105. *The Apparent Dipole Moments of the Chlorinated Methanes in the Liquid, Dissolved, and Gaseous States.*

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For CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4, the apparent moments (Debye–Clausius–Mosotti formulæ) in the states given in the title are respectively: 1·19, 1·69, 1·86; 1·14, 1·55, 1·57; 0·97, 1·13, 1·01; and *ca.* 0, 0, 0 (solvent: C_6H_6 in each case). Methylene dichloride thus slightly contravenes those "rules" which relate μ_{gas} to $\mu_{solution}$ *via* the algebraic sign of the Kerr constant of the solute, which for this substance is negative.

Certain empirical equations for the solvent effect are examined and the generality of their applicability tested.

The substances indicated by the title form a set of readily available related simple structures which are representative of the three chief types of solute molecules encountered in dipole moment measurements, *i.e.*, those with extension respectively (*a*) along the dipole axis (CH_3Cl), (*b*) unequally around it (CH_2Cl_2), (*c*) symmetrically across it ($CHCl_3$), and (*d*) equally about a centre (CCl_4). The original purpose of the present communication was to examine the variations with state of the apparent moments (as indicated by the Debye–Clausius–Mosotti formulæ) of these four compounds *vis à vis* the algebraic signs and magnitudes of their Kerr constants.

Several of the data required for our discussion were already on record in the literature (references below); we have checked or supplemented these where necessary. Dielectric-constant measurements on the system C_6H_6–CH_3Cl do not appear to have been made previously. Table I shows the relevant polarisations at 25° and the moments calculated therefrom, the temperature-invariant term of the Debye equation being used as the true distortion polarisation (${}_{D}P$) in each case.

Table II contains ratios extracted from Table I, together with Sachsse's values for the molar Kerr constants (*Physikal. Z.*, 1935, **36**, 357). It is apparent at once that "rules" requiring the sign of the solvent effect, $\delta\mu$, to be a reversal of that for the electric double refraction, K, are disobeyed by methylene dichloride as a solute, and by this substance and chloroform as undiluted liquids. The comparisons involving *pure* chloroform deserve comment since hitherto this liquid has been regarded as one for which $\delta\mu$ is positive (or $\mu^2_{liq.}/\mu^2_{gas}$ greater than unity; Le Fèvre and Le Fèvre, *J.*, 1935, 1747; Le Fèvre, "Dipole Moments," Methuen, 1938, p. 45; Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374). Such a result was due to the use of the molecular refraction as an approximation for the true distortion polarisation (thus if, in Table I, instead of ${}_{D}P_{CHCl_3} = 25·3$ c.c., $[R_L]_D = 21·4$ c.c. were used, μ would appear as $1·0_7$ D., *i.e.*, 0·06 D. larger than μ_{gas}). With methylene dichloride, however, μ_{gas} exceeds $\mu_{liq.}$ by both methods of calculation ($\mu_{liq.} = 1·22$ with $[R_L]_D = 16·4$; Vogel, *J.*, 1948, 1849). The "negative" solvent action of benzene on this substance, although slight, resembles in order that reported recently for sulphur dioxide (Le Fèvre and Ross, *J.*, 1950, 283). Thus there are now known two substances, showing definitely negative Kerr constants, for which the $\mu_{C_6H_6}/\mu_{gas}$ ratios are *less than unity.*

TABLE I.

P in c.c.; μ in D.	CH_3Cl.	CH_2Cl_2.	$CHCl_3$.	CCl_4.	P in c.c.; μ in D.	CH_3Cl.	CH_2Cl_2.	$CHCl_3$.	CCl_4.
$({}_{T}P)_{gas}$ ...	85·3	70·6	46·3	28·1	$({}_{O}P)_{liq.}$* ...	29·1	26·8	19·4	*ca.* 0
${}_{D}P$	13·6	20·0	25·3	28·1	$({}_{O}P)_{liq.}$† ...	71·7	60·1	31·9	2·3
$({}_{O}P)_{gas}$ ...	71·7	50·6	21·0	*ca.* 0	μ_{gas}	$1{\cdot}8_6$	$1{\cdot}5_7$	$1{\cdot}0_1$	*ca.* 0
$({}_{T}P_{\infty})_{C_6H_6}$	72·4	69·4	51·7	28·0	$\mu_{C_6H_6}$	$1{\cdot}6_9$	$1{\cdot}5_5$	$1{\cdot}1_3$	*ca.* 0
$({}_{O}P_{\infty})_{C_6H_6}$	58·8	49·4	26·4	*ca.* 0	$\mu_{liq.}$*	$1{\cdot}1_9$	$1{\cdot}1_4$	$0{\cdot}9_7$	*ca.* 0
$({}_{T}P)_{liq.}$ ...	42·7	46·8	44·7	28·0	$\mu_{liq.}$†	$1{\cdot}8_6$	$1{\cdot}7_0$	$1{\cdot}2_4$	0·3

* Apparent values by the Clausius–Mosotti–Debye equations.
† Apparent values by the Onsager equation.

