154. *The Magnitude of the Solvent Effect in Dipole-moment Measurements. Part IV. Determination of Distortion Polarisation and its Additivity in the Alkyl and Aryl Halides.*

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By combining dielectric-polarisation data for ethyl bromide in the liquid and the vapour state, it was shown in Part II (J., **1940**, 752) that some of the uncertainty concerning the magnitude of the atom polarisation (P_A) could be eliminated. In this paper methods for deciding the distribution of the polarisation of binary liquid mixtures between their components are discussed, and the necessary data are presented to extend the above elimination method for the determination of the distortion polarisation (P_{E+A}) to compounds of all four halogens. It is also found that the polarisation of non-polar hydrocarbons, and the values of P_{E+A} obtained by this elimination can, for certain halogen compounds, be expressed as the sum of contributory values assigned to each atom or bond. Values of P_{E+A} for carbon, hydrogen, and all four halogens in compounds of the type RX are calculated, and it is shown that, whereas the electron polarisation (P_E) increases, P_A appears to exhibit a general tendency to decrease in ascending the series from fluorine to iodine.

Sources of Error in Dipole-moment Measurements.—Dipole-moment measurements made in the vapour phase are subject to two main sources of error arising first out of deviations from ideal-gas behaviour, and secondly out of the impracticability of direct determination of the atom polarisation. Measurements made in the liquid phase are also liable to two sources of error, arising in this case from the solvent effect and from the atom polarisation.

Deviations of the vapour from ideal-gas behaviour can be eliminated by suitable corrections such as those used by McAlpine and Smyth (*J. Amer. Chem. Soc.*, 1933, **55**, 459; cf. Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 499), and in the liquid, the solvent effect can be calculated by the appropriate equation as described in Part II (*loc. cit.*). Provided these corrections can be applied to any particular case, there remains only one main source of error which is common to both phases, *viz.*, that due to the atom polarisation. This error could, it is true, be removed in the case of the vapour by making use of the temperature variation of the polarisation, which obeys the Debye expression, $P = a + b/T$. However, as was shown by Groves and Sugden (J., 1937, 1779), it is in many cases difficult to make accurate measurements over such a suitable and sufficient range of temperature as to give the constant a in the above formula with the necessary precision. This results in an experimental error which may be too great to give a satisfactory value for P_A. P_{E+A} could similarly be obtained from the solvent-effect equation $P_S = P_{E+A} + Z(\varepsilon - 1)^4/(\varepsilon + 2)^4 + Y/\varepsilon$ by making use of three values of the partial polarisation (P_S) determined for different dielectric constants to give the three unknowns P_{E+A}, Z, and Y; however, here again, the error of calculation for P_{E+A} is too great for this method to have any value. The above Debye expression cannot be applied directly to the temperature variation of the polarisation of liquids, because of the considerable temperature coefficient of the solvent effect. Disregard of this variation of the solvent effect with temperature has led to the recording of abnormally low values for moments, when these have been calculated from the dependence on temperature of the polarisation in dilute solutions (cf. Smyth and McAlpine, *J. Chem. Physics*, 1935, **3**, 347), and to a rise in the *apparent* moment of certain substances if calculated at a series of rising temperatures, as has indeed been noted by Jenkins (*Trans. Faraday Soc.*, 1934, **30**, 739). In the present state of our knowledge of the solvent effect as developed in this series it is not practicable to make the necessary solvent-effect corrections to measurements in suitable solvents over a sufficiently wide range of temperature.

From these considerations of the errors to which the polarisation is liable, it appears that the sole uncertainty, necessarily remaining in both vapour and liquid measurements, is centred in P_{E+A}. It should therefore be possible both to eliminate it as a source of error and to determine its magnitude, by a comparative study of suitable measurements made in both phases, in which uncertainties due to ideal-gas deviations in the one phase and the solvent effect in the other have been corrected. The method employed by Groves and Sugden (*loc. cit.*; cf. Sugden, *Trans. Faraday Soc.*, 1934, **30**, 734) in which the ratio $P_{E+A}/[R_L]_D$ is taken as 1·05 is a useful approximation for certain classes of substance, but as shown by Cartwright and Errera (*Proc. Roy. Soc.*, 1936, *A*, **154**, 138), Watson and Ramaswamy (*ibid.*, 1936, *A*, **156**, 144), and Coop and Sutton (J., 1938, 1269), much higher

TABLE I.

Polarisation Constants of Non-polar Hydrocarbons at 20°.

	Liquid.								Vapour.	
	P_E.	$[R_L]_D$.	$P^{liq.}_{E+A} + Z\frac{(\varepsilon-1)^4}{(\varepsilon+2)^4}$ (electric poln.), obs.	Z (derived poln. coeff.).[3]	$\frac{(\varepsilon-1)^4}{(\varepsilon+2)^4}$.	$Z\frac{(\varepsilon-1)^4}{(\varepsilon+2)^4}$.	$P^{liq.}_{E+A}$.	$P^{liq.}_{E+A}$ (calc.).[4]	$P^{vap.}_{E+A}$ (electric poln.), obs.	$P^{vap.}_{E+A}$ (calc.).[7]
n-C_5H_{12}	24·7[1]	25·3[1]	25·3[1]	—	—	—	—	24·8	25·2[5]	25·2
n-C_6H_{14}	29·2[1]	29·9[1]	29·9[1]	143	0·00295	0·42	29·5	29·3	29·9[5]	29·8
n-C_7H_{16}	33·7[1]	34·5[1]	34·5[1]	163	0·00314	0·50	34·0	33·9	34·2[5]	34·4
n-C_8H_{18}	38·2[1]	39·1[1]	39·0[1]	—	—	—	—	38·4	—	—
n-C_9H_{20}	42·9[1]	43·8[1]	43·7[1]	—	—	—	—	42·9	—	—
n-$C_{10}H_{22}$	47·4[1]	48·4[1]	48·3[1]	—	—	—	—	47·5	—	—
n-$C_{11}H_{24}$	51·9[1]	53·1[1]	52·9[1]	—	—	—	—	52·0	—	—
n-$C_{12}H_{26}$	56·4[1]	57·7[1]	57·3[1]	—	—	—	—	56·5	—	—
C_6H_6	25·1[6]	26·2[2]	26·6[2]	90	0·00802	0·72	25·9	25·9	—	—

