584. *Atom Polarisation. Part I. The Solvent-effect Theory and its Application to the Molecular Refraction and Polarisation of* n-*Paraffins in the Liquid State.*

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By means of new measurements of the refractive indices and dielectric constants of all the *n*-paraffins from *n*-pentane to *n*-heptadecane, and by application of the solvent-effect theory it is possible to express molecular refractions and polarisations in both the liquid and the gaseous state in terms of series and constitutive constants of both electron and atom polarisation for the various bonds and atoms, and also in terms of anisotropic factors associated with them in the liquid state. These anisotropic factors are related to the size and shape of the molecules in a manner precisely analogous to the solvent-effect constants which determine the magnitude of the solvent-effect in dipole-moment measurements by the solution method.

Evaluation of the Parameters of the Solvent-effect Equation.—Both theory and experiment indicate (*J.*, 1937, 1915; 1940, 752; 1942, 358) that the molecular polarisation of liquids and also the partial polarisation P_S of any one component of a binary liquid mixture are composed, not only of the three simple terms, electron, atom, and orientation polarisation arising from the natural mobilities of the electrons, atoms, and molecules respectively, but also of modifications of these by solvent effects. Among these solvent effects are the cavity field (which, together with the orientation polarisation, is given by Y/ε) and the reaction field $[Z(\varepsilon - 1)^4/(\varepsilon + 2)^4]$ where Y and Z depend on solute shape and are related quite simply to the values which the molecular polarisation of the liquid would have if the dielectric constant could attain the values of unity and infinity. The unknowns, Y and Z, can be calculated from the solvent-effect equation

$$P_S = P_{E+A} + (Y/\varepsilon) + [Z(\varepsilon - 1)^4/(\varepsilon + 2)^4] \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

as previously described (*loc. cit.*), whereas the third unknown, the elastic polarisation P_{E+A} cannot in general be measured directly. Because of this the value of P_{E+A} has frequently been assumed to have a fixed arithmetical ratio to the molecular refraction, although it has actually been found to vary within wide limits (cf. Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144). The value of P_{E+A} can, however, be estimated by the elimination method previously described (*J.*, 1940, 752, Fig. 4) provided that vapour measurements can be made on the substance. It was concluded from the data for non-polar compounds that the differences between P_{E+A} values for simple substances in liquid and in vapour form are in general not more than 0·2, and hence that the values given by the elimination method would also not have an error greater than $\pm 0{\cdot}2$. When this method was applied to methyl and ethyl iodides (*J.*, 1941, 864, Table IV) it was found that, although the ratio of the elastic polarisation to the molecular refraction ($P_{E+A}/[R]_D$) for these substances had quite different values (1·13 and 1·10 respectively), the values of P_{E+A} itself were separated by an increment of 4·8, approximating to that for the molecular refraction of these substances. From this isolated case it could be concluded that the atom polarisation is not a fixed percentage of the refraction and that it changes by only a small amount in passing from the first to the next member of the series.

There is no doubt that the atom polarisation is much more susceptible to constitutive changes than is the electron polarisation, but there is no evidence to show that, in the simplest types of saturated aliphatic compounds, constant terms for each atom cannot be applied to the atom polarisation just as they can to the molecular refraction. The atomic terms in the case of molecular refraction are not absolutely constant even in such a relatively simple series as the chlorinated methanes (Stevels, *Trans. Faraday Soc.*, 1937, **33**, 1381), and it appears from the scanty evidence available that in comparisons of atom polarisation and molecular refraction as constitutive properties there is a difference not of kind but only of degree.

In attempts to define the extent to which atom polarisation is a constitutive property, the simplest series, that of the straight-chain paraffins, has been re-examined. Dornte and Smyth (*J. Amer. Chem. Soc.*, 1930, **52**, 3546) measured the dielectric constants of the liquid *n*-paraffins from C_5 to C_{12} and found that the elastic polarisation P_{E+A}, like the molecular refraction $[R]$ and the electron polarisation P_E, is additive within the series. Hence we concluded (*J.*, 1941, 864) that by difference the atom polarisation P_A should be additive for these compounds. From an approximate treatment of Dornte and Smyth's figures it is seen that $P_{E+A} = 2{\cdot}2 + 4{\cdot}61c$ (where c is the number of carbon atoms) and $P_E = 2{\cdot}0 + 4{\cdot}53c$; then if our assumptions are correct, $P_A = 0{\cdot}2 + 0{\cdot}08c$. This means that if the atom polarisation is to be treated within the series as an additive property, the term for 2H is 0·2, whilst the increment for CH_2 is only 0·08. Thus there is an anomaly which would apparently make it impossible to deduce realistic atomic terms for carbon and hydrogen from these figures. If such a calculation is made, it indicates that the atom polarisation term for carbon would have a negative value ($-0{\cdot}12$), whilst that for hydrogen (0·1) would be large and much larger than the value (0·007) which can be deduced from the data of Watson and Ramaswamy (*loc. cit.*) for hydrogen gas.