TABLE II.

	CH_3Cl.	CH_2Cl_2.	$CHCl_3$.		CH_3Cl.	CH_2Cl_2.	$CHCl_3$.
$\mu^2_{soln.}/\mu^2_{gas}$	0·820	$0{\cdot}97_6$	1·26	*$\delta\mu_{liq.}/\mu_{gas}$	−0·360	−0·274	−0·040
*$\delta\mu_{soln.}/\mu_{gas}$	−0·0914	$-0{\cdot}01_3$	+0·119	$K \times 10^{12}$	41	−13·7	−28
$\mu^2_{liq.}/\mu^2_{gas}$	0·406	0·530	0·924				

* $\delta\mu = \mu_{solution}$ or μ_{liquid} minus μ_{gas}.

EXPERIMENTAL.

Data Sources.—Those relating to total polarisations are listed in three groups, by state. In each case the reference providing information for Table I is placed first, others following in chronological order. Although a complete survey of the literature was made, we here omit obviously incorrect or rough determinations.

(*a*) *Gaseous Dielectrics.*—Some authors quote equations for $(\varepsilon - 1)_{T^\circ}$ or $({}_{T}P_{gas})_{T^\circ}$. Others give individual observations of $(\varepsilon - 1)_{T^\circ}$. The forms used are indicated.

Methyl chloride.

μ, D.	Results as :	Authors.	Reference.
1·86	$P = 13{\cdot}6 + 21{,}351/T$	Smyth and McAlpine	*J. Chem. Physics*, 1934, **2**, 499.
1·97	$\varepsilon - 1 = 0{\cdot}0_3116 + 2{\cdot}828/T$	Sänger	*Physikal. Z.*, 1926, **27**, 556.
1·69	Individual $(\varepsilon - 1)_T$	Sircar	*Indian J. Physics*, 1928, **3**, 197.
1·89	One $(\varepsilon - 1)_{100^\circ}$ value	(Calc. by Höjendahl, Thesis, Copenhagen, 1928, from data by Pohrt, *Ann. Physik*, 1913, **42**, 569).	
1·86	$P = 14{\cdot}72 + 21{,}208/T$	Sänger and Steiger	*Helv. Physica Acta*, 1929, **2**, 130, 411.
1·86	Final μ only	Sänger	*Ibid.*, 1930, **3**, 161.
1·86	Individual $(\varepsilon - 1)_{T^\circ}$	Fuchs	*Z. Physik*, 1930, **63**, 824.
1·86	$P = 14{\cdot}1 + 21{,}390/T$	Sänger, Steiger and Gächter	*Helv. Physica Acta*, 1932, **5**, 200.
1·92	$P = 8{\cdot}66 + 22{,}730/T$	Ramaswamy	*Proc. Indian Acad. Sci.*, 1936, *A*, **4**, 108.

N.B.—Mean of last 8 values = 1·86 D.

Methylene dichloride.

1·58	$P = 19{\cdot}98 + 15{,}064/T$	Maryott, Hobbs, and Gross	*J. Amer. Chem. Soc.*, 1941, **63**, 659.
1·59	$\varepsilon - 1 = 0{\cdot}0_21356 + 1{\cdot}170/T$	Sänger	*Loc. cit.*, 1926.
1·62	Individual $(\varepsilon - 1)_{T^\circ}$	Mahanti and Sengupta	*J. Indian Chem. Soc.*, 1928, **5**, 673.
1·53	$P = 18{\cdot}74 + 14{,}470/T$	Ramaswamy	*Loc. cit.*

N.B.—Mean of last 3 values = 1·58 D.

Chloroform.

1·01	$P = 25{\cdot}28 + 6251/T$	Maryott, Hobbs and Gross	*Loc. cit.*
0·95	$\varepsilon - 1 = 0{\cdot}0_22127 + 0{\cdot}4328/T$	Sänger	*Loc. cit.*, 1926.
1·05	Individual $(\varepsilon - 1)_{T^\circ}$	Sircar	*Loc. cit.*
0·99	$P = 24{\cdot}72 + 6096/T$	Ramaswamy	*Loc. cit.*
1·02	$P = 24{\cdot}92 + 6491/T$	Ramaswamy	*Loc. cit.*

N.B.—Mean of last 4 values = 1·00 D.

Carbon tetrachloride.

0	$\varepsilon - 1 = 0{\cdot}0_22645 + 0{\cdot}0348/T$	Sänger	*Loc. cit.*, 1926.
0	$P = 28{\cdot}14 + 0/T$	Ramaswamy	*Loc. cit.*

(*b*) *Solutions in Benzene.*—These are tabulated under self-explanatory headings except that col. 5 shows the moments obtained *via* the true distortion polarisations (cf. Table I), while col. 6 contains those from the figures given by the original authors, who used for ${}_{E}P + {}_{A}P$ the refractivities in parentheses.