[1] Dornte and Smyth, *J. Amer. Chem. Soc.*, 1930, **52**, 3546. [2] Goss, J., 1935, 727. [3] See Table VI. [4] By summation of atomic contributions, see Table II. [5] Kubo, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, **26**, 242. [6] McAlpine and Smyth, *J. Amer. Chem. Soc.*, 1933, **55**, 453 (cf. Groves and Sugden, J., 1934, 1094; Ramaswamy, *Proc. Ind. Acad. Sci.*, 1936, **1**, 108). [7] From $P^{vap.}_{E+A} = P^{liq.}_{E+A} + A_E(\varepsilon - 1)/(\varepsilon + 2)$, see Table III.

values for this ratio (or the analogous ratio P_{E+A}/P_E) are quite common. Moreover, for the majority of substances, measurements in the vapour state are impossible owing to lack of volatility. Where both vapour and liquid measurements are available, the elimination and determination of P_{E+A} can be effected as has been outlined in Part II (*loc. cit.*), and this will now be discussed in more detail, and for additional substances. It is also now shown that, within certain restricted limits, P_{E+A} can be treated as an additive property, in which it somewhat resembles the molecular refractivity. Hence, it should be possible to determine P_{E+A} for the volatile members of a series by this elimination method, and thence by adding appropriate increments, to calculate P_{E+A} for the higher non-volatile members.

Derivation of the Distortion Polarisation for Liquid Paraffins.—The additive character of the electric polarisation for the non-polar series of normal paraffins in the liquid state has been demonstrated by Dornte and Smyth (*J. Amer. Chem. Soc.*, 1930, **52**, 3546), who found that the values (Table I) increase in a regular sequence just as do their molecular refractivities. The values can be reproduced by the sum of polarisations either for each atom or for each bond, the molecular values obtained being the same in each case. In Table II polarisations for carbon and hydrogen atoms are recorded, from which it is possible to calculate values for the electric polarisations of the liquid paraffins which agree very closely with the experimental values. The electric polarisation of non-polar liquids is composed, according to the solvent-effect equation suggested in Part I (Goss, J., 1937, 1918), of the two terms, $P^{\text{liq.}}_{E+A} + Z(\varepsilon - 1)^4/(\varepsilon + 2)^4$. The term involving the derived polarisation coefficient, Z, is quite small, but as it is found to be additive, the increment for CH_2 being 0·07D. (see Table I), $P^{\text{liq.}}_{E+A}$ is necessarily also additive.

TABLE II.

*Atomic Contributions to P_{E+A} at 20°.**

	Liquid.				Vapour.	
	P_E.	$[R_L]_D$.	$P^{\text{liq.}}_{E+A} + Z\frac{(\varepsilon-1)^4}{(\varepsilon+2)^4}$ (electric poln.).	$P^{\text{liq.}}_{E+A}$.	$P^{\text{vap.}}_{E+A}$.	$P_A = (P_{E+A} - P_E)$.
C	2·36	2·42	2·40	2·37	2·40	0·04
H	1·08	1·10	1·10	1·08	1·10	0·02
CH_2	4·52	4·62	4·60	4·53	4·60	0·08
C_6H_6	25·1	26·2	26·6	25·9	26·8	1·7
F in RX	0·9[1, 2]	1·0	—	6·5	6·5	5·6
Cl in RX	5·7[3]	6·0	—	9·8	9·8	4·1
Br in RX	8·5[1]	8·9	—	13·5	13·5	5·0
I in RX	13·2[1]	14·0	—	16·6	16·6	3·4
F in CX_4	0·9	1·0	—	—	1·9[4]	1·0
Cl in CX_4	5·7	6·0	6·4	6·3	6·3	0·6
Cl in $C_6H_4X_2$ ...	5·7	6·0	—	—	6·7[5]	1·0

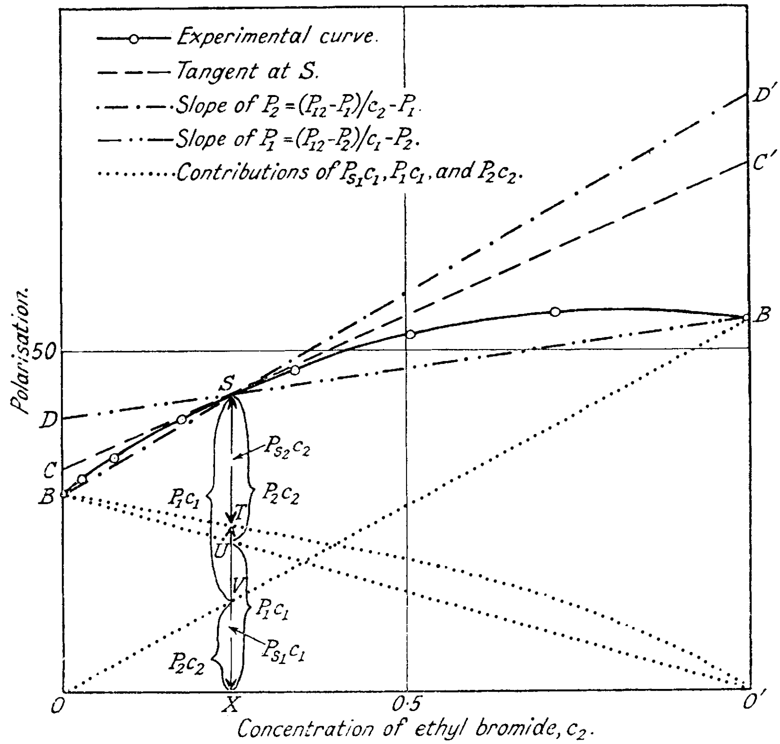
* Calculated from Tables I and IV or the data of: [1] Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 499. [2] McAlpine and Smyth, *ibid.*, 1935, **3**, 55. [3] Smyth, Morgan, and Boyce, *J. Amer. Chem. Soc.*, 1928, **50**, 1536. [4] Watson, Kane, and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 130; cf. Fuoss, *J. Amer. Chem. Soc.*, 1938, **60**, 1633. [5] Groves and Sugden, J., 1937, 1782.

