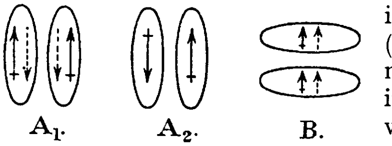
411. *Relation between Molecular Orientation Polarisation of Substances in the Liquid, Dissolved, and Gaseous States.*

By (Mrs.) Catherine G. Le Fèvre and Raymond J. W. Le Fèvre.

One of us recently suggested (this vol., p. 773) that the relation ${}_0P_1/{}_0P_2 = K(\varepsilon_2 + 2)/(\varepsilon_1 + 2)$ held between the orientation polarisations (${}_0P_1$ and ${}_0P_2$) developed by a molecule when surrounded by media of dielectric constants ε_1 and ε_2 respectively. With the aid of some new measurements now recorded and data collected from the literature we have examined its application to (*a*) 30 pairs of solutions, (*b*) 38 solutions and the solutes in the vapour state, (*c*) 58 solutions and the (liquid) solutes in bulk, and (*d*) 27 substances in the pure liquid and gaseous conditions. Only for class (*a*) is K found to be *ca.* unity; it is larger than 1·5 in 10 cases in class (*b*), in 24 cases in class (*c*), and in 15 cases in class (*d*). It is thus obvious that the rule as stated above has no general applicability.

Discussion.—Throughout comparisons (*b*), (*c*), and (*d*) the most striking of the substances for which K is large are water, phenol, chloroform, ether, hydrogen cyanide, and certain alcohols, esters, and amines (see tables, p. 1750). In some of the instances the results may be attributed to association in the liquid state, for it is evident that a large K will result when the orientation polarisation in the medium of higher dielectric constant is not reduced sufficiently relatively to the value which this factor has in the medium of lower ε; as pointed out by Bury and Jenkins (J., 1934, 688), an increase of total polarisation—and therefore, if the distortion polarisation is independent of the state (liquid, dissolved, or gaseous), a parallel exaltation of ${}_0P$—could be caused by association. Water, the alcohols, and phenol are strongly associated (Sidgwick, "Electronic Theory of Valency," Oxford, 1927, p. 134; Martin and Collie, J., 1932, 2658; Martin, *Trans. Faraday Soc.*, 1934, **30**, 759; Bernal and Fowler, *J. Chem. Physics*, 1933, **1**, 515; Hennings, *Z. physikal. Chem.*, 1935, *B*, **28**, 267), and accordingly an explanation is available for these compounds. It is also possible that the high value of K for certain esters is due to the use of calculated values of ${}_0P_{\text{vap.}}$, which, owing to the intramolecular rotation of dipolar groups, may be smaller than the true figures for the temperature at which comparison is made.

There remain several substances for which the orientation polarisation in the liquid or the dissolved state is of the same order as, or even greater than, that in the vapour, in contradiction to the general belief that polarisation and moment of a compound are always higher in the gaseous form than in solution. Such behaviour can be qualitatively understood when the mutual influences of the molecules involved are considered in conjunction with their shapes. Molecules may be roughly divided into two classes: A, where the principle moment lies along, and B, where it is at 90° to, the axis of maximum polarisability, which is in general the longest axis. Such molecules are taken broadly as prolate and oblate spheroids respectively. In the liquid state, under the influence of intermolecular attractive forces, the molecules may tend to form aggregates having a certain structure (phenomenon of cybotaxis; Stewart, *Physical Rev.*, 1930, **35**, 291, 726). Because, in the formation of these complexes, dipolar are outweighed by van der Waals forces (as in *iso*pentane and ethyl ether; *idem, ibid.*), such cybotactic units will in the first case contain either or both of the arrangements shown in A_1 or A_2—the more stable disposition being that in which the maximum number of atoms are in contact. Type B cannot be imagined as aggregating except in the manner shown. A unit such as A_2 will be effectively almost non-polar; in addition, as we proceed from a gas at low pressure to a pure liquid, intermolecular distance diminishes and mutual induction of dipoles therefore becomes stronger. Thus the net effect should be, since $\mu \propto \sqrt{{}_0P}$, that molecules of type A should show a diminished, and molecules of type B an increased, orientation polarisation in the liquid state compared with the gaseous. (By similar reasoning, the different effects of solvent molecules of type A or B on a solute of either kind at infinite dilution can be predicted: a solvent of type A will be more effective in apparently reducing the orientation polarisation of a solute of its own type than in apparently increasing the corresponding polarisation of one of type B; again, a solvent of type B will cause smaller diminution of polarisation of an A-type solute than it will an increase of polarisation of a solute of the second kind.)