Significance of Field Anisotropy in the Application of the Solvent-effect Equation.—In order to understand the significance of these anomalous values of the atomic terms for carbon and hydrogen, it is necessary to recall that in addition to the cavity and reaction fields delimited by the solvent-effect equation (1), the investigation of liquid mixtures (*J.*, 1940, 752) has shown that there is also a general field anisotropy which is, however, not readily susceptible to precise experimental delineation except as a deviation in the partial polarisation of components of the mixtures in the higher concentration ranges. This field anisotropy is of particular importance in the case of non-polar liquids because then the first modifying term (Y/ε) of the solvent-effect equation is zero and the remaining terms become of relatively greater significance. The existence of two modifying terms with non-polar compounds has been recognised for some time (*J.*, 1935, 727), but, as a rigid evaluation of a field anisotropy of this kind is a difficult problem (*J.*, 1941, 864; cf. Govinda Rau, *Proc. Indian Acad. Sci.*, 1935, **1**, *A*, 498), the effect is designated x; although it is used here to explain certain seeming anomalies in the polarisation of the paraffins, no precise attempt is being made at this stage to relate its absolute value to the structures concerned, and only its relative values amongst a limited number of similar compounds is considered.

The polarisation of liquids can therefore be represented by the general expression

$$P_S = P_{E+A} + (Y/\varepsilon) + [Z(\varepsilon - 1)^4/(\varepsilon + 2)^4] + x \quad . \quad . \quad . \quad . \quad (2)$$

of which the solvent-effect equation is one special case. For polar substances, x is usually small in comparison with the other terms, and consequently for such substances the effective terms are contained in the solvent-effect equation (1) already proposed (*J.*, 1937, 1915). For non-polar compounds Y is zero, but x is of comparatively greater significance so that, whilst the expression $P_S = P_{E+A} + [Z(\varepsilon - 1)^4/(\varepsilon + 2)^4]$ is sufficiently accurate for dilute solutions of non-polar substances, for concentrated solutions and pure non-polar liquids the equation must be written

$$P_S = P_{E+A} + [Z(\varepsilon - 1)^4/(\varepsilon + 2)^4] + x \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

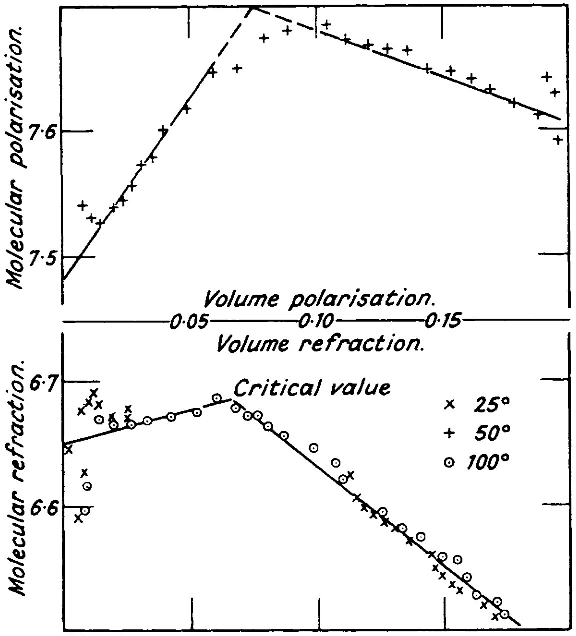
When considering the special case of a pure non-polar liquid at a fixed temperature and pressure for which the dielectric constant has a definite value, it is possible to simplify equation (3) to

$$P_S = P_{E+A} + x' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $x' = [Z(\varepsilon - 1)^4/(\varepsilon + 2)^4] + x$.