The Significance of Partial Polarisations.—The values of $Z(\varepsilon - 1)^4/(\varepsilon + 2)^4$ employed in the calculation of $P^{\text{liq.}}_{E+A}$ for hexane and heptane are obtained from mixtures with ethyl bromide and ethyl iodide respectively. The partial polarisation P_{S1} for the non-polar (X_1) and P_{S2} for the polar (X_2) component of these mixtures, which are tabulated in Table V, are so defined as to conform to Lewis's nomenclature (*Z. physikal. Chem.*, 1908, **61**, 144). For example, $P_{S2} = \delta P'/\delta n_2$, where P' is the total polarisation of n_1 molecules of X_1 and of n_2 molecules of X_2. The *apparent* molar polarisations P_1 and P_2 have been defined by Debye ("Handbuch der Radiologie," 1925, **6**, p. 628), as, *e.g.*, $P_2 = (P - P_1)/c_2 + P_1$. The partial and the apparent molar polarisations become identical only at infinite dilution, but both of them add up to the total molar polarisation of the mixture $P = P_{S1}c_1 + P_{S2}c_2 = P_1c_1 + P_2c_2$ at all concentrations. At the same time, for any one concentration, represented in Fig. 1 by the point S on the experimental curve BB', there is only one value of P_{S1} or of P_{S2} corresponding, in accordance with a theorem due to

Roozeboom (" Die Heterogenen Gleichgewichte," 1904, II, i, p. 288; cf. Lewis and Randall, " Thermodynamics," 1923, p. 38), to the intercepts OC or $O'C'$ of the tangent CSC'. On the other hand, there are two values of P_1 given by OB and OD and two of P_2 given by $O'B'$ and $O'D'$, intercepts of the chords BSD' and DSB'. Similarly, although the ordinates, such as TX of the curve BTO' represent the contribution $P_{S1}c_1$ of the non-polar component to the polarisation, yet there are two different values of P_1c_1, namely UX and SV. A choice between the two values of P_1c_1 was made by Debye (*ibid.*, p. 630) by assuming that " die zur Geraden BO' gehören Ordinaten dürfen sehr Näherung als die Beiträge des Benzols zur Polarisation angesehen werden "; *i.e.*, that the non-polar component probably behaves as an ideal solvent.

FIG. 1.

Polarisation of ethyl bromide and hexane at 20°.

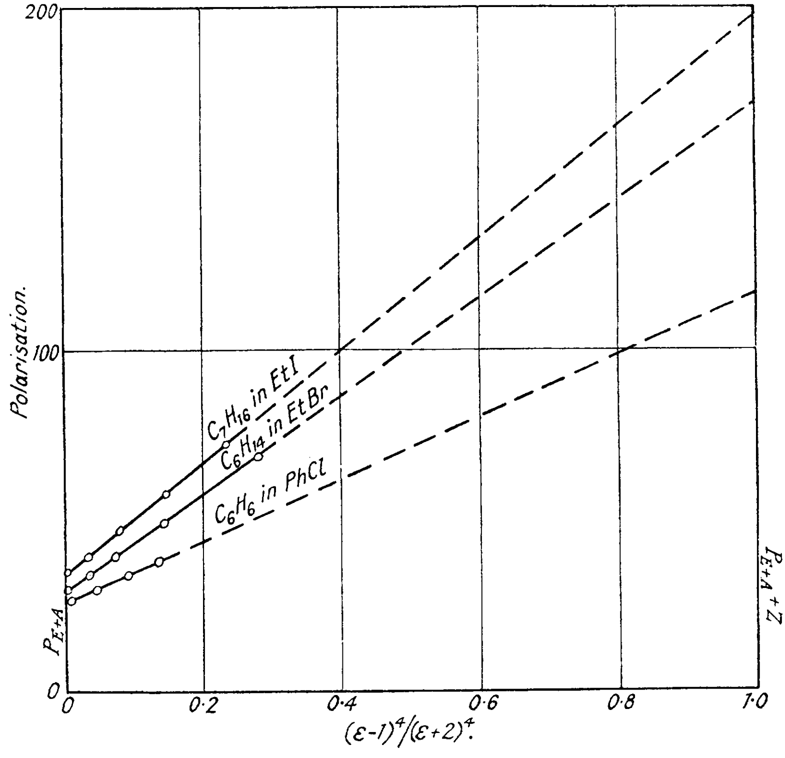


Now, although Williams (*J. Amer. Chem. Soc.*, 1926, **48**, 1888) has shown that this is approximately true for non-polar liquids in a medium of low dielectric constant, there is no evidence to show that the polarisation of any liquid is proportional to concentration at higher values of ε. On the other hand, the partial polarisations given by Lewis's formulæ, $P_{S1} = \delta P'/\delta n_1$ and $P_{S2} = \delta P'/\delta n_2$, not only provide unambiguous polarisation coefficients under all conditions of electric field and concentration, but enable us to express the polarisation of the components of many such mixtures in terms of three fundamental properties (dipole moment, distortion polarisation, and molecular shape) of the component, and of the temperature and dielectric constant of the medium; this is done by means of the solvent-effect equation $P_S = P_{E+A} + Z(\varepsilon - 1)^4/(\varepsilon + 2)^4 + Y/\varepsilon$ as described in earlier parts of this series (*loc. cit.*). For non-polar liquids Y is zero (see Table VI), and P_S is directly proportional to $(\varepsilon - 1)^4/(\varepsilon + 2)^4$ and is independent of the polar component of the mixture. P_S values for *n*-hexane and *n*-heptane are plotted against $(\varepsilon - 1)^4/(\varepsilon + 2)^4$, whence the Z coefficients (see Table IV) are obtained directly from the slope of the straight lines passing through the points determined as shown in Fig. 2.