It is therefore evident that the correct expression for the ratio ${}_0P_{\text{liq.}}/{}_0P_{\text{gas}}$ will not be simply $1-(\varepsilon-1)/(\varepsilon+2)$, as required by the formula previously given, but rather $1-(\varepsilon-1)/(\varepsilon+2)f$, where f may be positive or negative and will relate to the geometry and polarisability of the molecules under consideration.

The following is an attempt to evaluate f. On the assumptions that the molecules of a fluid are optically and electrically anisotropic, and that the polarisation field acting on a molecule in a dense fluid varies with its orientation relatively to the external field, Raman and Krishnan (*Proc. Roy. Soc.*, 1927, *A*, **117**, 589) have deduced the volume polarisation of a substance as

$$\frac{\varepsilon-1}{\varepsilon+2}=\nu\left[\frac{4\pi}{3}\frac{\alpha_1+\alpha_2+\alpha_3}{3}+\frac{\varepsilon-1}{\varepsilon+2}\Psi\right]+\frac{\nu}{3kT}\left[\frac{4\pi\mu^2}{3}+\frac{\varepsilon-1}{\varepsilon+2}\Theta\right]$$

Rewriting this to apply to the total molecular polarisation of a liquid, we have

$$P=\frac{\varepsilon-1}{\varepsilon+2}\cdot\frac{M}{d}=\frac{4\pi N}{3}\cdot\frac{\alpha_1+\alpha_2+\alpha_3}{3}+\frac{\varepsilon-1}{\varepsilon+2}\Psi N+\frac{N}{3kT}\left[\frac{4\pi\mu^2}{3}+\frac{\varepsilon-1}{\varepsilon+2}\Theta\right]$$

in which M is the molecular weight, d the density, and N Avogadro's number. Now Müller's experiments (*Physikal. Z.*, 1933, **34**, 689) have shown that for a given substance in solution the orientation polarisation alone appears to be measurably affected by the nature of the medium; changes in the total polarisation consequent upon changes in the state of aggregation can therefore be related to changes in the ${}_0P$ factor; if this be taken as the difference between the total polarisation and the molecular refractivity, we have

$${}_0P=\left[\frac{\varepsilon-1}{\varepsilon+2}-\frac{n_D^2-1}{n_D^2+2}\cdot\frac{M}{d}\right]=\frac{N}{3kT}\left[\frac{4\pi\mu^2}{3}+\frac{\varepsilon-1}{\varepsilon+2}\cdot\Theta\right]$$

Division throughout by the true ${}_0P$ (*i.e.*, the ${}_0P_{\text{gas}}=4\pi N\mu^2/9kT$) gives the desired relation

$${}_0P_{\text{liq.}}/{}_0P_{\text{gas}}=1+3\Theta(\varepsilon-1)/(\varepsilon+2)4\pi\mu^2$$

For solutions, where f_1 and f_2 are the mol.-fractions of the solute and solvent respectively and other symbols are as before

$${}_0P_1f_1+{}_0P_2f_2=\left[\frac{\varepsilon-1}{\varepsilon+2}-\frac{n_D^2-1}{n_D^2+2}\right]\frac{M_1f_1+M_2f_2}{d}=$$

$$\frac{N}{3kT}\left[f_1\left\{\frac{4\pi\mu_1^2}{3}+\frac{\varepsilon-1}{\varepsilon+2}\cdot\Theta_1\right\}+f_2\left\{\frac{4\pi\mu_2^2}{3}+\frac{\varepsilon-1}{\varepsilon+2}\cdot\Theta_2\right\}\right]$$

but at infinite dilution (when $f_1=0$) ${}_0P_1$ is given by an expression similar to that for the pure liquid except that ε is now the *D.C.* of the solvent. The ratio of the two ${}_0P$ values is therefore of the same form.