A third special case of the general expression (2) occurs for molecules such as hydrogen and nitrogen, which do not absorb rotational quanta (cf. Thompson, *J.*, 1944, 183) and for which both the reaction field and the field anisotropy are zero. For these substances $P_S = P_{E+A}$, and they behave in the same way as the single spherical molecule considered by Lorentz (*Ann. Physik*, 1880, [iii], **9**, 641), so that even at high pressures (cf. Uhlig, Kirkwood, and Keyes, *J. Chem. Physics*, 1933, **1**, 155) they obey the classic expression $P = (\varepsilon - 1)M/(\varepsilon + 2)d$.

Variation of the polarisation of carbon dioxide with field anisotropy: $P_S = P_{E+A} + x'$ *(data of Michels and Kleerekoper).*



Variation of the refraction of carbon dioxide with field anisotropy: $[R] = (P_E + \text{dispersion}) + x'$ *(data of Michels and Hamer).*

Effect of Field Anisotropy on Polarisation and Refraction in the Liquid and Gaseous States.—As an examples of the application of expression (4) and the analogous expression for molecular refraction, *viz.*,

$$[R] = (P_E + \text{dispersion}) + x' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

data for the molecular polarisation and refraction of carbon dioxide over a wide range of pressures taken from the experimental results of Michels and Hamer (*Physica*, 1937, **4**, 995) and of Michels and Kleerekoper (*ibid.*, 1939, **6**, 586) are plotted in the figure as a function of volume polarisation and volume refraction respectively. After allowance has been made for the authors' own estimate of possible errors it is seen that for each curve there is a change in direction at a critical value of the volume polarisation (p_C) or volume refraction (r_C) which can be calculated from the critical data since $p_C = P_{E+A}/V_C$ and $r_C = [R]/V_C$ where V_C is the critical molecular volume, and whence $p_C = 0{\cdot}076$ and $r_C = 0{\cdot}067$ in agreement with the figure. The values of x' are quite different for the two cases of refraction and polarisation because, as will be seen later in the case of the paraffins, although P_A is only a small fraction of P_E, the anisotropic effect associated with atoms is of necessity a relatively larger proportion of the whole. Again as the graphs are linear on either side of the critical values, x' must be related to the change in molecular volume. This also is to be expected as x' is a property of the shape of the polarisation ellipsoid.

Since the effect of lowering temperature is to lower the molecular polarisation and, on that part of the curve which includes the liquid values, the effect of lowering pressure is to raise the polarisation, it follows that the values of the molecular polarisation at the boiling points do not differ so greatly from the critical value. The difference which is observed is related to the increase in molecular volume between the critical point and the boiling point, which, at least for similar compounds, is an approximately constant fraction of the whole (cf. Young, *Phil. Mag.*, 1894, [v], **37**, 1), whereas the values of x' at the temperature of measurement must depend on the further increase in molecular volume up to the point of observation. As more extensive data are available for boiling points than for critical points it is preferable that when required, for example in cases when the gas values are not available, x' should be expressed in terms of the (b. p. — 20°) interval rather than the more strictly accurate (critical point — 20°) interval.

For the homologous series of liquid *n*-paraffins there is only a slight change in the magnitude of the increments of molecular volume in passing up the series; therefore, if the above conclusions about the relationship between the field anisotropy and molecular volume are correct, there should be, within the limits of experimental error, no appreciable change in the homologous series increment of x' for the (b. p. — 20°) interval. However, it is known that the boiling points of the *n*-paraffin series increase in a regular manner but with *decreasing* increments (cf. Deanesly and Carleton, *J. Physical Chem.*, 1941, **45**, 1104) and, if our deduction is correct that x' increases (in a negative sense) with a *fixed* increment on passage up the homologous series, then it follows that the temperature coefficients of the polarisations should increase regularly, but with *increasing* increments. This has been observed by Dornte and Smyth (*loc. cit.*). The decreases in the increments of the boiling points and the increases of the polarisation temperature coefficients just counterbalance each other and it is from this circumstance that the observed constant increment of the liquid molecular refractions for homologous series arises.