The Relationship between the Distortion Polarisation of Liquid and Vapour Hydrocarbons.—The possibility of a difference between the two values of P_{E+A} for the liquid and the vapour phase for certain compounds has already been discussed (Goss, J., 1935, 727). In the case of benzene it was then shown that the difference between the electric polarisation of the two phases can be interpreted on the basis of the Raman–Krishnan theory of field anisotropy in the liquid state, and also that the liquid possesses what was then termed a "false" polarisation. This is now, owing to our increased knowledge of the polarisation of liquids, seen to be identical with the solvent-effect term $Z(\varepsilon - 1)^4/(\varepsilon + 2)^4$ discussed in the preceding paragraphs.

FIG. 2.

Partial molar polarisations at 20° of non-polar hydrocarbons.



Although, as Govinda Rau (*Proc. Ind. Acad. Sci.*, 1935, **1**, 498) has pointed out, the evaluation of the field anisotropy is not rigid, the results are found to be of the right order for simple types of compounds. The contribution of the anisotropy has therefore been calculated for four of the paraffin hydrocarbons and is set out in Table III. The optical

TABLE III.

Anisotropy coefficients and polarisation axes.

	30°															20°.	
					$\alpha_1 + \alpha_2 + \alpha_3$.	α_1.	α_2.	α_3.									
	$P_E^{vap.}$.	$r^{vap.}$.[1]	$r^{liq.}$.[1]	$\beta \times 10^6$.[2]	(All $\times 10^{25}$).				p_1.	p_2.	p_3.	s_1.	s_2.	s_3.	A_E.	A_E.	$A_E\frac{(\varepsilon-1)}{(\varepsilon+2)}$.
n-C_5H_{12}.	25·26	0·0132	0·072	235	299	124	88	88	2·01	5·28	5·28	−2·18	1·09	1·09	1·59	1·62	0·36
n-C_6H_{14}	29·85	0·0149	0·099	169	353	147	103	103	1·87	5·35	5·35	−2·32	1·16	1·16	2·06	2·10	0·48
n-C_7H_{16}	34·50	0·0158	0·126	121·4	408	172	118	118	1·58	5·50	5·50	−2·61	1·31	1·31	2·85	2·91	0·69
n-C_8H_{18}	39·12	0·0186	0·129	110·4	463	199	132	132	1·15	5·71	5·71	−3·04	1·52	1·52	4·30	4·39	1·06
EtBr	19·1	0·023	0·250	144·20	226	102	62*	62*	2·51	5·03	5·03	−1·68	0·84	0·84	1·36	1·39	1·02
C_6H_5Cl	31·2	0·049	0·58	79·82	368	146†	146†	76	3·64	3·64	5·29	−0·55	−0·55	1·10	1·56	1·59	0·97

[1] Krishnan, *Phil. Mag.*, 1925, [vi], **50**, 697; Rao, *Indian J. Physics*, 1927, **2**, 7, 61, 179; Krishnan and Rao, *ibid.*, 1929, **4**, 39 (cf. Cabannes, "La diffusion moléculaire de la lumière," 1929).

[2] Tyrer, J., 1914, **105**, 2534; Freyer, Hubbard, and Andrews, *J. Amer. Chem. Soc.*, 1929, **51**, 766.

* Assumed equal. † Assumed equal.

polarisation axes α_1, α_2, and α_3 are calculated from the formulæ given by Krishnan (*Proc. Roy. Soc.*, 1929, *A*, **126**, 155), $P_{\text{E}} = 4\pi N(\alpha_1 + \alpha_2 + \alpha_3)/9$ and

$$\alpha_1/\alpha_3 = \{4 + 2r^{\text{vap.}} + \sqrt{(4 + 2r^{\text{vap.}})^2 - 4(2 - 9r^{\text{vap.}})(2 - 4r^{\text{vap.}})}\}/(4 - 18r^{\text{vap.}})$$

where $r^{\text{vap.}}$ is the depolarisation factor for the vapour. It is necessary for the substance to have an axis of symmetry for these formulæ to be applicable. Similarly, the components of the polarisation field p_1, p_2, and p_3 are calculated from $p_1 + p_2 + p_3 = 4\pi$ and Krishnan's equation (10), which may be expressed as

$$p_1 = \frac{\dfrac{n^2 - 1}{4\pi n}\sqrt{\dfrac{45r^{\text{liq.}}\boldsymbol{R}T\beta M}{d(6 - 7r^{\text{liq.}})}} + (n^2 + 1)\alpha_3 - \alpha_1}{(\alpha_1 + \alpha_3/2)(n^2 - 1)/4\pi}$$

