358. *The Direct Calculation of True Dipole Moments from Measurements on Solutions or Pure Liquids.**

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An empirical relationship is presented whereby for a given molecule μ_{gas} may be obtained from $\mu_{solution}$ or μ_{liquid}. Comparisons made by application to a number of polar liquids, representative of different molecular shapes, show that the new equation is superior to others previously proposed.

A number of empirical equations, connecting apparent dipole moments obtained from solutions in benzene with the true values determined in the gaseous states, were recently reviewed by Angyal, Barclay, and Le Fèvre (*J.*, 1950, 3370). The most satisfactory seemed to be that—listed as (1) below—proposed earlier by Barclay and Le Fèvre (*J.*, 1950, 556). Unfortunately, however, its applicability did not extend beyond non-polar solvents. Attempts have accordingly been made to remedy this defect. As a result, a new expression can now be submitted, which, used wholly or in part, enables the ratios μ_{liquid}/μ_{gas} or $\mu_{solution}/\mu_{gas}$ to be calculated *a priori* more accurately than by other relationships previously recorded. In support of this claim, tests on the representative series of molecules used before (references above) will now be summarised.

* In this and subsequent papers on dipole moments from these laboratories, subscripts 1 and 2 will refer, respectively, to the solvent and solute. This is the reverse of the convention formerly adopted in our papers.—R. J. W. Le F.

Equations Examined.—In these, subscripts 1 and 2 indicate solvent and solute respectively, ε is the dielectric constant, d the density, and n the refractive index, e is the base of Napierian logarithms, and x^2 a quantity dependent on the shape of the dissolved molecule under consideration. Values of x^2 have been derived from scale-drawings incorporating Stuart's "Wirkungsradien" (*Z. physikal. Chem.*, 1935, *B*, **27**, 350); if A is the measurement along the axis of $\mu_{\text{resultant}}$ and C is the lesser of the other two dimensions perpendicular to A, then generally $x^2 = (C^2 - A^2)/(\text{greatest length})^2$. The ξ used by Ross and Sack (*Proc. Phys. Soc.*, 1950, **63**, 893) also reflects the molecular structure; it can be ascertained quickly from curves reproduced in the paper just cited.

The equations now to be considered are numbered for subsequent reference:

$$(1)\quad \frac{\mu^2_{\text{soln.}}}{\mu^2_{\text{gas}}} = 1 + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\left(\mathrm{e}^{x^2} - \frac{n_1^2}{n_2^2}\right)$$

$$(2)\quad \frac{\mu^2_{\text{soln.}}}{\mu^2_{\text{gas}}} = 1 + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\left[\mathrm{e}^{x^2} - (\mathrm{e} - \mathrm{e}^{x^2})^{3(n_1^2 - n_2^2)(1 - \mathrm{e}^{x^2})^2}\right]$$

$$(3)\quad \frac{\mu^2_{\text{soln.}}}{\mu^2_{\text{gas}}} = 1 + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\left[\mathrm{e}^{x^2} - (\mathrm{e} - \mathrm{e}^{x^2})^{3(n_1^2 - n_2^2)(1 - \mathrm{e}^{x^2})^2}\right] - \frac{1{\cdot}69\,\mathrm{e}^{x^2}(\varepsilon_1 - 1)(n_2^2 + 1)\,|\varepsilon_1 - n_2^2|}{\varepsilon_1^2 n_2^2(\mathrm{e}^{x^2} + 1)(\mathrm{e}^{M_2/d_2A_2B_2C_2})}$$

$$(4)\quad \frac{\mu_{\text{soln.}}}{\mu_{\text{gas}}} = \frac{3\varepsilon_1}{(\varepsilon_1 + 2)} \cdot \frac{1 + (n_2^2 - 1)\xi}{\varepsilon_1 + (n_2^2 - \varepsilon_1)\xi}$$

$$(5)\quad \frac{\mu^2_{\text{liq.}}}{\mu^2_{\text{gas}}} = 1 + \frac{\varepsilon - 1}{\varepsilon + 2}(\mathrm{e}^{x^2} - 1) - \frac{1{\cdot}69\,\mathrm{e}^{x^2}(\varepsilon - 1)(n^2 + 1)(\varepsilon - n^2)}{\varepsilon^2 n^2(\mathrm{e}^{x^2} + 1)(\varepsilon^{M/dABC})}$$

$$(6)\quad \frac{\mu^2_{\text{liq.}}}{\mu^2_{\text{gas}}} = \text{as No. (5) but with numerical constant} = 1{\cdot}70$$

$$(7)\quad \mu^2_{\text{gas}} = \frac{9kTM}{4\pi Nd} \cdot \frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2 + 2)^2}$$