Substance.	Temp.	No. of solns. examined.	$_{\infty}P_T$, c.c.	μ, D.	μ, D.	References.
CH_3Cl	25°	6	72·4	1·69	1·72(11·5) *	Present Work.
CH_2Cl_2	25	12	69·4	1·55	1·60(16·4) *	Present Work.
	25	5	70·0	1·56	1·61(15·8)	Mahanti and Das Gupta (*J. Indian Chem. Soc.*, 1929, **6**, 411).
	25	1	66·3	1·50	1·55(16·2)	Müller and Sack (*Physikal. Z.*, 1930, **31**, 815).
	20	1	68·1	1·51	1·59(15)	Müller (*ibid.*, 1933, **34**, 689).
$CHCl_3$	25	15	51·7	1·13	1·21(21·4)	Le Fèvre (*Trans. Faraday Soc.*, 1950, **46**, 1).
	25	4	47·5	1·04	1·10(21·3)	Williams and Krchma (*J. Amer. Chem. Soc.*, 1927, **49**, 1676).
	18	3	55·4	1·19	1·27(21·3)	Hassel and Uhl (*Z. physikal. Chem.*, 1930, *B*, **8**, 187).
	25	1	51·2	1·12	1·18(21·3)	Müller and Sack (*loc. cit.*).
	20	1	51·9	1·12	1·21(21·2)	Müller (*loc. cit.*).
	25	4	52·1	1·14	1·22(21·4)	Le Fèvre and Russell (*J.*, 1936, 491).
CCl_4	25	6	28·0	0	0 (26·5) *	Present Work.
	25	4	28·3	0	0 (28·3)	Williams and Krchma (*loc. cit.*).
	20	1	28·7	0	0 (26·1)	Müller (*Physikal. Z.*, 1933, **34**, 689).

* Values from Vogel (*J.*, 1948, 1842.)

(*c*) *Pure Liquids.*—

Substance.	ε^{25}.	d_4^{25}.	$_TP_{\text{liq.}}$, c.c.	Reference.
CH_3Cl	9·68	$0{\cdot}878_5$	42·7	Extrapolated from values recorded by Ulrich and Nespital (*Z. physikal. Chem.*, 1932, *B*, **16**, 221), Morgan and Lowry (*loc. cit.*), and Goss (*J.*, 1934, 696, 1467).
CH_2Cl_2	8·93	1·3169	46·8	Present work.
	8·92	1·3175	$46{\cdot}7_5$	Morgan and Lowry (*loc. cit.*).
$CHCl_3$	4·724	1·4790	44·7	Le Fèvre and Rayner (*J.*, 1938, 1921 ; cf. Ball, *J.*, 1930, 570).
	4·642	—	—	Harris (*J.*, 1925, **127**, 1049).
	4·770	1·4796	45·0	Williams and Krchma (*loc. cit.*).
	4·670	1·4780	44·4	Smyth and Morgan (*loc. cit.*).
	4·899	—	—	Matsuike (*Proc. Imp. Acad. Tokyo*, 1929, **5**, 29).
	4·745	1·4800	44·8	Morgan and Lowry (*loc. cit.*).
	4·722	1·4797	44·7	Jenkins (*J.*, 1934, 480).
	4·709	—	—	Davies (*Phil. Mag.*, 1936, **21**, 1).
CCl_4	2·2270	1·5844	28·18	Le Fèvre (*Trans. Faraday Soc.*, 1938, **34**, 1127).
	2·219	—	—	Harris (*loc. cit.*).
	2·230	1·5835	28·24	Williams and Krchma (*loc. cit.*).
	$2{\cdot}210_5$	$1{\cdot}584_2$	27·92	Stranathan (*Physical Rev.*, 1928, **31**, 653).
	2·197	—	—	Matsuike (*loc. cit.*).
	2·231	1·5820	28·27	Morgan and Lowry (*loc. cit.*).
	2·225	1·5836	28·17	Fairbrother (*J.*, 1932, 43).
	$2{\cdot}227_7$	1·5848	28·19	Jenkins (*loc. cit.*).
	$2{\cdot}226_6$	—	—	Davies (*loc. cit.*).
	2·2276	1·5846	28·18	Miller (*J. Amer. Chem. Soc.*, 1942, **64**, 117).

Present Measurements.—Methyl chloride (from methyl alcohol, zinc chloride, and hydrochloric acid ; Morris and Taylor, *J. Amer. Chem. Soc.*, 1924, **46**, 755), dried by passage through 10% potassium hydroxide solution, concentrated sulphuric acid, and a tower of solid potassium hydroxide, was dissolved in sodium-dried benzene, etc., as described by Le Fèvre and Ross (*loc. cit.*) for sulphur dioxide. The methylene dichloride was a commercial specimen. After standing for several hours over calcium chloride, it was distilled (b. p. 40·1°; d_4^{25} 1·3169) before use. Measurements were made by usual procedures (Le Fèvre, " Dipole Moments," Methuen, 2nd Edn., 1948, pp. 31—42) on apparatus already noted (Le Fèvre and Ross, *loc. cit.* ; Calderbank and Le Fèvre, *J.*, 1948, 1949). Extrapolation methods, and symbols used, are explained elsewhere (*Trans. Faraday Soc.*, 1950, **46**, 1) and need not be repeated here.