where $r^{\text{liq.}}$ is the depolarisation factor for the liquid, β is the isothermal compressibility, and s_1, s_2, s_3 are the amounts by which p_1, p_2, p_3 respectively differ from the isotropic field. Then $A_{\text{E}} = -N(\alpha_1 s_1 + \alpha_2 s_2 + \alpha_2 s_3)/3$, where A_{E} is the molecular anisotropy factor as previously defined (Goss, *loc. cit.*) and the contribution to the electric polarisation is $A_{\text{E}}(\varepsilon - 1)/(\varepsilon + 2)$. The values of this contribution to the polarisation are recorded for the hydrocarbons in Table III. At first sight they appear not to be additive in character but this is due to the large temperature coefficient of A_{E} (*loc. cit.*). Krishnan and Rao (*Indian J. Physics*, 1929, **4**, 39) have shown that the anisotropy exhibits a maximum value at low temperatures, falling to zero at higher temperatures. It follows from their work that at 20° the value of $A_{\text{E}}(\varepsilon - 1)/(\varepsilon + 2)$ has about its maximum value in the case of octane, whereas for the lower hydrocarbons the values at 20° are below their maxima. Comparison of the data in Tables I and III shows that the anisotropy contributions $A_{\text{E}}(\varepsilon - 1)/(\varepsilon + 2)$ for these paraffin hydrocarbons, after allowance for the deviations from the maxima (see above), are numerically equal, within the limits of experimental error, to the reaction field contribution $Z(\varepsilon - 1)^4/(\varepsilon + 2)^4$. The relationship between the liquid and the vapour polarisation can thus be expressed for non-polar liquids as $P^{\text{vap.}}_{\text{E+A}} = P^{\text{liq.}} - Z(\varepsilon - 1)^4/(\varepsilon + 2)^4 + A_{\text{E}}(\varepsilon - 1)/(\varepsilon + 2)$, which is the same formula as that derived experimentally for benzene (Goss, *loc. cit.*, p. 729) where the supposed " false " orientation polarisation K is now identified as the reaction field contribution of the solvent effect, *i.e.*, $Z(\varepsilon - 1)^4/(\varepsilon + 2)^4$ (see Part II). Since for the paraffins, and rather by coincidence, $Z(\varepsilon - 1)^4/(\varepsilon + 2)^4 \approx A_{\text{E}}(\varepsilon - 1)/(\varepsilon + 2)$, the electric polarisation is identical for liquid and vapour. For benzene, $A_{\text{E}}(\varepsilon - 1)/(\varepsilon + 2)$, which has been previously calculated (J., 1935, 727), is slightly greater than $Z(\varepsilon - 1)^4/(\varepsilon + 2)^4$ as may be seen from the data in Tables I and II.

Derivation and Additivity of the Distortion Polarisation of Alkyl and Aryl Halides.—Having established the additive character of the contributions of carbon and hydrogen to $P_{\text{E+A}}$ and also to the experimental values of the polarisation, we now extend the additive principle to the halogens. Suitable data are available for the seven compounds listed in Table IV. The treatment for ethyl bromide has already been dealt with briefly in Part II (J., 1940, 757 *). It was then assumed without supporting or rebutting evidence that $P^{\text{vap.}}_{\text{E+A}}/P^{\text{liq.}}_{\text{E+A}} = 1{\cdot}05$; an estimate of the ratio has now been made by assessing A_{E} as in the case of the above hydrocarbons. It is necessary in making the calculation to assume an average value for two of the three axes, and consequently the calculated anisotropy factor is not precise, but is, however, of the correct order of magnitude. This calculation has been carried out for ethyl bromide and chlorobenzene, and from the results given in Table III it will be seen that $A_{\text{E}}(\varepsilon - 1)/(\varepsilon + 2)$ is not greater than 5% of $P_{\text{E+A}}$, and hence, that the ratio $P^{\text{vap.}}_{\text{E+A}}/P^{\text{liq.}}_{\text{E+A}}$ for both these substances can be taken as approximating to unity.

Consequently, for this type of substance the determination of the moment and of $P_{\text{E+A}}$ can be carried out by the method employed in Part II for ethyl bromide with sufficient accuracy if $P_{\text{E+A}}$ is assumed to have the same value for both liquid and vapour. The appropriate data for the substances mentioned are collected in Fig. 3 and Table IV.

The values of P_{O} at 20° are obtained in the following manner: from vapour polarisations recorded in the literature there is subtracted the value for $P_{\text{E+A}}$ corresponding to

* *Errata.* On this page lines 36 and 43 : *for* P_{A} *read* $P_{\text{E+A}}$.

TABLE IV.

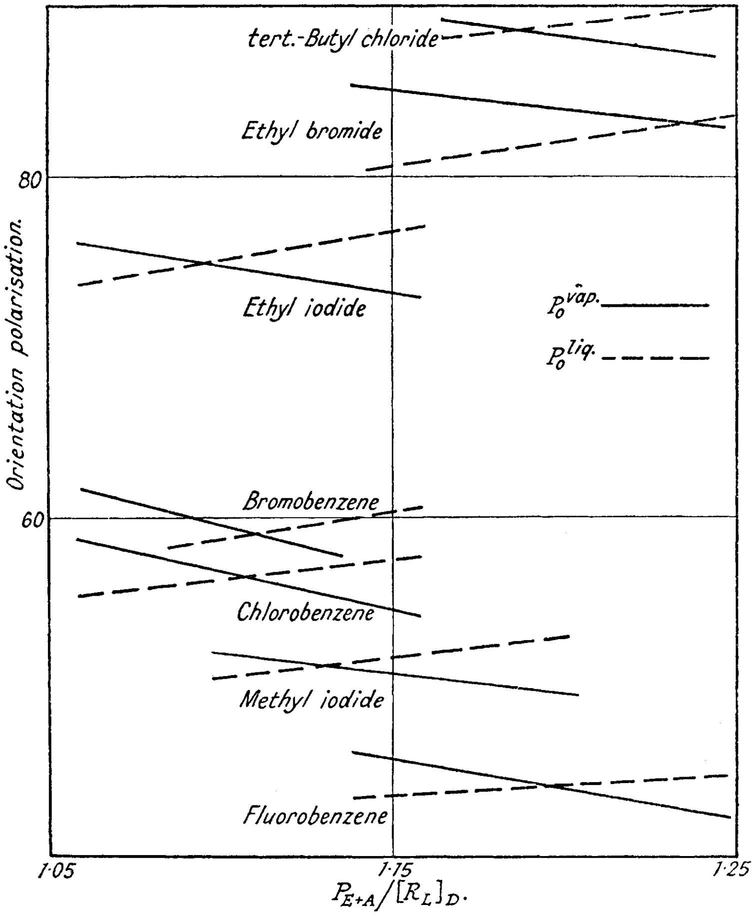
Polarisation data leading to the evaluation of P_{E+A} at 20°.