Equation (1) was advanced by Barclay and Le Fèvre (*J.*, 1950, 556). Although this gave results in good agreement with experiment for many solutes, yet there were some (*e.g.*, paraldehyde, sulphur dioxide, and trimethylamine) where it was less satisfactory. We therefore sought a substitute for the term n_1^2/n_2^2 in (1). In this—and other empirical approaches underlying the present paper—we have been guided by intuitive guesses very similar to those set out before (*J.*, 1950, 3370). These we would now amend to read: (*a*) that x^2, being concerned with areas, may be a measure of hindrance to rotation, so that $\exp x^2$ (or perhaps $1 - \exp x^2$) may reflect the non-randomness of rotational modes about the greatest and least axis of length of the solute molecule, and (*b*) that a second term is needed having some relation to the exclusion from spherical distribution of the centres of the molecules surrounding the solute in the directions collinear and perpendicular to its resultant moment, and—in consequence—to the disturbance from isotropy of its polarisable solvent environment.

For the requirement of (*b*) the introduction of $(\mathrm{e} - \mathrm{e}^{x^2})$ seemed reasonable, since such a factor could express the degree of elongation of the molecule in a direction at right angles to the dipole axis. Because x^2 must (by its definitition) be less than unity, it followed that e would be the maximum value for $\exp x^2$. Thus for an imaginary plane structure (*i.e.*, one with negligible thickness), whose resultant dipole axis is perpendicular to the plane, $(\mathrm{e} - \mathrm{e}^{x^2})$ would be zero; its values for other extreme shapes were obvious: notably it could never become negative so that quantities such as:

$$(\mathrm{e} - \mathrm{e}^{x^2})^{9(\varepsilon_1 - n_2^2)(1 - \mathrm{e}^{x^2})^2/\varepsilon_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

or

$$(\mathrm{e} - \mathrm{e}^{x^2})^{3(n_1^2 - n_2^2)(1 - \mathrm{e}^{x^2})^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B)$$

would be entirely real.

(A) and (B) were the two most promising alternatives to n_1^2/n_2^2 found after many trials. When equations containing them were applied to the test substances in Table IV of the paper by Barclay and Le Fèvre (*loc. cit.*) both proved better than the original equation (1).

However, if used on solutions of nitrobenzene in several solvents (Cleverdon and Smith, *Trans. Faraday Soc.*, 1949, **45**, 109), an equation with (B) was superior to one with (A). Thus we selected equation (2) as the best replacement for (1).

Nevertheless, equation (2) was still limited in usefulness to cases where the solvent was non-polar. To make it general an extra term was accordingly devised. This addition clearly had to vanish if ε were unity (when $\mu_{soln.} = \mu_{gas}$), and to be zero or very small if the solvent were non-polar. These desiderata were met by utilising the factors $(\varepsilon - 1)$ and $(\varepsilon - n^2)$. Of many possible " third terms " tried, that shown in equation (3) was the most successful.

The full form of the new equation now proposed is (3); in application to pure liquids this becomes (5) or (6). For solutions in non-polar solvents the third term is small and equation (2) may be used successfully. In equations (1), (2), (3), and (5) refractive indexes for the Na_D line are employed. The change in the numerical constant from equation (5) to equation (6) is caused by taking, whenever available, $n^2_{eff.}$ instead of n^2_D in the latter [the " effective " refractive index is estimated by equating the distortion polarisation to $(n^2_{eff.} - 1)M/(n^2_{eff.} + 2)d_{liq.}$]. Equation (4) is due to Ross and Sack (*loc. cit.*); here also $n^2_{eff.}$ has been introduced as far as possible, but when it is unknown the procedure recommended by Ross and Sack has been followed and the n^2 corresponding to $1{\cdot}05[R_L]_D$ has been adopted. Equation (7) is Onsager's (*J. Amer. Chem. Soc.*, 1936, **58**, 1486); it is included now for comparison because Böttcher (*Physica*, 1939, **6**, 59) has already shown it to be fairly satisfactory for many polar substances. Here again $n^2_{eff.}$, rather than n^2_D, has been used if available.