Relationship between Polarisation and Refraction of the Liquid and Gaseous States for the n-*Paraffins*.—The present investigation of the physical properties of hydrocarbons was undertaken in an endeavour to provide experimental values for the polarisation of all the *n*-paraffins which are liquid at 20°, and to measure the molecular refractions on the same samples. Particular attention has been paid to the purification of the compounds and to the accuracy of the measurements so that, by correlation with the existing values for the gaseous *n*-paraffins, it should be possible to evaluate the field anistropy and to find some explanation for the two apparent anomalies in the recorded polarisation and refraction data.

The first of these anomalies has already been mentioned and concerns the apparent values of P_A for the paraffins, as calculated from liquid data. The second is concerned with the increment for the CH_2 group in certain series of liquid aliphatic compounds. Whilst the increment is constant throughout each series, there is a variation, as Vogel (*J.*, 1943, 636) has pointed out, from one series to another by amounts which, although small, are greater than the experimental error. These small variations are not due to the polar group because the first member of each series has been omitted.

Molecular Refractions of the Liquid n-*Paraffins*.—Values for the molecular refraction of six liquid *n*-paraffins were recorded by Wibaut and Langedijk (*Rec. Trav. chim.*, 1940, **59**, 1220) who concluded that the increment for each CH_2 in the case of $[R]_D^{20}$ is 4·636, and that the values for the series are given by 2·078 + 4·636*c*. In the interpretation of our own results for the thirteen paraffins from *n*-pentane to *n*-heptadecane, we have given relatively greater weight to the values for the lower members, both because these are more readily obtained in a state of high purity, and also because the values for the higher members include a much larger molecular weight with proportionate increase in the error of calculation. Our value for the set of molecular refractions is 2·09 + 4·638*c* for which a comparison is made with the experimental values in Table V. This value of 4·638 for the increment is actually identical with that of Wibaut and Langedijk, when allowance is made for the fact that we have used the 1940 value of 12·01 for the atomic weight of carbon. Other smoothed values recorded for the liquid *n*-paraffins are those of Deanesly and Carleton (*loc. cit.*) which were based in part on selected values of density and refractive index published before 1941; their value for the series constant is 2·075 + 4·640. Vogel (*J.*, 1936, 133) obtained a value of the constant for hydrogen by a procedure which includes data for the alkyl halides which, as he admits, have different values for the increment. Vogel's alternative procedure, which is based on the hydrocarbon results alone, leads to 2·09 + 4·643*c* where the constant for hydrogen is identical with our own. The constant for the increment is obtained in Vogel's case by the method of least squares which gives equal weight to all the individual values.

Deanesly and Carleton (*loc. cit.*) have calculated smoothed densities for these paraffins by plotting a mean curve through the increments of the molecular volumes calculated from their selected data. Contrary to Deanesly and Carleton (*loc. cit.*, footnote, p. 1106), we believe that the molecular volumes of these paraffins must lie on a smooth curve, because if the molecular volumes at the boiling points and also the boiling points themselves lie on smooth curves as indicated by Egloff and Kuder (*J. Physical Chem.*, 1941, **45**, 836) then the molecular volumes at any given temperature should also lie on a smooth curve. We disagree slightly with Deanesly and Carleton's molecular-volume increment curve, the upper end of which is based on their determination of the density of *n*-hexadecane from fuel oil. Our own determination of this density is concordant with that of Wibaut, Hoog, Langedijk, Overhoff, and Smittenborg (*Rec. Trav. chim.*, 1939, **58**, 329); and so a new curve (not shown, but the data for which are included in Table V) slightly modified from that of Deanesly and Carleton has been drawn, giving smoothed values for the molecular volume which approach a value of 16·327 on extrapolation and are intermediate between those of Deanesly and Carleton and those of Calingaert and Hladky (*J. Amer. Chem. Soc.*, 1936, **58**, 153). From these smoothed values a new set of smoothed densities has been calculated by Deanesly and Carleton's method. Our experimental values (Table V) of d_4^{20} for all the hydrocarbons from *n*-pentane to *n*-heptadecane are in good agreement with these smoothed values. Smoothed values for the refractive indices of these paraffins obtained from our smoothed molecular volumes and our series value for the molecular refractions (Deanesly and Carleton's method) are in good agreement with our experimental values (see Table V) and those of other authors.

