to 1.0 molar. The transference number varies from about 0.47 to 0.30 over this range.

2. Several equations purporting to express the transference number as a function of the con-

centration and the problem of extrapolation of transference numbers to infinite dilution are discussed.

Polarization and Dielectric Constant of Liquids

BY JEFFRIES WYMAN, JR.

There is much evidence that the dielectric constant is a linear function of the polarization per unit volume in the case of the more polar liquids for which the Clausius–Mosotti relationship ceases to hold. This appears to be almost the only conceivable interpretation of the strikingly simple behavior of a variety of strongly polar molecules in solvents of high dielectric constant.[1] It is in accord with the temperature variation of the dielectric constant of polar liquids, and the change of dielectric constant with density, under pressure, at constant temperature (see below). If we suppose the linear function to approximate direct proportionality, it offers a ready explanation of such a simple empirical relationship as that submitted by Girard,[2] according to which for water and the aliphatic alcohols the product of molecular weight times the dielectric constant is nearly constant; for in these cases the electric moments and consequently the molecular polarizations are all about the same, and therefore the polarizations per cc. should be inversely proportional to the molecular volumes or, roughly, to the molecular weights.[3] Onsager, in the following paper in THIS JOURNAL, develops a theoretical argument for a linear relation between dielectric constant and polarization in strongly polar media.

The problem of determining the two constants of this inferred linear relationship between dielectric constant and polarization is of course of great interest and the present paper is an attempt to deal with it from a purely empirical point of view.[4] There are of course no cases of polar

liquids in which we have exact independent knowledge of the polarization with which to correlate the dielectric constant. We may, however, calculate ideal or hypothetical values of the polarizations per unit volume for such liquids by making use of the values of the electric moments and molar polarizations obtained from measurements on the vapor or on dilute solutions in non-polar solvents and by taking account of the density. Clearly, such ideal, calculated values of the polarization per unit volume cannot be supposed in general to be realized more than approximately, but, nevertheless, apart from special cases of strongly associated liquids such as those forming hydrogen bonds, they may be expected to be fairly representative of the actual values. We may then try the effect of comparing these calculated values of the polarization with the observed values of the dielectric constant, to see whether or not the linear relation shows up. If it does, there is justification of our procedure of making use of the calculated values of the polarization and we may then proceed to determine the magnitude of the two constants. This in fact is what has been done.

By reference to the section of the "International Critical Tables" (Vol. VI) devoted to the dielectric constant of liquids and to the recent extensive table of electric moments and polarizations given in the *Transactions of the Faraday Society*,[5] it was possible to pick out about 140 cases of liquids with a dielectric constant greater than 5 and for which the electric moments and polarizations had been determined. In most of these the dielectric constant is pretty well known, although in some, accompanied in Table I below by a question mark, it has been measured only at very high frequencies, several times 10[8] cycles per second, and the values may be too low, the more so in the case of the larger molecules, owing to anomalous dispersion. On the other hand the

(1) See J. Wyman, THIS JOURNAL, **56**, 536 (1934).

(2) P. Girard, *Trans. Faraday Soc.*, **30**, 763 (1934).

(3) As a matter of fact Cohn has pointed out that Girard's relationship is improved if we multiply the dielectric constant in each case not by the molecular weight but by the molecular volume. E. J. Cohn, "Annual Review of Biochemistry," Annual Review of Biochemistry, Ltd., Stanford University P. O., California, Vol. IV, 1935, p. 100.

(4) An attempted derivation of the relation based on a modification of the underlying assumptions of the classical theory with regard to the internal field has been suggested but appears far too special.[1]

(5) *Trans. Faraday Soc.*, **30** (1934).

values of the polarizations are much less certain, showing in some cases a twofold variation or more. This appears to be due in part to differences in the conditions under which the measurements were made and in part to experimental discrepancies. From these data were calculated the ideal values of the polarization per cc. for the liquids for comparison with the dielectric constant.