	$[R_L]_D$.	Assumed values of P_{E+A}.			$P_O^{liq.}$, calc. by solvent-effect equations.			$P_O^{vap.}$, calc. from vapour data.			P_{E+A}, point of inter-section, Fig. 3.	P_{E+A}, calc. from Table II.	P_O, point of inter-section, Fig. 3.
$P_{E+A}/[R_L]_D$ =		1·05	1·15	1·25	1·05	1·15	1·25	1·05	1·15	1·25			
PhF	26·1	27·4	30·0	32·6	42·4	43·6	44·7	49·5	45·8	42·1 [1]	31·3	31·3	43·9
PhCl	31·2	32·8	35·9	—	55·2	57·5	—	59·1	54·5	— [1]	34·6	34·6	56·5
PhBr	34·0	35·7	39·1	—	57·1	60·2	—	62·1	56·9	— [2]	37·7	38·3	59·0
Bu$^\gamma$Cl	25·8	27·1	29·7	32·2	85·5	87·9	90·0	92·6	89·7	86·8 [3]	30·6	29·3	88·2
EtBr	19·1	20·1	22·0	23·9	77·6	80·6	83·5	87·3	85·0	82·7 [4]	23·6	23·6	83·2
MeI	19·4	20·4	22·3	—	49·5	51·8	—	53·3	50·8	— [4]	21·9	21·9	51·2
EtI	24·2	25·4	27·8	—	73·4	76·7	—	76·4	73·1	— [4]	26·7	26·7	75·1

[1] McAlpine and Smyth, *J. Chem. Physics*, 1935, **3**, 55. [2] Groves and Sugden, J., 1935, 971. [3] Wiswall and Smyth, *J. Chem. Physics*, 1941, **9**, 356. [4] Smyth and McAlpine, *ibid.*, 1934, **2**, 499.

FIG. 3.

Variation of calculated values of $P_O^{vap.}$ and $P_O^{liq.}$ with assumed values of P_{E+A}.



1·05, 1·15, or 1·25 times $[R_L]_D$; by substituting the resulting values of P_O at the respective temperatures in the Debye expression, $0{\cdot}01273\sqrt{P_O T}$, and taking a mean value as the dipole moment, it is possible by the same expression to calculate the value of $P_O^{\text{vap.}}$ at 20°. Again using the same figures for P_{E+A}, and the recorded polarisations at 20° of suitable binary liquids mixtures, we calculate $P_O^{\text{liq.}}$ by means of the solvent-effect equation (see above) and the intercept ratio $P_O^{\text{liq.}} = Y/[3\sqrt[4]{(Z + P_{E+A})/P_{E+A} - 2}]$ as described in Part II (*loc. cit.*). Both $P_O^{\text{vap.}}$ and $P_O^{\text{liq.}}$ bear a linear relationship to $P_{E+A}/[R_L]_D$ and have a point of intersection corresponding to values of P_{E+A} and P_O which are common to both liquid and vapour.

TABLE V.

Partial molar polarisation at 20°.

PhF in CCl_4 (see Table VII); P_{E+A} = 31·3.

c_2.	P_{S2}.	P_{S1}.
0·00000	71	28·2
0·00728	71	28·2
0·01443	71	28·2
0·02454	70	28·2
0·04220	69	28·3
0·07594	68	28·4
0·14836	65	28·6
0·25702	62	30
0·50159	58	33
0·75252	57	36
1·00000	56·3	38

PhCl in CCl_4 (recalc. from Goss, J., 1937, 1918); P_{E+A} = 34·6. .

c_2.	P_{S2}.	P_{S1}.
0·00000	82·5	28·1
0·00806	82·0	28·1
0·01531	81·5	28·1
0·03142	81	28·2
0·04812	80	28·2
0·08478	78	28·3
0·18906	73	29
0·47942	65	33
0·89470	62	39
1·00000	61·8	41

EtBr in CCl_4 (recalc. from Goss, J., 1940, 755); P_{E+A} = 23·6.

c_2.	P_{S2}.	P_{S1}.
0·00000	97	28·2
0·01326	95	28·2
0·02255	94	28·3
0·03601	92	28·3
0·04647	91	28·3
0·08538	86	28·6
0·12218	83	29·1
0·23730	73	31
0·55515	59	40
0·79674	56	46
1·00000	55·3	53

PhBr in CCl_4 (see Table VII); P_{E+A} = 38·3.

c_2.	P_{S2}.	P_{S1}.
0·00000	83	28·2
0·00832	82·5	28·2
0·01754	82	28·2
0·02809	81	28·2
0·05227	80	28·3
0·09717	77	28·5
0·19572	73	29·2
0·30140	70	30
0·48043	66	33
0·73379	63	37
1·00000	62·6	40

Bu$^\gamma$Cl in CCl_4 (see Table VII); P_{E+A} = 29·3.

c_2.	P_{S2}.	P_{S1}.
0·00000	122	28·2
0·00687	121	28·2
0·00822	121	28·2
0·01271	120	28·2
0·02719	118	28·3
0·04086	116	28·4
0·08017	112	28·8
0·17989	103	30
0·40869	90	36
0·77657	83	45
1·00000	82·2	50

EtI in CCl_4 (see Table VII); P_{E+A} = 26·7.