We have not ourselves measured the dispersion of these hydrocarbons, as concordant values for their dispersions are already available in the results of Dornte and Smyth, Wibaut and Langedijk, and Vogel (*loc. cit.*), who agree in indicating that $[R]_D - [R]_\alpha = 0{\cdot}01 + 0{\cdot}020c$ and $[R]_\beta - [R]_D = 0{\cdot}03 + 0{\cdot}050c$; when combined with our value $[R]_D = 2{\cdot}09 + 4{\cdot}638c$, this gives $[R]_\alpha = 2{\cdot}08 + 4{\cdot}618c$ and $[R]_\beta = 2{\cdot}12 + 4{\cdot}688c$, in good agreement with the series constants for $[R]_\alpha$ and $[R]_\beta$ given by Wibaut and Langedijk (*loc. cit.*) after due allowance for the lower atomic weight of carbon used by these authors.

A similar series value for the constant P_E has been obtained by application of the dispersion formula $n_\lambda^2 = n_\infty^2 + k/\lambda^2$ to the values for the refractive index corresponding to the series constants for molecular refraction at different wave-lengths.

It is found that

$$P_E = 2{\cdot}02 + 4{\cdot}534c \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

which gives values of P_E for the individual hydrocarbons in good agreement with those calculated by Dornte and Smyth (*loc. cit.*).

Molecular Polarisations for the Liquid n-*Paraffins*.—As one of the main objects of this work we have measured, with the apparatus previously described (*J.*, 1933, 1343; 1935, 730; 1940, 893), the dielectric constants of these *n*-paraffins, in order to make available molecular polarisations and refractions measured on the same pure samples of the hydrocarbons. By the methods employed for the molecular refraction, we find that our experimental values for the series of *n*-paraffins can be expressed as

$$P_{E+A} = 2{\cdot}24 + 4{\cdot}61c \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

This value of 4·61 for the increment is concordant with that found by Dornte and Smyth (*loc. cit.*) when allowance is made for the fact that they base their measurements of dielectric constant on a standard value for benzene of 2·276, whereas we employ 2·2825. By a calculation similar to that used for refractive index, the smoothed dielectric constants have been obtained from the series constant (7) and the smoothed molecular volumes, and these are found to be in good agreement with the experimental values (Table V).

Finally to complete the set of properties for the liquid paraffins we obtain the series constant of the atom polarisation by subtraction of expressions (6) and (7) to give $P_A = 0{\cdot}22 + 0{\cdot}076c$. These series constants for the liquid *n*-paraffins are summarised in Table II. As previously stated the carbon and hydrogen constants corresponding to this series constant for P_A are anomalous because the figures indicate that P_A for hydrogen in these compounds is 0·11, or 11% of P_E, and this is far above the value of P_A for gaseous hydrogen (Table I). In any case the negative value so obtained for carbon is anomalous as P_A itself cannot be negative.

Series Constants of the Gaseous n-*Paraffins*.—The experimental data (see Table IV) for the gaseous *n*-paraffins are of necessity less accurate than those for the liquids, but it can be seen by comparison with the values calculated from the series constants in Table II that there is reasonably good agreement between the experimental values and the series constants (obtained by giving special weight to the lower members because, as with the liquids, relatively greater accuracy is obtained in this way). We find that for the *n*-paraffins in the gaseous state, $P_E = 1·85 + 4·60c$, $P_{E+A} = 1·86 + 4·67c$, whence $P_A = 0·01 + 0·07c$. These series constants lead to values for P_A for the elements which are entirely reasonable and probable, that for carbon (see Table I) being positive instead of negative as it is for the liquids, whilst the constant for hydrogen, calculated on the assumption that all the C–H bonds are equivalent, is in agreement with the value for gaseous hydrogen. The value of P_E for the hydrogen molecule is of course different from the hydrogen constant for the paraffins because it depends on the H–H bond in one case and C–H in the other. P_A however depends on the mobility of the hydrogen nucleus in both cases.

TABLE I.

Constitutive refraction and polarisation constants for the n-*paraffins.*

	$[R]_D$.	P_E.	P_{E+A}.	P_A.	P_A, as % of P_E.
		Liquid state.			
CH_4 extrapolated	6·728	6·554	6·85	0·296	5
CH_2 increment	4·638	4·534	4·61	0·076	2
2H by difference	2·09	2·02	2·24	0·22	11
H	1·045	1·01	1·12	0·11	11
C	2·548	2·514	2·37	−0·144	−6
		Gaseous state.			
CH_4	6·60	6·45	6·53	0·08	1·2
CH_2 increment	4·70	4·60	4·67	0·07	1·5
2H by difference	1·90	1·85	1·86	0·01	0·5
H	0·95	0·925	0·93	0·005	0·5
C	2·80	2·75	2·81	0·06	2·2
H_2 gas	2·08	2·035	2·05	0·015	0·7

TABLE II.