Two points of interest arise from this result.

(1) The sign of Θ is opposite to that of the Kerr constant, which for the majority (class A) of compounds is positive (Briegleb and Wolf, *Fortschr. Chem.*, 1931, **21**, Pt. 3). As a consequence, Θ is negative and the ratio ${}_0P_{\text{liq.}}/{}_0P_{\text{gas}}$ therefore fractional. For such cases the observed polarisations for solution or for liquid are less than those for vapour—a relative order of magnitude which has been realised experimentally by several workers

who have thus been led to conclude that it is general. On the basis of the expression now proposed, there should exist a minority of compounds *which should exhibit larger polarisations in the dissolved or liquid than in the gaseous condition*; such substances should be those having *negative* Kerr constants (*i.e.*, shape of type B) and therefore positive Θ values. Relevant evidence is sparse, but it is significant that, among the available results, chloroform, ether, and certain amines display the predicted variations of polarisation. The first is a particularly satisfactory example in this connexion because, not only has its dielectric constant in the liquid state been carefully determined at the ordinary temperature (Ball, J., 1930, 570), so that its apparent orientation polarisation at this temperature can be calculated with certainty, but also its Kerr constant B (*ca.* -3×10^{-7}) is one of the largest negative values listed by Briegleb and Wolf (*loc. cit.*). It will be noted that its ${}_{0}P$ in the liquid (bulk) state is 23·7 c.c., in contrast to the *highest* recorded value in the vapour state (from the measurements of Sircar, *Indian J. Physics*, 1928, **3**, 197) which is only 22·8 c.c. The results of Sänger (*Physikal. Z.*, 1926, **27**, 556) would indicate an even greater disparity in the same direction. The contrast with substances of class A, *e.g.*, ethyl bromide or chlorobenzene (${}_{0}P_{\text{liq.}}/{}_{0}P_{\text{vap.}} = 37/91$ and $31/59$ respectively) is unmistakable. Bromoform also has a negative Kerr constant and should, in the present respect, duplicate the behaviour of chloroform, but the one (unconfirmed) determination in the gas phase (Braunmühl, *ibid.*, 1927, **28**, 141) is much too high for this to be true. We note, however, (*a*) that in the dipole-moment measurements made on *solutions* of chloroform, bromoform, and iodoform (see *Trans. Faraday Soc.*, 1934, Appendix, for references) the results for the second compound lie *between* those for the first and the third, so that by analogy there should not be the great difference reported in the vapour data; and (*b*) that the total polarisation of bromoform as a *pure liquid* (*ca.* 47 c.c., see p. 1750) is of the same order as the polarisation (48—51 c.c.) found by other workers for infinitely dilute solutions in carbon disulphide, benzene, etc.

(2) In many cases Θ can be considered as of the order $-4\pi\mu^2/3$; substitution for Θ in the above equation then gives ${}_{0}P_{\text{liq.}}/{}_{0}P_{\text{gas}} = 1 + (1 - \varepsilon)/(\varepsilon + 2) = 3/(\varepsilon + 2)$, which is identical with the purely empirical result discussed and illustrated previously, and from which (by relation through the ${}_{0}P_{\text{gas}}$) the expression set out at the beginning of this paper is at once derivable. The degree of correctness of this simplification for some of the applications made in the present inquiry can vary from case to case; calculations from the collected data have shown that by no means in all instances does the ratio between the experimental values of Θ and $4\pi\mu^2/3$ approach -1. Goss (J., 1934, 697) states that this equality "is unlikely, and has not so far been found to exist except where $\mu = 0$; indeed it is evident that at the critical point Θ vanishes, while μ retains its usual value." Thus, one obvious deficiency underlying the empirical rule is evident.

Data.—In the following tables are given the data for the compounds discussed above, figures for a few other cases having been included for comparison. Because the empirical rule was under test, we have shown values for ${}_{0}P$, but since these have been taken throughout as the difference between total polarisation and the molecular refractivity for sodium light, the data now collected serve to illustrate how two definite types of molecules exist, in one of which the total polarisation in the pure state is of the same order as, and in the other of which it is considerably less than, the total polarisation in the infinitely dilute (non-polar solvents) and/or gaseous states.

