane | 174·0 | — | 0·7300 | 194·88 | — | 1·4118 | 0·24872 | — | 48·47 | — |
| | 30. | 4-Propylheptane | 161·8 | —12·2 | 0·7360 | 193·31 | —1·57 | 1·4141 | 0·24994 | 122 | 48·32 | —0·15 |
| $C_{15}$ | 31. | 2-Methyltetradecane | — | — | 0·7656 | 277·44 | 1·16 | 1·4304 | 0·25853 | —085 | 71·73 | 0·07 |
| | 32. | n-Pentadecane | — | — | 0·7688 | 276·28 | — | 1·4320 | 0·25938 | — | 71·66 | — |
| $C_{16}$ | 33. | n-Hexadecane | — | — | 0·7739 | 292·60 | — | 1·4347 | 0·26077 | — | 76·30 | — |
| | 34. | 3-Methylpentadecane | — | — | 0·7749 | 292·21 | —0·39 | 1·4350 | 0·26094 | 017 | 76·25 | —0·05 |
| $C_{32}$ | 35. | n-Dotriacontane | — | — | 0·8141 | 553·80 | — | 1·4559 | 0·27178 | — | 150·51 | — |
| | 36. | 11-Decyldocosane | — | — | 0·8127 | 554·75 | 0·95 | 1·4543 | 0·27096 | —082 | 150·31 | —0·20 |

Data for n-paraffins $C_5$ to $C_{16}$ are smoothed values from Part I (*loc. cit.*), $C_{32}$ being extrapolated from the series constants calculated from them.

Data for the branched-chain paraffins are :

$C_5$ to $C_8$. Concordant values of Wibaut and Langedijk (*loc. cit.*); Forziati, Glasgow, Willingham, and Rossini (*J. Nat. Bur. Stand.*, 1946, **36**, 129);
Edgar and Calingaert (*loc. cit.*); and from the present work.

No. 24. Vogel (*J.*, 1946, 133).

Nos. 25 and 27. White and Glasgow (*J. Nat. Bur. Stand.*, 1937, **19**, 423).

No. 28. Horton (*J. Amer. Chem. Soc.*, 1947, **69**, 182).

Nos. 31 and 34. Lunshof, van Steenis, and Waterman (*Rec. Trav. chim.*, 1947, **66**, 348).

No. 36. Whitmore, Sutherland, and Cosby (*J. Amer. Chem. Soc.*, 1942, **64**, 1360).

paraffins has indeed been noted by Edgar and Calingaert (*J. Amer. Chem. Soc.*, 1929, **51**, 1540) although, as may be seen from Table II, their particular method of comparing the effect of chain branching on these properties is only approximately true.

It is to be concluded that the molecular refraction exaltations at the boiling points, like those of the molecular volume, are almost always negative for the paraffins. *iso*Butane is an exception, but this does not invalidate our conclusions in general because the precise values of $x'$ are not known. Boiling-point data are only used as an approximation where gas data are not available (see Part I, *loc. cit.*). This conclusion is confirmed by the values for this apparently exceptional case of *iso*butane which, by extrapolation of the known values for its homologues as shown in Fig. 3, would appear to have a positive $\Delta[R]$ of about 0·1 c.c. and has in fact at its boiling point a $\Delta[R]$ of +0·05 and a $\Delta(M/d)$ of +1·3. Nevertheless, in the gaseous state (Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144) *iso*butane has the expected negative exaltation ($\Delta[R] = -0·02$). The position of *neo*pentane is similar to that of *iso*butane and the approximate data for both of these hydrocarbons extrapolated to 20° from their recorded constants at low temperatures have beeen included in Figs. 2, 3, and 4, and it will be seen that the points lie on the natural extensions of the appropriate curves.

Since the molecular dimensions [R] and $M/d$ of the various isomers exhibit related exaltations, it follows that the volume refraction [or refraction per c.c., $r = (n^2 - 1)/(n^2 + 2)$], which is also the quotient $[R]/(M/d)$, will give the same characteristic curves with sharp change of direction when the values are plotted against molecular weight as in Fig. 4. The change of direction is seen to occur at the usual positions for the various homologous series. The volume refraction is in many ways the most satisfactory function to employ in the investigation of these hydro-carbon exaltations because it does not include the molecular weight, which in the molecular functions has the arithmetical effect of exaggerating errors of measurement for the higher members of the series, as can be seen by a comparison of Figs. 3 and 4.

Our conclusion that the exaltations of molecular refractions at 20° for homologous series are not constant for the lower members appears to conflict with Wibaut and Langedijk (*loc. cit.*), who find that the increments of molecular refraction for branched-chain series such as those terminated by *iso*propyl or *tert.*-butyl groups are " the same " or " differ but *little* " (their italics) from the increment for the normal paraffin series. It is evident, however, that they do observe differences, especially in the 2 : 3-dimethyl series, because they record, but do not plot, the molecular refraction for 2 : 3-dimethylbutane, which from their viewpoint appears to have an unexpectedly high value, until it is noted that its boiling point is low in comparison with the higher members of the series. As we have already indicated, Wibaut and Langedijk's general-isation for molecular refractions of these series should be strictly true only at the boiling points and especially in the gaseous state. At 20° the variations in the (b. p. − 20°) interval cause the apparent irregularities, but in proceeding higher up the series the boiling points become smoothly related to the molecular weight just as in the series of normal paraffins.