Series constants for refraction and polarisation.

	Liquid *n*-paraffins.	Gaseous *n*-paraffins.	Field anisotropy, *x'* (by difference).
$[R]_\beta$	2·12 + 4·688*c*	1·92 + 4·75*c*	0·20 − 0·062*c*
$[R]_D$	2·09 + 4·638*c*	1·90 + 4·70*c*	0·19 − 0·062*c*
$[R]_\alpha$	2·08 + 4·618*c*	1·89 + 4·68*c*	0·19 − 0·062*c*
P_E	2·02 + 4·534*c*	1·85 + 4·60*c*	0·17 − 0·066*c*
P_{E+A}	2·24 + 4·61*c*	1·86 + 4·67*c*	0·38 − 0·06*c*
P_A	0·22 + 0·076*c*	0·01 + 0·07*c*	0·21 + 0·006*c*

TABLE III.

Bond and atom constants for the refraction and polarisation of the n-*paraffins with the corresponding anisotropic factors at 20° (in parentheses).*

	$[R]_\beta$.	$[R]_D$.	$[R]_\alpha$.	P_E.	P_A.
C–C	1·415(−0·131)	1·400(−0·126)	1·395(−0·126)	1·375(−0·118)	—
C–H	1·667(0·035)	1·650(0·32)	1·642(0·032)	1·612(0·026)	—
C	—	—	—	—	0·060(−0·204)
H	—	—	—	—	0·005(0·105)

TABLE IV.

Molecular refraction and polarisation of the gaseous n-*paraffins.*

	Recorded values.*					Calculated from series constants in Table III.				
	$[R]_\beta$.	$[R]_D$.	$[R]_\alpha$.	P_E.	P_{E+A}.	$[R]_\beta$.	$[R]_D$.	$[R]_\alpha$.	P_E.	P_{E+A}.
Methane	6·67	6·60	6·57	6·45	6·53	6·67	6·60	6·57	6·45	6·53
Ethane	11·43	11·31	11·26	11·07	11·16	11·42	11·30	11·25	11·05	11·20
n-Propane	16·26	16·09	16·02	15·73	16·04	16·17	16·00	15·93	15·65	15·87
n-Butane	20·92	20·68	20·59	20·20	20·65	20·92	20·70	20·61	20·25	20·54
n-Pentane	—	—	—	—	25·18	—	—	—	—	25·21
n-Hexane	—	—	—	—	29·90	—	—	—	—	29·88
n-Heptane	—	—	—	—	34·18	—	—	—	—	34·55

* Values for CH_4 to C_4H_{10}, Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144.
Values for C_5H_{12} to C_7H_{16}, Kubo, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, **26**, 242; cf. Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 571.

TABLE V.

Physical constants related to the refraction and polarisation of the liquid n-*paraffins.*