Table 1 sets out the numerical data required for testing the equations. The apparent dipole moments shown under $\mu_{liq.}$ or $\mu_{C_6H_6}$ have been calculated from the differences between the total polarisations of the substances (as pure liquids or at infinite dilution in benzene) and the distortion polarisations recorded from measurements on gaseous dielectrics, except in those instances where gaps occur under $n^2_{eff.}$ in Table 1 when $[R_L]_D$ has of necessity replaced $_DP$ (for source references, see Barclay and Le Fèvre, *loc. cit.*; Angyal, Barclay, and Le Fèvre, *loc. cit.*). The values of ξ quoted to three figures are those estimated from the geometrical dimensions of the molecules by Ross and Sack (*loc. cit.*); the remainder have been derived from the corresponding lengths A, B, and C by the method described by these authors.

Table 2 shows the relative success with which the various equations will give μ_{gas} from $\mu_{C_6H_6}$ or $\mu_{liq.}$.

TABLE 1. *Numerical data required.*

Substance	M_2	d_4^{25}	$(n^2_D)^{25}$	$(n^2_{eff.})^{25}$	ε^{25}	$\mu_{liq.}$	$\mu_{C_6H_6}$	A	B	C	ξ
CH_3Cl	50·49	0·8785	1·751	1·929	9·68 [1]	1·19	1·69	5·27	3·80	3·80	0·267
CH_2Cl_2	84·94	1·3175	2·0295	2·349	8·93 [1]	$1{\cdot}14_5$	1·55	4·10	6·10	3·60	0·38
$CHCl_3$	119·39	1·4790	2·0825	2·368	4·724 [1]	$0{\cdot}97_5$	1·13	4·10	6·50	6·50	0·364
$CH_3{\cdot}CN$	41·05	0·7772	1·800	—	36·7 [2]	1·36	3·11—3·51	5·95	3·80	3·80	0·22
$CH_3{\cdot}NO_2$ ...	61·04	1·1362	1·9040	—	27·75 [3]	$1{\cdot}32_5$	3·02—3·13	5·20	4·50	3·80	0·27
$COMe_2$	58·08	0·7863	1·8400	—	19·11 [4]	1·52	2·74	5·15	6·54	3·80	0·315
Paraldehyde	132·16	0·9896	1·989	2·499	12·93 [5]	$1{\cdot}74_5$	1·87	3·80	9·50	9·50	0·59
SO_2	64·06	1·369	1·763	1·911	13·20 [6]	1·14	1·61	3·44	5·00	3·08	0·354
NMe_3	59·11	0·6267	1·808	—	2·44 [7]	0·72	0·86	3·82	6·55	6·55	0·47
$Ph{\cdot}CH_3$	92·13	0·8657	2·2320	—	2·366 [8]	0·34	0·34	8·25	6·05	3·80	0·20
PhCl	112·56	1·1011	2·3180	2·554	5·612 [3]	1·15	1·59	8·08	6·05	3·16	0·181
$Ph{\cdot}NO_2$	123·11	1·1986	2·4045	2·633	34·89 [9]	1·69	3·95	8·00	6·05	2·90	0·236
Ph·CN	103·12	1·0013	2·329	—	25·20 [8]	1·71	3·74—3·97	8·95	6·05	2·90	0·15

References : n^2_D and $n^2_{eff.}$ values : Barclay and Le Fèvre (*J.*, 1950, 556).

ε values : [1] Barclay and Le Fèvre (*loc. cit.*). [2] Le Fèvre and Le Fèvre (*J.*, 1935, 1747). [3] Ulich and Nespital (*Z. physikal. Chem.*, 1932, *B*, **16**, 221). [4] Åkerlof (*J. Amer. Chem. Soc.*, 1932, **54**, 4125). [5] Le Fèvre, Mulley, and Smythe (*J.*, 1950, 290). [6] Le Fèvre and Ross (*J.*, 1950, 283). [7] Le Fèvre and Russell (*Trans. Faraday Soc.*, 1947, **43**, 374). [8] Le Fèvre (*ibid.*, 1938, **34**, 1127). [9] Drude (*Z. physikal. Chem.*, 1897, **23**, 309).

TABLE 2. *Calculations of* μ_{gas} *by equations* (1)—(7).