*Relationships between Refraction and Total Polarisation, and their Use as Criteria of Purity.*— The relationship which we have suggested for the exaltations of the molecular volume and the refraction of the branched-chain paraffins, namely, the dependence on the exaltation of the boiling point, as expressed by curves such as those in Figs. 1—4 found for the various homologous series, can be used to check the structures of paraffins presumed to belong to them and to decide between different values of physical constants recorded in the literature. The purity of the hydrocarbons, irrespective of whether they belong to any particular series, may also be checked by the equivalence (2). For this purpose, a precise knowledge of the true value of [R] is not necessary because, owing to the high dielectric constants of polar impurities, these will cause a large change in $\Delta P_{E+A}$ whereas $\Delta[R]$ is only slightly altered. This may be illustrated by measurements which we have made on certain samples of the paraffins enumerated in Table III. We find that if, for a given sample, the relationship $\Delta[R] = \Delta P_{E+A}$ holds true within narrow limits ($\pm 0·06$) to include possible inequalities in the respective values of $x'$ as well as errors of experiment, the sample is then found to have a correct value for its density (to within $\pm 0·0002$). When, however, the exaltation of the total polarisation is higher than that of the refraction (by more than 0·06), indicating the presence of polar impurities, the density is also in error by a small amount. In the case of these particular compounds the densities and refractive indices for highly purified samples are accurately known, but this is not essential and the method can be successfully applied to new members of the paraffin series for which other constants are not accurately known. Additional help in judging the structure and purity of samples may be obtained from the fact that the molecular volumes must fall into their proper order and, as shown by Edgar and Calingaert (*loc. cit.*), the refractive indices and dielectric constants must fall

approximately into a similar sequence for a given set of isomers. In all, a sensitive test of purity is available, as well as methods for the prediction of the properties of new compounds.

TABLE III.

*Equivalence of* $\Delta[R]_D$ *and* $\Delta P_{E+A}$ *and detection of polar impurities in non-polar* $C_7$ *and* $C_8$ *hydrocarbons by comparison of exaltation.*

| Sample no. | Hydrocarbon. | $[R]_D$. | $P_{E+A}$. | $\Delta[R]_D$. | $\Delta P_{E+A}$. | $d_4^{20}$: lit. val. | $d_4^{20}$: sample. | Diff. of $\Delta[R]_D$ and $\Delta P_{E+A}$. | Diff. between values of density. |
|---|---|---|---|---|---|---|---|---|---|
| \( C_7. \) | | | | | | | | | |
| 1. | 2 : 2-Dimethylpentane | 34·62 | 34·60 | 0·06 | 0·09 | 0·6739 | 0·6737 | 0·03 | −0·0002 |
| 2. | 2-Methylhexane | 34·59 | 34·56 | 0·03 | 0·05 | 0·6787 | 0·6789 | 0·02 | 0·0002 |
| 3. | *n*-Heptane | 34·56 | 34·51 | — | — | — | — | — | — |
| 4. | 3-Methylhexane | 34·47 | 34·37 | −0·09 | −0·14 | 0·6870 | 0·6870 | −0·05 | 0 |
| 5. | 3 : 3-Dimethylpentane | 34·33 | 34·34 | −0·23 | −0·17 | 0·6933 | 0·6934 | 0·06 | 0·0001 |
| 6. | 2 : 3-Dimethylpentane | 34·33 | 34·31 | −0·23 | −0·20 | 0·6951 | 0·6951 | 0·03 | 0 |
| 7. | 3-Ethylpentane | 34·28 | 34·17 | −0·28 | −0·34 | 0·6984 | 0·6984 | −0·06 | 0 |
| \( C_8. \) | | | | | | | | | |
| 8. | 2 : 5-Dimethylhexane | 39·26 | 39·19 | 0·07 | 0·07 | 0·6941 | 0·6941 | 0 | 0 |
| 9. | *n*-Octane | 39·19 | 39·12 | — | — | — | — | — | — |
| 10. | 3-Ethylhexane | 38·94 | 38·86 | −0·25 | −0·26 | 0·7136 | 0·7136 | −0·01 | 0 |
| 11. | 3 : 4-Dimethylhexane | 38·87 | 38·75 | −0·32 | −0·37 | 0·7195 | 0·7195 | −0·05 | 0 |
| 12. | 2 : 3 : 3-Trimethylpentane | 38·77 | 38·67 | −0·42 | −0·45 | 0·7262 | 0·7262 | −0·03 | 0 |
| 13. | 3-Ethyl-3-methylpentane... | 38·72 | 38·67 | −0·47 | −0·45 | 0·7274 | 0·7274 | 0·02 | 0 |