Methyl chloride in benzene at 25°.

10^5w_1.	ε^{25}.	$\alpha\varepsilon_2$.	d_4^{25}.	βd_2.	10^5w_1.	ε^{25}.	$\alpha\varepsilon_2$.	d_4^{25}.	βd_2.
0	2·2725	—	0·87378	—	2810	2·4367	5·84	0·87552	0·0619
1370	2·3563	6·12	0·87459	0·0591	2876	2·4384	5·77	0·87560	0·0633
2080	2·3944	5·86	0·87507	0·0620	3418	2·4817	6·12	0·87605	0·0664
2558	2·4246	5·95	0·87540	0·0633					

Whence mean $\alpha\varepsilon_2 = 5{\cdot}94$; mean $\beta d_2 = 0{\cdot}0626$; and $_{\infty}P_1 = 72{\cdot}4$ c.c.

Methylene chloride in benzene at 25°.

$10^5 w_1$.	ε^{25}.	$\alpha\varepsilon_2$.	d_4^{25}.	βd_2.	$10^5 w_1$.	ε^{25}.	$\alpha\varepsilon_2$.	d_4^{25}.	βd_2.
821·8	—	—	0·87599	0·280	6,794	2·4925	3·14	0·89326	0·286
1204	2·3108	3·18	—	—	6,830	2·5117	3·50	0·89365	0·291
1374	2·3120	2·89	0·87769	0·285	8,933	2·5565	3·18	—	—
1722	2·3289	3·27	0·87875	0·289	9,443	2·6027	3·50	0·90128	0·291
2795	2·3602	3·17	0·88217	0·300	12,660	2·6965	3·35	0·91165	0·299
2859	2·3641	3·20	0·88219	0·294	15,010	2·7781	3·37	0·91964	0·306
5088	2·4357	3·21	0·88867	0·293					

Whence (by least squares) $\alpha\varepsilon_2 = 3{\cdot}12 + 2{\cdot}13w_1$; $\beta d_2 = 0{\cdot}286 + 0{\cdot}107w_1$; and ${}_{\infty}P_1 = 69{\cdot}4$ c.c.

The dielectric constant of pure methylene chloride at 25° (*viz.*, 8·93) was read from a graph of condenser reading against ($\varepsilon - 1$), obtained from the following standards: air, $\varepsilon = 1$; C_6H_6, $\varepsilon = 2{\cdot}27$; C_6H_5Cl, $\varepsilon = 5{\cdot}61$; o-$C_6H_4Cl_2$, $\varepsilon = 9{\cdot}82$.

*Carbon tetrachloride in benzene at 25°.**

$10^6 w_1$	0	9251	11,034	18,951	20,522	30,908	33,461
ε^{25}	2·2725	2·2724	2·2724	2·2723	2·2723	2·2718	2·2714
d_4^{25}	0·87378	0·87759	0·87810	0·88131	0·88189	0·88609	0·88710

$\Sigma(\varepsilon_{12} - \varepsilon_2)/\Sigma w_1 = -0{\cdot}019$; $\Sigma(d_{12} - d_2)/\Sigma w_1 = 0{\cdot}398$; whence ${}_{\infty}P_1 = 28{\cdot}0$ c.c.

* Recorded at University College, London, 1938—39, with the apparatus of Le Fèvre and Russell (*Trans. Faraday Soc.*, 1947, **43**, 374).

DISCUSSION.

Attempts to relate the variation of the apparent moment of a substance with its state (compare Glasstone, *Ann. Reports*, 1936, **33**, 117, for references not explicitly given here) may be roughly divided into four classes, *viz.*, (*a*) empirical methods of correction for solvent influence, (*b*) *a priori* introduction of factors, for solute and/or for medium, not included in the Clausius–Mosotti–Debye treatment, (*c*) new fundamental models for dielectric polarisation, and (*d*) the addition to the approaches under (*b*) and (*c*) of the conception of hindered rotation, or quasi-crystallinity, in liquids.

Proposals under (*a*) by Müller, Jenkins, Arkel and Snoek, Sugden, Henriquez, *et al.*, like those under (*d*) by Debye (*Physikal. Z.*, 1935, **36**, 100, 193; *Chem. Rev.*, 1936, **19**, 171), Fowler (*Proc. Roy. Soc.*, 1935, *A*, **149**, 1), Kincaid and Eyring (*J. Chem. Physics*, 1938, **6**, 620), and Kirkwood (*J. Chem. Physics*, 1939, **7**, 911; *Ann. N.Y. Acad. Sci.*, 1940, **40**, 315), cannot—in the forms as published—cover those cases (Le Fèvre and Russell, *loc. cit.*; Le Fèvre and Ross, *J.*, 1950, 283; Le Fèvre, Mulley, and Smythe, *J.*, 1950, 290) where $\mu_{\text{soln.}}/\mu_{\text{gas}}$ or $\mu_{\text{liq.}}/\mu_{\text{gas}}$ are greater than unity. Onsager's equation, which falls under (*c*), if used literally, fails with methylene chloride and chloroform (cf. Table I); Wilson's modification (*Chem. Rev.*, 1939, **25**, 377) of it to cover the anisotropy of the solute molecules is an improvement, but one of limited practical usefulness since for most compounds Kerr constant polarisability data are lacking.