In the preparation of the tables, a difficulty lay in the fact that most dielectric-constant measurements on substances as vapours have been carried out at temperatures considerably above those at which the available related observations for the liquid or dissolved states have been made. In the previous paper ${}_{0}P$ data for four substances were extrapolated graphically back to room temperature for comparison with results on solutions. These extrapolations were inaccurate, and we have therefore thought it better to calculate the ${}_{0}P$ at the lower temperatures from the recorded dipole moment—deduced in most cases from the temperature dependence of the polarisation over the higher temperature range. We have ${}_{0}P = 4\pi N\mu^2/9kT = \mu^2/0{\cdot}01273^2T$ c.c. Such a treatment is justifiable for those molecules in which no rotation of dipolar groups occurs and for which, therefore, the moment should be temperature-invariant.

The dielectric constants and densities marked with an asterisk were obtained experimentally by use of methods detailed in our previous papers. The headings in the tables have their usual significance.

Comparison of Molecular Orientation Polarisation Values for the Dissolved and the Vapour State.

	T.	S_1.	ϵ_1.	${}_TP_1$.	$[R_L]_D$.	${}_OP_1$.	$\mu_{vap.}$.	${}_OP_2$.	*K*.
MeI	25°	C_6H_6	2·2725	72	19·3	52·7	1·66	57·1	1·32
EtI	25	C_6H_6	2·2725	86	24·3	61·7	2·0	82·8	1·06
$CHCl_3$	25	C_6H_6	2·2725	47·5	21·4	26·1	1·05	22·8	1·63
	25	CCl_4	2·227	49·8	21·4	28·4	1·05	22·8	1·76
	20	C_6H_{14} †	1·912	51·0	21·4	29·6	1·05	23·2	1·66
PhCl	25	C_6H_6	2·2725	82	31·1	50·9	1·69	59·1	1·23
PhMe	25	CCl_4	2·227	23·7	31·1	2·6	0·35	2·5	1·44
$Me{\cdot}CO_2Me$	25	C_6H_6	2·2725	84	18·1	65·9	1·67	57·8	1·63
$H{\cdot}CO_2Et$	25	C_6H_6	2·2725	96·3	18·0	78·3	1·92	76·3	1·46
$Me{\cdot}CO_2Et$	25	CCl_4	2·227	87·0	22·3	64·7	1·76	64·1	1·42
$Me{\cdot}CO_2C_5H_{11}$	25	C_6H_6	2·2725	109·0	36·2	72·8	1·70	59·8	1·73
$COMe_2$	25	CCl_4	2·227	170	16·2	153·8	2·84	167·0	1·30
$COCl_2$	0	CCl_4	2·2748	44·5 *	17·1	27·4 *	1·18	31·6	1·23
Et_2O	25	CCl_4	2·227	56·0	22·2	33·8	1·14	26·9	1·77
	25	C_6H_6	2·2725	54·5	22·2	32·3	1·14	26·9	1·71
H_2O	25	$C_4H_8O_2$ ‡	2·306	82·0	3·7	78·3	1·79	66·4	1·69
MeOH	20	C_6H_6	2·280	65·2	8·2	57·0	1·68	59·4	1·37
EtOH	25	CCl_4	2·227	73·5	12·8	60·7	1·69	58·9	1·45
HCN	20	C_6H_6	2·280	154	6·5	147·5	2·88	174·7	1·20
PhCN	20	C_6H_6	2·280	340	31·6	308·4	4·39	405·9	1·08
$NHEt_2$	25	C_6H_6	2·2725	54	24·2	29·8	0·94	18·3	2·32
NEt_3	25	C_6H_6	2·2725	51	33·7	17·3	0·82	13·9	1·77
$MeNO_2$	25	C_6H_6	2·2725	219	12·5	206·5	3·78	295·9	0·99
$EtNO_2$	20	C_6H_6	2·280	232	17·0	215·0	4·03	342·1	0·90

† Hexane. ‡ Dioxan.

Comparison of Molecular Orientation Polarisation Values for the Solute in Bulk and in Solution.