Substance	By (1)	By (2)	By (3)	By (4)	By (5)	By (6)	By (7)	μ_g (found)
CH_3Cl	1·89	1·85	1·92	1·85	1·96	1·91	1·76	1·86
CH_2Cl_2	1·59	1·57	1·60	1·48	1·58	1·55	1·57	1·57
$CHCl_3$	1·02	1·01	1·03	1·09	0·98	0·94	1·08	1·01
$CH_3{\cdot}CN$	3·49—3·94	3·49—3·94	3·60—4·06	3·58—4·04	3·96	3·98	3·58	3·94—3·98
$CH_3{\cdot}NO_2$ ...	3·30—3·42	3·27—3·39	3·36—3·49	3·29—3·41	3·17	3·19	3·04	3·42
$COMe_2$	2·95	2·87	2·98	2·88	3·04	3·04	2·98	2·85—3·02
Paraldehyde	1·60	1·48	1·52	1·50	1·65	1·59	2·72	1·44
SO_2	1·70	1·63	1·69	1·64	1·59	1·58	1·90	1·62
NMe_3	0·78	$0{\cdot}74_5$	0·77	0·80	0·67	0·67	0·74	0·64
$C_6H_5{\cdot}CH_3$ ...	0·37	0·37	0·37	$0{\cdot}38_5$	0·37	0·37	0·34	0·37
C_6H_5Cl	1·74	1·72	1·73	1·81	1·67	1·64	1·34	1·73
$C_6H_5{\cdot}NO_2$ ...	4·29	4·25	4·27	4·21	4·24	4·24	3·96	4·24
$C_6H_5{\cdot}CN$ ...	4·09—4·34	4·07—4·32	4·07—4·32	4·43—4·70	4·31	4·33	3·58	4·39

Finally, Table 3 presents the ratios of ${}_{\rm O}P_{\rm soln.}/{}_{\rm O}P_{\rm gas}$ (*i.e.*, $\mu^2_{\rm soln.}/\mu^2_{\rm gas}$) forecast by equations (1), (2), (3), and (4) for one solute, nitrobenzene, in a range of polar and non-polar solvents, the properties of which have been conveniently listed by Cleverdon and Smith (*loc. cit.*).

TABLE 3. *Calculations of* ${}_{\rm O}P_{\rm soln.}/{}_{\rm O}P_{\rm gas}$ *for solutions of nitrobenzene by equations* (1)—(4).

Solvent	$E_{25°}{}^{\rm solvent}$	$(n^2_{\rm D})_{25}{}^{\rm solvent}$	By (1)	By (2)	By (3)	By (4)	${}_{\rm O}P_{\rm s}/{}_{\rm O}P_{\rm g}$ (found)
n-Hexane	1·887	1·8847	0·92	0·95	0·90	0·95	0·91
Di*iso*amyl	1·976	1·9973	0·90	0·93	0·89	0·94	0·88
*cyclo*Hexane	2·016	2·0221	0·89	0·92	0·89	0·93	0·88
Decalin	2·162	2·16	0·87	0·89	0·87	0·90	0·86
Dioxan	2·204	2·0171	0·88	0·91	0·90	0·89	0·85
CCl_4	2·228	2·1656	0·86	0·88	0·87	0·89	0·86
p-Xylene	2·260	2·2317	0·85	0·87	0·86	0·88	0·85
C_6H_6	2·273	2·2417	0·85	0·87	0·85	0·88	0·87
CS_2	2·633	2·6360	0·76	0·72	0·70	0·81	0·75
Et_2O	4·250	1·8295	0·82	0·90	0·78	0·53	0·57
$CHCl_3$	4·724	2·0825	0·75	0·81	0·68	0·48	0·55
C_6H_5Cl	5·612	2·3180	0·67	0·69	0·47	0·39	0·34
$C_6H_5{\cdot}NO_2$	34·89	2·4045	0·47	0·47	0·16	0·020	0·16

Conclusions.—From Table 2 it may be seen that values of $\mu_{\rm gas}$ predicted by equations (2) and (3) agree in the main with the observed values within differences not in excess of the experimental errors. The latter are of the order of 2%, 1% in the value of $\mu_{C_6H_6}$, and 1% in the observed value of $\mu_{\rm gas}$. Moreover, both (2) and (3) give figures for $\mu_{\rm gas}$ which are, on the whole, more correct than those computed by either (1) (the Barclay–Le Fèvre equation) or (4) (the Ross–Sack equation).