In group (*b*) there are the *a priori* treatments of Weigle, Higasi, and Frank, together with others involving the constants ψ and θ of Raman and Krishnan (*Proc. Roy. Soc.*, 1928, *A*, **117**, 589; cf. Goss, *Trans. Faraday Soc.*, 1934, **30**, 751; Le Fèvre and Le Fèvre, *J.*, 1935, 1747; and the criticisms of Jenkins and Bauer, *J. Amer. Chem. Soc.*, 1936, **58**, 2435). In a general way, these approaches have successfully forecast whether $\mu_{\text{soln.}}/\mu_{\text{gas}}$ for a given molecule is above or below unity. In cases where the structure can be credibly regarded as spheroidal, the (*b*) theories have often given approximately quantitatively correct ratios. Unfortunately, in many practical instances, however, neither the ellipsoids defining the anisotropy of polarisability or of "shape" are bodies of rotation. The following table illustrates this point

	(1).			(2).			(3).		
	b_1.	b_2.	b_3.	b_1.	b_2.	b_3.	*A*.	*B*.	*C*.
CH_3Cl	1	0·764	0·764	1	0·827	0·827	1	$0{\cdot}750_5$	0·7505
CH_2Cl_2	—	—	—	1	1·193	0·952	1	1·488	0·878
$CHCl_3$	1	1·349	1·349	1	1·233	1·233	1	1·585	1·585
CCl_4	—	—	—	—	—	—	—	—	—

for the chloromethanes. Under (1) are given the relative polarisabilities recorded for the gaseous materials (Stuart and Volkmann, *Ann. Physik*, 1933, **18**, 140), under (2) the same but for solutions in carbon tetrachloride (Sachsse, *Physikal. Z.*, 1935, **36**, 357), and under (3) the relative effective dimensions (see later) of the molecules. In each case the property measured along the dipole axis is taken as unity.

Several of the relations previously published for solvent action in this field can be cast into general forms typified by : $\mu^2_s/\mu^2_g = 1 + A(\varepsilon - 1)/(\varepsilon + 2)$. For CH_3Cl, CH_2Cl_2, and $CHCl_3$, the results in Table I require A to be *ca.* $-0{\cdot}60$, $-0{\cdot}067$, and $+0{\cdot}87$, respectively. We find that these figures correspond to exp $x^2 - (n^2_2)_{\text{Eff.}}/(n^2_1)_{\text{Eff.}}$, where $n^2_{\text{Eff.}}$ is calculated from the distortion polarisation of solvent or solute, *i.e.*, $(n^2_{\text{Eff.}} - 1)M/(n^2_{\text{Eff.}} + 2)d_{\text{liq.}}$, and x^2 is obtained by the following procedure : Scale drawings are constructed from the known X-ray or electron-diffraction data (in the cases just named these are from Sutton and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 473; in other instances below, dimensions are those recommended by Pauling and Huggins, *Z. Krist.*, 1934, **87**, 205, and Schomaker and Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37) and the " Wirkungsradien " of Stuart (*Z. physikal. Chem.*, 1935, *B*, **27**, 350) superimposed. The maximum measurements along, and in the two perpendicular directions to, the axis of the molecular resultant dipole moment are then read off and recorded as ratios with $A = 1$. Length A is consistently taken parallel to $\mu_{\text{resultant}}$; of B and C (if different), C is made the lesser, x^2 follows as $(C^2 - A^2)/A^2$ when $A > B$ or C, $(C^2 - A^2)/B^2$ when $A < B > C$ and $(C^2 - A^2)/C^2$, when $A < B$ or C. The equation indicated is therefore :

$$\mu^2_{\text{soln.}}/\mu^2_{\text{gas}} = 1 + (\varepsilon - 1)[(\exp x^2 - (n^2_2)_{\text{Eff.}}/(n^2_1)_{\text{Eff.}}]/(\varepsilon + 2) \quad . \quad . \quad . \quad (1)$$

This is tested in Table III. It is seen that the calculated and observed ratios are in reasonable agreement.

TABLE III.