	M. p.,	B. p.,	d,		M/d,	$\Delta M/d$,	n_D,		ε,		$[R]_D$,		P_{E+A},	
	observed.		smoothed.	observed.	smoothed.		observed.		smoothed.	observed.	smoothed.	observed.	smoothed.	observed.
n-Pentane ...	—	36·0°	0·62631	0·62605	115·192	—	1·3578	1·3577	1·8439	1·8437	25·280	25·29	25·29	25·30
n-Hexane	—	68·6	0·65940	0·65955	130·683	15·491	1·3750	1·3750	1·8900	1·8900	29·918	29·91	29·90	29·89
n-Heptane ...	—	98·2	0·68374	0·68377	146·543	15·860	1·3877	1·3878	1·9241	1·9249	34·556	34·56	34·51	34·53
n-Octane	—	125·6	0·70263	0·70278	162·563	16·020	1·3975	1·3975	1·9506	1·9517	39·194	39·18	39·12	39·14
n-Nonane	—	150·7	0·71773	0·71757	178·689	16·126	1·4054	1·4054	1·9722	1·9725	43·832	43·84	43·73	43·75
n-Decane	—	173·7	0·73005	0·72994	194·885	16·196	1·4118	1·4118	1·9896	1·9891	48·470	48·48	48·34	48·33
n-Undecane ...	—	—	0·74036	0·74024	211·126	16·241	1·4171	1·4169	2·0037	2·0049	53·108	53·09	52·95	52·98
n-Dodecane ...	—	216·2	0·74904	0·74871	227·395	16·269	1·4217	1·4217	2·0163	2·0160	57·746	57·77	57·56	57·56
n-Tridecane ...	—	—	0·75654	0·75624	243·681	16·286	1·4256	1·4258	2·0275	2·0261	62·384	62·44	62·17	62·13
n-Tetradecane	4·5°	—	0·76306	0·76314	259·979	16·298	1·4290	1·4291	2·0370	2·0368	67·022	67·03	66·78	66·77
n-Pentadecane	9·5	—	0·76879	0·76862	276·285	16·306	1·4320	1·4320	2·0452	2·0452	71·660	71·68	71·39	71·40
n-Hexadecane	18·1	—	0·77387	0·77378	292·597	16·312	1·4347	1·4348	2·0526	2·0518	76·298	76·33	76·00	75·97
n-Heptadecane	—	—	0·77840	0·7780	308·914	16·317	1·4370	1·4368	2·0593	2·0578	80·936	80·94	80·61	80·57

Values for $C_{17}H_{36}$ extrapolated from	t.	d.	n_D.	ε.
	25°	0·7745	1·4348	2·0526
	30	0·7711	1·4328	2·0474
	35	0·7676	1·4309	2·0422

M. p. and b. p. may be compared with the data of Deanesly and Carleton, *J. Physical Chem.*, 1941, **45**, 1104.

Observed values of densities and refractive indices up to hexadecane may be compared with those of: Egloff, "Physical Constants of Hydrocarbons," Vol. I, 1939; Deanesly and Carleton, *loc. cit.*; Dornte and Smyth, *J. Amer. Chem. Soc.*, 1930, **52**, 3546; Wibaut, Hoog, Langedijk, Overhoff, and Smittenberg, *Rec. Trav. chim.*, 1939, **58**, 329; Wibaut and Langedjik, *ibid.*, 1940, **59**, 1220; Vogel, *J.*, 1946, 133; Forziati, Glasgow, Willingham, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 129.

Observed values of dielectric constant up to dodecane may be compared with those of Dornte and Smyth, *loc. cit.*

Smoothed values of $[R]_D$ and P_{E+A} are taken from Table III. Other smoothed values calculated as indicated in the text.

Field Anisotropy for the n-*Paraffins expressed as Series and Constitutive Constants.*—Eisenlohr (*Z. physikal. Chem.*, 1911, **75**, 585) computed, in the case of molecular refraction, constitutive constants which depend on fundamental values for carbon and hydrogen obtained from a number of aliphatic series. It is evident that when the values in Table II for the liquid and gaseous states are compared, the constants for carbon and hydrogen derived from the liquid data are not even in the correct proportion when compared with the gaseous values, and that they are only approximately of the right order. The values of $[R]_D^{20}$ need correcting by the expression (7), whereby the anisotropic effect x' accounts for the difference between the gaseous and the liquid constants for the series. In Table II the field anisotropy corresponding to $[R]$, P_E, P_{E+A}, and P_A respectively is expressed as the several differences between the series constants for the gas and liquid states, and in this way we derive series constants for x', in which the third decimal place is included for calculating purposes. The field anisotropy is thus found to be a constitutive property as has already been indicated from theoretical considerations.