S_1.	*T*.	ϵ_1.	d_1.	${}_TP_1$.	$[R_L]_D$.	${}_OP_1$.	S_2.	ϵ_2.	${}_TP_2$.	${}_OP_2$.	*K*.
MeI	25°	6·533*	2·2463*	40·99	19·3	21·7	C_6H_6	2·2725	72	52·7	0·82
EtI	25	7·244*	1·9187*	54·9	24·3	30·6	C_6H_6	2·2725	86	61·7	1·07
$CHCl_3$	25	4·724	1·4681	45·08	21·4	23·7	C_6H_6	2·2725	47·5	26·1	1·43
PhCl	25	5·610	1·1010	61·9	31·1	30·8	C_6H_6	2·2725	82·0	50·9	1·08
PhBr	25	5·397*	1·4879*	62·7	34·0	28·7	C_6H_6	2·2725	82·0	48·0	1·04
o-$C_6H_4Cl_2$	20	7·50	1·3048	77·1	36·0	41·1	C_6H_6	2·280	145·5	109·5	0·83
PhMe	25	2·378	0·8543	33·9	31·1	2·8	CCl_4	2·227	33·7	2·6	1·12
$H{\cdot}CO_2Et$	25	7·16*	0·9161*	54·3	18·0	36·3	C_6H_6	2·2725	96·3	78·3	0·99
$Me{\cdot}CO_2C_5H_{11}$	25	4·73*	0·8664*	74·2	36·2	38·0	C_6H_6	2·2725	109	72·8	0·82
$Me{\cdot}CO_2Me$	25	6·680*	0·9255*	52·3	18·1	34·2	C_6H_6	2·2725	84	65·9	1·05
$Me{\cdot}CO_2Et$	25	6·030*	0·8938*	61·7	22·3	39·4	CCl_4	2·227	87·0	64·7	1·16
COMePh	25	17·39	1·0237	99·1	36·3	62·8	C_6H_6	2·2725	214·5	178·2	1·60
$COCl_2$	0	4·724	1·414	38·4	17·1	21·3	CCl_4	2·2748	48·7*	27·4*	1·23
Et_2O	25	4·362	0·7079	55·2	22·2	33·0	C_6H_6	2·2725	54·5	32·3	1·52
H_2O	25	79·45	0·9971	17·4	3·7	13·7	$C_4H_8O_2$	2·306	82	78·3	3·31
MeOH	20	31·2	0·7915	36·8	8·2	28·6	C_6H_6	2·280	65·2	57·0	3·86
EtOH	25	24·69	0·7852	52·0	12·8	39·2	CCl_4	2·227	73·5	60·7	4·08
n-PrOH	20	22·2	0·8035	65·4	17·5	47·9	C_6H_6	2·280	82·7	65·2	4·15
sec.-BuOH	25	*ca.* 14	0·7987	75·3	22·2	53·1	C_6H_6	2·2725	89	66·8	*ca.* 3
iso-AmOH	25	14·0	0·8110	88·2	26·8	61·4	CCl_4	2·227	86	59·2	3·93
tert.-AmOH	18	11·58	0·8136	84·27	26·8	57·5	C_6H_6	2·241	85·2	58·4	3·15
$C_6H_5{\cdot}OH$ [3]	70	9·161	1·0307	66·7	31·0	35·7	C_6H_6	2·188	70·1	39·1	2·43
$CH_2Ph{\cdot}OH$	20	13·0	1·0420	82·9	32·4	50·5	$C_{10}H_{18}$	2·16	103·0	70·6	2·58
$C_6H_{12}O$ §	25	15·0	0·9435	87·3	28·9	58·4	C_6H_6	2·2725	105	46·6	4·99
PhCN	25	25·19	1·0006	91·6	31·6	60	C_6H_6	2·2725	338·5	306·9	1·24
$NHEt_2$	25	4·169	0·7007	53·5	24·2	29·3	C_6H_6	2·2725	54	29·8	1·42
NEt_3	25	*ca.* 3·1	0·7236	57·5	33·7	23·8	C_6H_6	2·2725	51	17·3	1·64
$Me_2N{\cdot}NO$	20	54	1·0061	69·61	19	50·6	C_6H_6	2·280	355·6	336	1·97
$MeNO_2$	20	27·75	1·1362	48·3	12·5	35·8	C_6H_6	2·280	205	192·5	1·29
$EtNO_2$	20	*ca.* 30	1·0430	65·2	17·0	48·2	C_6H_6	2·280	232	215·0	1·67
m-$NO_2{\cdot}C_6H_4Me$	20	23·8	1·1575	104·6	37·4	67·2	C_6H_6	2·280	406	368·6	1·10
$CHBr_3$	25	4·398*	2·8750*	46·7	30·2	16·5	C_6H_6	2·273	51	20·8	1·19
							CS_2	2·64	48	17·8	*ca.* 1·3