Substance.	*B*.	*C*.	$n^2_{\text{Eff.}}$.	Exp $x^2 - (n^2_2/n^2_1)_{\text{Eff.}}$.	${}_0P_s/{}_0P_g$ (calc.).	${}_0P_s/{}_0P_g$ (found).
CH_3Cl	0·721	0·721	1·929	—0·598	0·82	0·82
CH_2Cl_2	1·488	0·878	2·349	—0·077	0·98	0·98
$CHCl_3$	1·585	1·585	2·368	+0·855	1·26	1·26
$C_6H_5NO_2$	$0{\cdot}752_5$	$0{\cdot}562_5$	2·633	—0·369	0·89	0·87 (1)
C_6H_5Cl	0·767	0·391	2·554	—0·481	0·86	0·84 (2)
C_6H_5Me	$0{\cdot}751_5$	0·485	2·215	—0·573	0·83	0·84 (3)
SO_2	1·453	0·895	1·911	—0·293	0·91	0·99 (4)
Paraldehyde	2·50	2·50	2·499	1·41	1·42	1·69 (5)

References.—Dipole moment values : (1) $\mu_g = 4{\cdot}24$ (Groves and Sugden, *J.*, 1934, 1094; 1935, 971), $\mu_{\text{Benzene}} = 3{\cdot}95$ (Le Fèvre, *Trans. Faraday Soc.*, 1950, **46**, 1). (2) $\mu_g = 1{\cdot}73$ (Groves and Sugden, *loc. cit.*), $\mu_{\text{Benzene}} = 1{\cdot}59$ (Le Fèvre, *loc. cit.*). (3) $\mu_g = 0{\cdot}37$ (McAlpine and Smythe, *J. Amer. Chem. Soc.*, 1933, **55**, 453; Baker and Groves, *J.*, 1939, 1144), $\mu_{\text{Benzene}} = 0{\cdot}34$ (Le Fèvre, Le Fèvre, and Russell, *J.*, 1935, 480). (4) $\mu_g = 1{\cdot}62$ (Le Fèvre, Ross, and Smythe, *J.*, 1950, 276), $\mu_{\text{Benzene}} = 1{\cdot}61$ (Le Fèvre and Ross, *J.*, 1950, 283). (5) $\mu_g = 1{\cdot}44$ (Le Fèvre, Mulley, and Smythe, *J.*, 1950, 290), $\mu_{\text{Benzene}} = 1{\cdot}87$ (*idem, ibid.*).

Special structures : Chlorinated methanes, Brockway and Sutton, *J. Amer. Chem. Soc.*, 1935, **57**, 473; nitrobenzene, James, King, and Horrocks, *Proc. Roy. Soc.*, 1935, *A*, **153**, 225; paraldehyde, see Le Fèvre, Mulley, and Smythe, *loc. cit.*, for refs.; sulphur dioxide, Schomaker and Stevenson, *J. Amer. Chem. Soc.*, 1940, **62**, 1270.

We next explored the possibility of modifying the equation of Le Fèvre and Le Fèvre (*J.*, 1935, 1747) along lines obvious from the discussion of the Raman–Krishnan expression by Govinda-Rao (*Proc. Indian Acad. Sci.*, 1935, **1**, 498), *viz.*, by taking θ as approximately equal to $\mu^2_1 S_1$ and writing S_1 as $4\pi(\delta - 1/3)$, so that

$${}_0P_s/{}_0P_g = 1 + 3\theta(\varepsilon - 1)/(\varepsilon + 2)4\pi\mu^2 = 1 + 3(\delta - 1/3)(\varepsilon - 1)/(\varepsilon + 2) \quad . \quad (2)$$

Estimations of δ were made by using the x^2 values as before and applying them in the equations of Maxwell (" Electricity and Magnetism," Vol. 2, Oxford, 1892, Article 438; cf. also Lord Rayleigh, " Scientific Papers," **4**, 307; Mascart and Joubert, " Leçons," 1896, paras. 52, 53, 276) as follows : (when x^2 positive) $\delta = (1/x^2) - \{(1 - x^2)^{\frac{1}{2}} \arcsin x\}/x^3$, or [when x^2 negative, regarding x^2 as $(-1)y^2$] $\delta = [(1 - y^2)/y^2][(1/2\,y) \ln \{(1 + y)/(1 - y)\} - 1]$. Table IV contains the results for a representative range of molecules; $3\delta - 1$, just as exp $x^2 - (n^2_2)_{\text{Eff.}}/(n^2_1)_{\text{Eff.}}$ (Table III), correctly forecasts the type of solvent effect; the former quantity, however, does not run parallel to it. Since intuitively it seemed that the appropriate relation might be ${}_0P_s/{}_0P_g$ (or μ^2_s/μ^2_g) $= 1 + \text{f}(\varepsilon, n^2_{\text{Eff.}})(3\delta - 1)$ many different types of $\text{f}(\varepsilon, n^2_{\text{Eff.}})$ were tried. Of these, several were promising, *e.g.*,

$${}_0P_s/{}_0P_g = 1 + {}_DP_1(\varepsilon_2 + 2)(3\delta - 1)d_2/M_1(\varepsilon_2 - 1) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where ${}_{\mathrm{D}}P_1$ is the distortion polarisation of the solute and M_1 its molecular weight. Six examples will show, however, that (3) acts in the right sense, but excessively :