The fundamental constants of the elastic polarisation are the values of P_E for each type of bond and of P_A for each atom in the gaseous state, whilst the corresponding values of $[R]$ include the effects of dispersion at the appropriate wave-length. The values of the bond constants are calculated on the assumption that every C–H bond in the normal paraffins is of identical value. Associated with these and included in Table III are the corresponding values of x' which represent the amounts of induced polarisation by which the constants of the relatively isolated gaseous molecules are changed, in accordance with equation (4), when the molecules are brought into proximity with one another in the liquid state. The molecular refractions and polarisations of the liquid hydrocarbons can therefore be obtained by summation of the appropriate terms, including the values of x' with due regard for their signs. As x' expresses an anisotropic effect it is related to the size and especially to the shape of the molecules, and is in this respect unlike the refraction and polarisation which are related to the mobilities of the component parts of the molecule. It will be seen from Table III that x' can have negative values and in this particular resembles the solvent effect of polar compounds, which can be either positive or negative with respect to the gas value. Thus it is noteworthy that the anisotropic factors for the atoms and particularly that for the hydrogen atom are large compared with those for the bonds. The signs of the values of x' agree with the changes in shape of the paraffin molecules and are consistent with the signs of the solvent effects previously noted (*J.*, 1940, 752), since on passage up the homologous series each carbon atom and C–C bond causes an elongation of the molecule which is known to be connected with an apparent decrease in the polarisation on passage from gas to liquid. Each hydrogen atom and C–H bond however causes a broadening of the molecule, normally connected with an apparent increase in polarisation. The net effect for each CH_2 group ($-0{\cdot}06$) is due to the net elongation.

These conclusions concerning the field anisotropy explain very simply the two anomalies noted above and found in the polarisation and refraction data of liquids. The first, which is concerned with the apparent atom polarisation of the liquid paraffins, arises because the anisotropic effect may be of negative sign, and because that part of it associated with the atoms is much larger than the atom polarisation itself. By contrast, the anisotropic effect of the bonds is smaller than the electron polarisation. The second anomaly, that the increments vary from one series to another, arises because x' is, as we have shown, a function of the boiling-point intervals of the homologous series concerned and, as these vary from one series to another, the differing values of the refraction increment observed by Vogel (*loc. cit.*) is to be expected and is unavoidable in the liquid state.

EXPERIMENTAL.

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

Preparation and Purification of Materials.—*n*-Pentane was prepared from 1-bromopentane by the method given in *Org. Synth.*, 1931, **11**, 85. The hydrocarbon was washed with 2-c.c. portions of concentrated sulphuric acid until the latter remained colourless (20 washings), then successively with water, dilute sodium carbonate solution, and again with water. After being dried (Na_2SO_4), it was fractionally distilled over sodium through a Widmer column, the middle fraction being used for measurements. This purification was repeated until the density and dielectric constant remained unchanged, and the same procedure was adopted for all the paraffins used for the determination of physical constants.

n-Hexane, *n*-octane, *n*-decane, and *n*-tetradecane were prepared by the Wurtz reaction according to Vogel's method (*J.*, 1946, 135). The appropriate alkyl bromides were obtained from the corresponding alcohols (B. D. H.).

n-Heptane was prepared by first converting *n*-propyl bromide into heptan-4-ol (*Org. Synth.*, Coll. Vol. II, 1943, p. 179), which was converted by boiling 48% hydrobromic acid into the corresponding bromide and thence into *n*-heptane by the method used for *n*-pentane except that di-*n*-butyl ether was replaced by diethyl ether.

n-Nonane was prepared from *n*-butyl bromide which was converted by the above methods first into nonan-5-ol and then by iodine and red phosphorus (Rieth and Beilstein, *Annalen*, 1863, **126**, 250) into 5-*iodononane*, b. p. 129°/53 mm. (Found : C, 43·1; H, 7·7; I, 49·2. $C_9H_{19}I$ requires C, 42·5; H, 7·5; I, 49·9%). 5-Iodononane was reduced to nonane by the method given in *Org. Synth.*, Coll. Vol. II, 1943, p. 320.

n-Dodecane and *n*-hexadecane were prepared by reduction (cf. above) of the corresponding primary iodides, the starting materials being dodecyl alcohol (I.C.I.) and cetyl alcohol (B.D.H.) respectively.

n-Pentadecane was prepared from pentadecan-8-ol, the starting material being heptaldehyde prepared from castor oil. The carbinol was converted by Rieth and Beilstein's method (*loc. cit.*) into 8-*iodopentadecane*, b. p. 148°/0·8 mm. (Found : C, 53·6; H, 9·2; I, 37·2. $C_{15}H_{31}I$ requires C, 53·2; H, 9·2; I, 37·5%), which was reduced to the paraffin by the method used for *n*-nonane.

n-Undecane, *n*-tridecane, and *n*-heptadecane supplied by Messrs. Carbon and Carbide Chemicals of New York were lent to us by Mr. R. S. Bradley. They were used without further treatment or characterisation.

The physical constants of the paraffins are recorded in Table V.

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