§ *cyclo*Hexanol.

Comparison of $_0$P *Values for Substances in the Liquid and the Gaseous State.*

S_1.	T.	ϵ_1.	$d^{t°}_{4°}$.	$[R_L]_D$.	$_0P_1$.	$\mu_{vap.}$.	$_0P_2$.	K.
MeI	25°	6·533*	2·2463*	19·3	21·7	1·66	57·1	1·08
EtBr	25	9·06*	1·4283*	19·1	36·5	2·09	90·5	1·49
EtI	25	7·244*	1·9187*	24·3	30·6	2·0	82·8	1·14
PhMe	18	2·347	0·8657	31·1	1·8	0·35	2·6	1·0
$CHCl_3$	25	4·724	1·4681	21·4	23·7	1·05	22·8	2·33
Et_2O	20	4·368	0·7135	22·2	32·7	1·14	27·4	2·53
$COCl_2$	0	4·724	1·414	17·4	21·4	1·18	31·5	1·52
Me_2CO	25	20·87	0·7863	16·2	47·9	2·84	167·0	2·19
Me·CHO	20	14·8	0·7799	11·6	30·5	2·69	152·4	1·12
Me·COCl	20	15·9	1·1051	16·9	42·2	2·68	151·3	1·66
PhCl	25	5·612 [1]	1·1011	31·1	30·8	1·69 [2]	59·1	1·32
$H{\cdot}CO_2Et$	14·5	9·1	0·9189	18·0	22·8	1·92	79·1	1·07
$H{\cdot}CO_2C_5H_{11}$	25	6·49*	0·8721*	31·6	23·1	1·90	76·3	0·86
$Me{\cdot}CO_2Me$	25	6·680*	0·9255*	18·1	34·2	1·67	57·8	1·71
$Me{\cdot}CO_2Et$	20	6·11	0·9005	22·3	39·3	1·76	65·2	1·63
$Me{\cdot}CO_2C_5H_{11}$	25	4·73*	0·8664*	36·2	38·0	1·70	59·8	1·43
H_2O	25	79·45	0·9971	3·7	13·7	1·79	66·35	5·61
MeOH	20	31·2	0·7915	8·2	28·4	1·68	59·4	5·29
EtOH	25	24·69	0·7952	12·8	39·2	1·686	58·9	5·92
NH_3	−33	22	0·675	5·6	14·3	1·48	56·3	2·03
HCN	0	96	0·7115	6·5	30·3	2·88	187·5	5·28
PhCN	25	25·19 [1]	1·0006	31·6	60·0	4·39 [2]	399·1	1·36
NMe_3	4	2·95	0·67	19·7	15·0	0·82	15·0	1·65
$NHEt_2$	21	3·58	0·7050	24·2	23·7	0·94	18·5	2·38
NEt_3	21	3·15	0·7280	33·7	24·2	0·82	14·1	2·38
$MeNO_2$	20	27·75	1·1362	12·5	35·8	3·78	300·9	1·18
$EtNO_2$	20	*ca.* 30	1·0430	17·0	48·2	4·03	342·1	1·5

References.—The above data are collected from the following sources: *Trans. Faraday Soc.*, 1934, Appendix; Landolt–Börnstein–Roth, "Tabellen"; International Critical Tables; Beilstein; Sugden, J., 1933, 772 [1]; Sugden and Groves, J., 1934, 1094 [2]; Martin, *Nature*, 1935, **135**, 909 [3].

UNIVERSITY COLLEGE (UNIVERSITY OF LONDON). [*Received, June 19th*, 1935.]