	$3\delta - 1$.	${}_{\mathrm{O}}P_s/{}_{\mathrm{O}}P_g$ (calc.).	${}_{\mathrm{O}}P_s/{}_{\mathrm{O}}P_g$ (found).		$3\delta - 1$.	${}_{\mathrm{O}}P_s/{}_{\mathrm{O}}P_g$ (calc.).	${}_{\mathrm{O}}P_s/{}_{\mathrm{O}}P_g$ (found).
CH_3Cl	−0·274	0·78	0·82	Paraldehyde...	+0·764	1·75	1·69
CH_2Cl_2	−0·055	0·96	0·98	SO_2	−0·238	0·88	0·99
$CHCl_3$	+0·428	1·27	1·26	$C_6H_5{\cdot}NO_2$ ...	−0·409	0·65	0·87

If our " δ " is used in place of the " ξ " of the Ross–Sack equation,

$$\frac{\mu_s}{\mu_g} = \frac{3\varepsilon}{(\varepsilon + 2)}\,\frac{1 + (n^2_{\text{Eff.}} - 1)\delta}{\varepsilon + (n^2_{\text{Eff.}} - \varepsilon)\delta} \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

cited in a previous paper (*J.*, 1950, 283), the ratios indicated are :

	${}_{\mathrm{O}}P_s/{}_{\mathrm{O}}P_g$ (calc.).		${}_{\mathrm{O}}P_s/{}_{\mathrm{O}}P_g$ (calc.).
CH_3Cl	0·80	Paraldehyde	1·56
CH_2Cl_2	0·98	SO_2	0·81
$CHCl_3$	1·29	$C_6H_5{\cdot}NO_2$	0·81

Expressions Useful in Practice.—To the above attempts may be urged the objections : (*a*) that the ${}_{\mathrm{D}}P$ for a given substance is difficult to measure accurately (examples of this occur in the tables on p. 557; sometimes the A of the Debye equation can be obviously too small without the μ_{gas} value becoming grossly incorrect, *e.g.*, Ramaswamy, *Proc. Indian Acad. Sci.*, 1936, *A*, **4**, 108, gives for acetone $P = 6 + 53650/T$, whence $\mu = 2{\cdot}95$; yet $[R_L]_{\mathrm{D}}$ for this substance is *ca.* 16 c.c.) ; and (*b*) that knowledge of $n^2_{\text{Eff.}}$ implies the existence of experiments from which μ_{gas} should be calculable directly. Since our underlying motive, for reasons set out elsewhere (" Dipole Moments," Methuen, 1938, p. 52), is to search for an *a priori* method whereby μ_{gas} may be estimated from observations on solutions, we regard (*b*) as serious, and proceed therefore to show the measure of success to be achieved with the accessible quantity n_{D}^2, instead of $n^2_{\text{Eff.}}$, in equations (1)—(4).

Table IV summarises our computations for benzene ($n_{\mathrm{D}}^2 = 2{\cdot}2417$ at 25°) as solvent. It

TABLE IV.

							μ_{gas}, calc., *via*				
	B.	*C.*	x_2.	δ.	$\mu_{C_6H_6}$.	n_{D}^2.	(1).	(2).	(3).†	(4).	$\mu_{\text{gas, obs.}}$
CH_3Cl ...	*	*	−0·520	0·242	1·69	1·7510 (*a*)	1·89	1·76	1·86	1·92	1·86
CH_2Cl_2 ...	*	*	−0·103$_5$	0·315	1·55	2·0295	1·59	1·56	1·57	1·61	1·57
$CHCl_3$ ...	*	*	+0·602	0·476	1·13	2·0825	1·02	1·06	1·02	1·02	1·01
$CH_3{\cdot}CN$ ...	0·639	0·639	−0·592	0·223	3·11—3·51	1·800	3·49—3·94	3·28—3·70	3·62—4·08	3·58—4·04	3·94—3·98
$CH_3{\cdot}NO_2$	0·865	0·731	−0·466	0·254	3·02—3·13	1·9040	3·30—3·42	3·13—3·56	3·26—3·38	3·35—3·47	3·42
$CO(CH_3)_2$	1·270	0·738	−0·282	0·291	2·74	1·8400	2·95	2·79	2·89	2·96	2·85—3·02
Paraldehyde ...	*	*	+0·840	0·588	1·87	1·989	1·60	1·68	1·50	1·56	1·44
SO_2	*	*	−0·094	0·254	1·61	1·763 (*b*)	1·70	1·67	1·70	1·81	1·62
$N(CH_3)_3$ ...	1·74	1·74	+0·670	0·489	0·86	1·808	0·78	0·80	0·71	0·79	0·64
$C_6H_5{\cdot}CH_3$	*	*	−0·765	0·168	0·34	2·2320	0·37	0·37	0·48	0·40	0·37
C_6H_5Cl ...	*	*	−0·847	0·132	1·59	2·3180	1·74	1·76	2·23	1·93	1·73
$C_6H_5{\cdot}NO_2$	*	*	−0·684	0·197	3·95	2·4045	4·23	4·22	4·79	4·46	4·24
$C_6H_5{\cdot}CN$	0·693	0·353	−0·875	0·117	3·74—3·97	2·329	4·09—4·34	4·16—4·42	5·77—6·13	4·62—4·91	4·39