Equation (5)—and also (6), which by utilising $n^2_{\rm eff.}$ instead of $n^2_{\rm D}$ gives slightly better results than (5)—forecasts values for μ_g (from observations solely on the pure liquids) which are essentially of a similar accuracy to those predicted by the equation of Barclay and Le Fèvre on benzene solutions. Equation (5) certainly yields results which are superior to those derived by (7) (the Onsager equation).

From the evidence of Tables 2 and 3, it appears (*a*) that by use of data obtained from solutions in benzene, the most probable value for μ_g is obtained by application of equation (2), and (*b*) by use of data obtained from pure liquids, the most satisfactory equation to apply is (5). Equation (6), utilising $n^2_{\rm eff.}$, will not be a form useful in practice because a knowledge of $n^2_{\rm eff.}$ implies the existence of "gas" measurements, which would themselves permit a direct calculation of μ_g.

We conclude by referring to the case of water, since among the 33 substances for which Böttcher (*loc. cit.*) estimated $\mu_{\rm gas}$ *via* the Onsager formula, this gave the worst result, *viz.*, $(\mu_{\rm gas})_{\rm calc.} = 3{\cdot}0$—$3{\cdot}1$D, in contrast to the observed figure of 1·8 D. In our recalculations the following data are used : $\varepsilon^{25} = 78{\cdot}42$ (Åkerlof and Oshrey, *J. Amer. Chem. Soc.*, 1950, **72**, 2844), $(M/d)^{25} = 18{\cdot}07$ c.c. (I.C.T., III, 25), distortion polarisation = 4·03 c.c. (Stranathan, *Phys. Review*, 1935, **48**, 538), $(n^2_{\rm D})^{25} = 1{\cdot}7756$ (I.C.T., VII, 13), $(n^2_{\rm eff.})^{25} =$

1·86; and $A : B : C = 2{\cdot}73 : 3{\cdot}35 : 2{\cdot}44$ (Angyal and Le Fèvre, *J.*, 1952, 1651); accordingly ${}_{\mathrm{T}}P_{\mathrm{liq.}} = 17{\cdot}40$ c.c., whence $\mu_{\mathrm{liq.}} = 0{\cdot}808$ D.

Appropriate substitutions in equations (5), (6), and (7) yield values for $(\mu_{\mathrm{gas}})_{\mathrm{calc.}}$ of 1·37, 1·40, and 3·10 D, respectively, against 1·84 D by direct measurement (cf. Angyal and Le Fèvre, *loc. cit.*). Böttcher (*loc. cit.*) quotes also ε, d, and n_{∞}^2 for water at 100°; these by equations (5) or (7) lead to $(\mu_{\mathrm{gas}})_{\mathrm{calc.}} = 1{\cdot}5$ or 3·0 D. It is seen that the predictions by (7) are some three times as high as those by (5) are low. Considering that between the H_2O molecules of water there are directed interactions of an exceptional kind (possibly producing pseudo-crystalline domains) not operative within organic liquids (for references, see Wells, "Structural Inorganic Chemistry," Oxford, 2nd Edn., 1950, pp. 427—432), we may claim that the applicability of equation (5) is not unsatisfactory. It is interesting that the abnormalities of physical properties shown by water do not occur with hydrogen sulphide, the dielectric constant of which according to Eversheim (*Ann. Physik*, 1904, **13**, 492) is 5·4 at 25° (measured under pressure). This value in conjunction with other quantities cited by Angyal and Le Fèvre (*loc. cit.*) yielded by equation (6) $(\mu_{\mathrm{gas}})_{\mathrm{calc.}} = 0{\cdot}92$ D. The experimental figure is 0·89 D. Equation (7) with the same data gives $(\mu_{\mathrm{gas}})_{\mathrm{calc.}} = 0{\cdot}95$ D.

[*Added, April 8th,* 1952.] Since the above paper was submitted, Everard, Kuman, and Sutton (*J.*, 1951, 2807) have redetermined $\mu_{C_6H_6}$ for $C_6H_5{\cdot}CN$ at 25° as 4·05 D. By using this figure in lieu of the 3·74—3·97 D given in Table 1, the following values for μ_{gas} are obtained:

By (1)	By (2)	By (3)	By (4)
4·43	4·41	4·41	4·80

The forecasts by (2) and (3) are seen to agree well with $\mu_{\mathrm{gas(obs.)}}$, *viz.*, 4·39 D (cf. Table 2).

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