c_2.	P_{S2}.	P_{S1}.
0·00000	90	28·2
0·00807	89	28·2
0·02288	88	28·2
0·04058	86	28·3
0·08197	81	28·5
0·11800	78	28·8
0·18076	74	29·6
0·29625	68	31
0·47188	61	35
0·75333	57	42
1·00000	55·7	48

MeI in CCl_4 (see Table VII); P_{E+A} = 21·9.

c_2.	P_{S2}.	P_{S1}.
0·00000	63	28·2
0·00630	63	28·2
0·01276	63	28·2
0·02095	62	28·2
0·02888	62	28·2
0·04282	61	28·3
0·07795	60	28·4
0·11363	58	28·6
0·18205	55	28·9
0·23209	53	29·3
0·32246	51	29·8
0·39028	49	31
0·49048	46	33
0·67196	43	37
0·85049	42	42
1·00000	41·8	46

PhCl in C_6H_6 *at* 25° (Smyth, Morgan, and Boyce, *J. Amer. Chem. Soc.*, 1928, **50**, 1536); $P_{E+A}(C_6H_6)$ = 25·9.

c_2.	P_{S2}.	P_{S1}.
0·0000	82	26·6
0·0786	77	27
0·1988	72	28
0·4007	67	30
0·6020	64	33
0·7048	63	34
1·0000	62·1	38

EtBr in C_6H_{14} (see Goss, J., 1940, 755); $P_{E+A}(C_6H_{14})$ = 29·3.

EtI in C_7H_{16} (Smyth and Stoops, *J. Amer. Chem. Soc.*, 1929, **51**, 3312); $P_{E+A}(C_7H_{16})$ = 33·9.

c_2.	P_{S2}.	P_{S1}.
0·0000	92	34·7
0·0328	89	34·7
0·0365	89	34·8
0·0843	85	35·0
0·1889	79	36
0·1430	68	40
0·6155	62	47
0·8035	58	58
1·0000	56·2	72

This method for the determination of P_{E+A} is necessarily restricted to compounds which have identical moments in the liquid and the vapour state. Where there is a possibility that, say, an alkyl chain may have more than one spatial arrangement (cf. Stuart, *Physikal. Z.*, 1930, **31**, 80) and consequently different resultant moments, the use of such compounds in the above procedure is inappropriate because $P_O^{\text{vap.}}$ and $P_O^{\text{liq.}}$ may not be identical. Further restrictions are imposed where the compounds are too volatile in the liquid or too unstable in the vapour state. We have therefore been confined, in our attempt to assess the additive character of the distortion polarisation of the alkyl and aryl halides, to the compounds listed above. Moreover, since the error of measurement of the polarisation of this type of compound is of the order of ± 0·5, this will also be the error in the calculation of P_{E+A}. However, the object of this work is not the evaluation of P_{E+A} to a high degree of accuracy, but only sufficiently to permit the establishment of additivity within certain limits, so that we can, at a later stage, apply the calculated values to the higher, non-volatile homologues of the series specified. As the probable errors in the case of these homologues will still be of the same order, the use of additive P_{E+A} coefficients, even with an error of ± 0·5, appears preferable to other methods of assessing P_{E+A}.

It will be seen from Table IV that the increments of $[R_L]_D$ and of P_{E+A} (determined by this elimination method) are from methyl to ethyl iodide identical at 4·8, so the additivity principle can be extended to iodine in the alkyl halides, the value of P_{E+A} for iodine being 16·6. Using this to calculate P_{E+A} for the higher alkyl iodides, we find that the ratio $P_{E+A}/[R_L]_D$, which is 1·13 for methyl iodide, falls regularly to 1·05 for hexyl iodide and to below 1·01 higher in the series. The contributory values of P_{E+A} for all the halogens can be obtained by subtracting from those of suitable halogen compounds the values for the alkyl and aryl residues calculated from the data for the hydrocarbons. Exaltations will arise from the presence of different types of bond (cf. Huggins, *J. Amer. Chem. Soc.*, 1941, **63**, 116), and allowance has been made for these in the " P_{E+A} calc." column of Table IV by making use of the known exaltations of the molecular refractivity. The values for bromine, chlorine, and fluorine have been calculated in this way from experimental data for ethyl bromide, chlorobenzene, and fluorobenzene, as there are data in the literature for the vapours of these substances which have been corrected to zero pressure.

The values of P_{E+A} obtained by the elimination method described, and also those given by addition from the contributory values found for the constituent atoms, are compared in Table IV. The figures for bromobenzene and *tert.*-butyl chloride are in satisfactory agreement when allowance is made for the fact that the error of calculation of the elimination method increases in the order $I < Br < Cl < F$, and also that the vapour polarisations for these compounds have not been corrected to zero pressure. Owing to the volatility of the alkyl fluorides, the only suitable data for fluorine are provided by fluorobenzene.

The values of P_{E+A} for the halogens given in this paper are not, of course, applicable to all states of combination; indeed, those for $C_6H_4X_2$ and CX_4 (see Table II) are considerably lower.

Values of P_E taken from the literature are included in Table II, whence P_A can be calculated by difference but is subject to the same probable error of about ± 0·5 as P_{E+A}; P_A does, however, appear to exhibit a tendency to increase from iodine to fluorine. The value for fluorine appears to be somewhat high, but it will be noticed from the data in Table II that the P_A ratio for F/Cl in the CX_4 series is 1·0/0·6, even greater than the ratio of 5·6/4·1 found for these monohalogen compounds. The high values of P_A for compounds containing fluorine have already been noted by Watson and Ramaswamy (*loc. cit.*).

TABLE VI.

Polarisation constants at 20°.