* See Table III. † Using $[R_L]_{\mathrm{D}}$ instead of ${}_{\mathrm{D}}P$. (*a*) Calc. from $[R_L]_{\mathrm{D}}$ *ex* Vogel's (*loc. cit.*) atomic constants. (*b*) *Ex* $[R_L]_{\mathrm{D}} = 9{\cdot}49$ (Nasini, *Gazzetta*, 1883, **18**, 296) and extrapolated density (Le Fèvre and Ross, *loc. cit.*).

Dipole-moment references additional to those beneath Table III : $CH_3{\cdot}CN$: $\mu_{C_6H_6} = 3{\cdot}11$ (Werner, *Z. physikal. Chem.*, 1929, *B*, **4**, 371), 3·51 (Eide and Hassel, *Chem. Ztg.*, 1930, **11**, 2234), 3·16 (Hunter and Partington, *J.*, 1932, 2812), 3·45 (Snoek, *Physikal. Z.*, 1934, **35**, 196), 3·51 (Lewis and Smyth, *J. Chem. Physics*, 1939, **7**, 1085) ; $\mu_{\text{gas}} = 3{\cdot}98$ (Ramaswamy, *loc. cit.*), 3·94 (Höjendahl, Thesis, 1928), 3·94 (Groves and Sugden, *J.*, 1937, 158). $CH_3{\cdot}NO_2$: $\mu_{C_6H_6}$ (see Faraday Soc. List), $\mu_{\text{gas}} = 3{\cdot}42$ (Smyth and McAlpine, *J. Amer. Chem. Soc.*, 1934, **56**, 1697). Acetone : $\mu_{C_6H_6} = 2{\cdot}74$ (see Faraday Soc. List) ; $\mu_{\text{gas}} = 2{\cdot}93$ to 3·02 (Stuart, *Z. Physik*, 1928, **51**, 490), 2·85 (Zahn, *Physikal. Z.*, 1932, **33**, 686). Trimethylamine : $\mu_{C_6H_6} = 0{\cdot}86$, $\mu_{\text{gas}} = 0{\cdot}64$ (Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374; cf. Brockway and Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036). Benzonitrile : ($\mu_{C_6H_6}$ see Faraday Soc. List), $\mu_{\text{gas}} = 4{\cdot}39$ (Groves and Sugden, *loc. cit.*).

will be noted that, by overall consideration, (1) and (2) seem preferable to (3) and (4) for the four aromatic molecules listed. In most cases (1) and (4) could give better results if n_γ were used instead of n_D, since n_γ is nearer to $n_{Eff.}$ than is n_D.

Variation of $\mu_{\text{Nitrobenzene}}$ *with Solvent.*—An empirical " rule," if of correct form, should also forecast the relative effects of different solvents upon a given solute. Table V shows the application of equations (1), (2), and (4), using n_D^2 instead of $n^2_{Eff.}$, to the figures conveniently tabulated for nitrobenzene in 12 solvents by Cleverdon and Smith (*Trans. Faraday Soc.*, 1949, **45**, 109) ($\mu_{gas} = 4{\cdot}24$).

TABLE V.

			${}_0P_s/{}_0P_g$, calc., *via* eqn. :			
Solvent.	ϵ_{25}.	$(n_D^2)_{25}$.	1.	2.	4.	${}_0P_s/{}_0P_g$, found.
n-Hexane	1·887	1·8847	0·94	0·91	0·87	0·91
Di*iso*amyl	1·976	1·9773	0·92	0·90	0·85	0·88
*cyclo*Hexane	2·016	2·0221	0·91	0·90	0·84	0·88
Decalin	2·162	2·16	0·89	0·89	0·81	0·86
Dioxan	2·204	2·0171	0·91	0·89	0·80	0·85
CCl_4	2·228	2·1656	0·89	0·88	0·80	0·86
p-Xylene	2·260	2·2317	0·87	0·88	0·79	0·85
C_6H_6	2·273	2·2417	0·87	0·88	0·79	0·87
CS_2	2·633	2·6360	0·79	0·86	0·71	0·75
Et_2O	4·250	1·8295	0·87	0·79	0·45	0·57
$CHCl_3$	4·722	2·0825	0·80	0·77	0·40	0·55
C_6H_5Cl	5·612	2·3180	0·72	0·75	0·32	0·34

For the nine non-polar solvents, all three relations predict drifts in the direction observed, and for this class (1) seems on the whole superior to (4). The latter, however, alone reflects the effects of the three polar media. Further, it should be repeated again that $n^2_{Eff.}$ properly enters (4), *not* n_D^2, which has been utilised only because for most substances it is a recorded (or easily determinable) datum.

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