(B) Hydrocarbon samples having high values of $\Delta P_{E+A}$ accompanied by high densities.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| \( C_7. \) | | | | | | | | | |
| 14. | 2 : 4-Dimethylpentane | 34·59 | 34·91 | 0·03 | 0·40 | 0·6728 | 0·6733 | 0·37 | 0·0005 |
| 15. | 2 : 3-Dimethylpentane | 34·30 | 34·74 | −0·26 | 0·23 | 0·6951 | 0·6956 | 0·49 | 0·0005 |
| \( C_8. \) | | | | | | | | | |
| 16. | 2 : 2-Dimethylhexane | 39·32 | 39·47 | 0·13 | 0·35 | 0·6953 | 0·6959 | 0·24 | 0·0006 |
| 17. | 2-Methylheptane | 39·26 | 39·41 | 0·07 | 0·29 | 0·6979 | 0·6982 | 0·22 | 0·0003 |
| 18. | 3 : 3-Dimethylhexane | 38·99 | 39·11 | −0·20 | −0·01 | 0·7100 | 0·7105 | 0·19 | 0·0005 |
| 19. | 2 : 3 : 4-Trimethylpentane | 38·88 | 38·93 | −0·31 | −0·19 | 0·7190 | 0·7194 | 0·12 | 0·0004 |

(A) Properties at 20° of hydrocarbon samples having $\Delta[R]_D = \Delta P_{E+A}$.

The values of $[R]_D$ in Section (A) and the literature values of $d$ are from concordant determinations recorded mainly by Wibaut and Langedijk (*loc. cit.*), Forziati, Glasgow, Willingham, and Rossini (*loc. cit.*), Edgar and Calingaert (*loc. cit.*), and this paper. Values of $P_{E+A}$ in Section (A) are calculated from the literature values of $d$. In Section (B), both $[R]_D$ and $P_{E+A}$ are from the actual constants of the samples.

Other data for samples 1, 2, 4, 5, and 6 are the values recorded by Smyth and Stoops (*loc. cit.*) after their dielectric constants have been corrected to allow for their method of calibration, using for benzene $\varepsilon^{25} = 2·279$. Samples 8 and 11 were prepared for these measurements. Samples 7, 10, and 12—19 inclusive were lent by the Institute of Petroleum Hydrocarbon Bank.

Data for the normal hydrocarbons from Part I of this series (*loc. cit.*) are included for comparison.

Smyth and Stoops (*J. Amer. Chem. Soc.*, 1928, **50**, 1883) concluded from their measurements of the $C_7$ isomers that $P_A$ appears to change a little in line with the changes in the values of $[R]$ and $P_E$. However, our criteria of purity being adopted for these hydrocarbons, three of their isomers would be rejected, and any slight fall in $P_A$ for the other five members which are included in Table II would be less than the unavoidable errors. Our measurements for the $C_8$ isomers show no indication of any regular variation in the value of $P_A$ which, if it occurred, would mean that $\Delta[R]$ would not equal $\Delta P_{E+A}$. The data in Table III indicate that within the limits of probable error $P_A$ is independent of the nature of the chain-branching as was assumed in our derivation of expression (2).

EXPERIMENTAL.

Density, dielectric constant, and temperature were measured as previously described (*J.*, 1940, 893), refractive index by means of an Abbé refractometer.

*Preparation and Purification of Materials.*—2 : 5-Dimethylhexane was prepared from sodium and *iso*butyl bromide (from Kahlbaum's *iso*butyl alcohol) and impurities were removed by successive washings with sulphuric acid; b. p. 108—109°/750 mm., $d_4^{20}$ 0·69407, $n_D^{20}$ 1·3928, $\varepsilon^{20}$ 1·9376. 3 : 4-Dimethylhexane was prepared similarly from *sec.*-butyl iodide; b. p. 117·5—118°/750 mm., $d_4^{20}$ 1·71955, $n_D^{20}$ 1·4045, $\varepsilon^{20}$ 1·9688.

Physical constants of samples lent by the Institute of Petroleum Hydrocarbon Bank were measured without further purification.

| | | B. p. | $d_4^{20}$. | $n_D^{20}$. | $\varepsilon$. |
|---|---|---|---|---|---|
| $C_7$. | 2 : 4-Dimethylpentane | 80·8° | 0·67335 | 1·3815 | 1·9195 |
| | 2 : 3-Dimethylpentane | 90·6 | 0·69557 | 1·3920 | 1·9533 |
| | 3-Ethylpentane | 93·2 | 0·69837 | 1·3935 | 1·9379 |
| $C_8$. | 2 : 2-Dimethylhexane | 107·0 | 0·69587 | 1·3937 | 1·9498 |
| | 2-Methylheptane | 117·2 | 0·69820 | 1·3952 | 1·9519 |
| | 3 : 3-Dimethylhexane | 111·8 | 0·71053 | 1·4000 | 1·9645 |
| | 3-Ethylhexane | 118·6 | 0·71361 | 1·4014 | 1·9617 |
| | 2 : 3 : 4-Trimethylpentane | 113·6 | 0·71941 | 1·4043 | 1·9738 |
| | 2 : 3 : 3-Trimethylpentane | 114·2 | 0·72623 | 1·4076 | 1·9780 |
| | 3-Ethyl-3-methylpentane | 118·4 | 0·72740 | 1·4078 | 1·9800 |