	P_{E+A}.	Z,[1]	Y.[1]	P_O.	μ.		P_{E+A}.	Z.[1]	Y.[1]	P_O.	μ.
PhF	31·3	68·9	88·4	43·9	1·44	MeI	21·9	34·3	92·1	51·2	1·56
PhCl	34·6	61·8	106·0	56·5	1·64	EtI	26·7	47·3	140·5	75·1	1·89
PhBr ...	38·3	47·6	99·3	59·4	1·68	C_6H_6 ...	25·9	90 [2]	0	0	0
Bu$^\gamma$Cl ...	29·3	102·0	206·9	87·5	2·04	C_6H_{14} ...	29·3	143	0	0	0
EtBr ...	23·6	48·3	163·3	83·2	1·99	C_7H_{16} ...	33·9	163	0	0	0

[1] Derived polarisation coefficients calculated by solvent-effect equation from data in Table V (cf. Fig. 2). [2] At 25°. The change in Z for 5° is unlikely to exceed the error of measurement.

EXPERIMENTAL.

Density, dielectric constant, and temperature were measured as previously described (Goss, J., 1933, 1343; 1935, 730; 1940, 893).

Preparation and Purification of Materials.—Fluorobenzene, prepared by the method of Bird and Ingold (J., 1938, 918), had $n_D^{20^\circ}$ 1·4667 (cf. Schiemann, *Z. physikal. Chem.*, 1931, *A*, **156**, 397), $d_{4^\circ}^{20^\circ}$ 1·0225 (cf. Young, *Proc. Roy. Dublin Soc.*, 1910, **12**, 374).

A B.D.H. sample of methyl iodide was washed with sodium carbonate, dried with calcium chloride, and fractionated twice. The middle fraction had $n_D^{20°}$ 1·5303 (cf. Cowley and Partington, J., 1938, 977). Ethyl iodide, similarly purified, had $n_D^{20°}$ 1·5128 (*loc. cit.*).

tert.-Butyl chloride was prepared from recrystallised *tert.*-butyl alcohol (B.D.H.) (*Organic Syntheses*, 1928, **8**, 50). Washing was carried out with ice-cold 1% sodium bicarbonate. The compound was carefully fractionated, the lower third of the distillate being collected. It had $n_D^{20°}$ 1·3855 (cf. Timmermans and Delcourt, *J. Chim. physique*, 1934, **31**, 85).

A B.D.H. sample of bromobenzene was shaken successively with dilute sulphuric acid, sodium carbonate, and water, dried with calcium chloride, and the middle third of the distillate collected. It had $n_D^{20°}$ 1·5600 (cf. Timmermans and Martin, *ibid.*, 1926, **23**, 745).

Densities and dielectric constants of these compounds and their mixtures with purified carbon tetrachloride, and the polarisations (P_{12}) for the binary mixtures calculated therefrom, are recorded in Table VII.

TABLE VII.

Polarisations at 20°.

c_2.	ε.	$d_{4°}^{20°}$.	P_{12}.	c_2.	ε.	$d_{4°}^{20°}$.	P_{12}.
Methyl iodide and carbon tetrachloride.							
0·00000	2·2366	1·5939	28·17	0·18205	2·7532	1·6778	33·34
0·00630	2·2545	1·5967	28·39	0·23209	2·9365	1·7028	34·80
0·01276	2·2737	1·5995	28·63	0·32246	3·242	1·7511	36·64
0·02095	2·2942	1·6030	28·87	0·39028	3·524	1·7896	38·09
0·02888	2·3174	1·6065	29·15	0·49048	3·939	1·8508	39·58
0·04282	2·3563	1·6127	29·60	0·67196	4·814	1·9776	41·28
0·07795	2·4567	1·6284	30·69	0·85049	5·898	2·1280	41·89
0·11363	2·5605	1·6449	31·72	1·00000	7·081	2·2673	41·76
Ethyl iodide and carbon tetrachloride.							
0·00000	2·2353	1·5939	28·15	0·18076	2·9933	1·6474	37·37
0·00807	2·2689	1·5962	28·64	0·29625	3·553	1·6834	42·19
0·02288	2·3296	1·6005	29·53	0·47188	4·449	1·7411	47·56
0·04058	2·4029	1·6056	30·54	0·75333	6·082	1·8406	53·10
0·08170	2·5758	1·6177	32·78	1·00000	7·719	1·9357	55·70
0·11800	2·7313	1·6284	34·62				
Fluorobenzene and carbon tetrachloride.							
0·00000	2·2365	1·5940	28·17	0·14836	2·6479	1·5107	34·09
0·00728	2·2570	1·5898	28·49	0·25702	2·9571	1·4496	37·86
0·01443	2·2755	1·5857	28·78	0·50159	3·748	1·3117	45·51
0·02454	2·3026	1·5801	29·20	0·75252	4·574	1·1682	51·37
0·04220	2·3511	1·5702	29·94	1·00000	5·472	1·0225	56·25
0·07594	2·4431	1·5513	31·29				
Bromobenzene and carbon tetrachloride.							
0·00000	2·2386	1·5940	28·20	0·19572	2·8826	1·5754	37·80
0·00832	2·2654	1·5935	28·64	0·30140	3·230	1·5653	42·17
0·01754	2·2954	1·5922	29·15	0·48043	3·833	1·5480	48·74
0·02809	2·3296	1·5913	29·70	0·73379	4·627	1·5223	56·14
0·05227	2·4080	1·5890	30·96	1·00000	5·431	1·4950	62·61
0·09717	2·5559	1·5849	33·21				
tert.-Butyl chloride and carbon tetrachloride.							
0·00000	2·2384	1·5942	28·19	0·08017	2·7132	1·5274	35·44
0·00687	2·2768	1·5882	28·84	0·17989	3·3561	1·4467	43·42
0·00822	2·2858	1·5872	28·98	0·40869	4·981	1·2676	57·94
0·01271	2·3100	1·5835	29·38	0·77657	7·942	0·9970	74·41
0·02719	2·3929	1·5714	30·70	1·00000	9·961	0·8434	82·21
0·04086	2·4750	1·5598	31·98				

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