TABLE I

Name	ε		p		ε + 1/8.5	
Water	78.54		4.24		9.34	
Prussic acid	95	116	3.98		11.3	11.9
Formic acid	62		1.08		7.39	
Acetic acid	7.1		0.43	0.96	0.96	
Ethyl formate	8.6		1.21		1.13	
Propyl formate	9.1		1.05		1.19	
Isobutyl formate	8.		0.93		1.06	
Amyl formate	7.7		.78		1.02	
Methyl acetate	7.3		1.03		0.98	
Ethyl acetate	6.4		0.78	1.11	.85	
Propyl acetate	6.3		.82	0.94	.86	
n-Butyl acetate	5.1		.80		.72	
Isobutyl acetate	5.6		.81		.77	
Phenyl acetate	5.3		.68	.77	.75	
Benzyl acetate	5.1		.77		.71	
Ethyl acetoacetate	15.9?		1.87		1.99	
Methyl propionate	5.5?		0.84	.93	0.75	
Ethyl propionate	5.7		.77	.87	.79	
Methyl butyrate	5.6?		.83		.78	
Ethyl butyrate	5.2		.75		.73	
Diethyl oxalate	8.2?		1.18		1.08	
Diethyl malonate	7.9	8.4	1.12		1.05	1.25
Methyl salicylate	9.0?		1.32		1.17	
Ethyl salicylate	8.6		1.55		1.13	
Ethyl cinnamate	6.6		0.95		0.90	
Methyl benzoate	6.9		.87		.93	
Ethyl benzoate	6.2		1.03	.82	.85	
Methyl nitrate	23.9		2.93		2.90	
Ethyl nitrate	19.7		2.4		2.41	
Propyl nitrate	14.2?		2.12		1.79	
Acetonitrile	38.8		4.1	5.21	4.65	
Propionitrile	27.7		3.54	4.37	3.37	
Butyronitrile	20.7?		3.13		2.55	
Benzonitrile	26.5		2.93	3.32	3.23	
Benzyl cyanide	18.3		2.32	2.58	2.27	
o-Tolunitrile	18.8?		2.94		2.23	
Phenyl isocyanate	5.7?	8.9?	1.42	1.32	0.79	1.17
Methyl n-thiocyanate	35.9?		4.2		4.31	
Methyl isothiocyanate	19.7?		3.24		2.42	
Ethyl n-thiocyanate	29.6		3.48		3.59	
Ethyl isothiocyanate	19.7		2.94		2.41	
Allyl isothiocyanate	17.5?		2.65		2.16	
Phenyl isothiocyanate	10.7?		1.77	2.02	1.37	
Ethyl mercaptan	8.0?		0.81		1.04	
Dimethyl sulfide	6.3?		.83		0.85	
Diethyl sulfide	7.2?		.77		.99	
Acetyl chloride	15.9		2.38		1.98	
Ethylidine chloride	10.9		1.15		1.39	
Ethylene chloride	10.5		0.63	1.12	1.34	
Propyl chloride	7.7?		1.02	1.18	1.02	
Allyl chloride	8.2		1.27		1.06	
Isoamyl chloride	6.4?		0.91		0.87	
t-Amyl chloride	9.5		1.04		1.24	
Benzal chloride	6.9?		1.02		0.93	
Benzyl chloride	7.0		0.94		.94	
Chloroacetone	29.8?		1.58		3.6	
Ethylene chlorohydrin	25.8		1.42	1.63	3.14	
Epichlorohydrin	22.9		1.14		2.79	
Chlorobenzene	5.9		0.74	0.85	0.81	
o-Chlorophenol	6.3	8.2	.69		0.86	1.08
m-Chloroaniline	13.3		2.02	1.76	1.68	
m-Chlorotoluene	5.4		0.81	0.96	0.75	
p-Chlorotoluene	6.2		.89	.97	.85	
Dichloroethylene-*cis*	9.22		1.08	1.28	1.18	
Chloroform	5.05		0.59	0.65	0.70	
Benzotrichloride	7.4?	6.4?	.98		.98	0.67
Ethyl bromide	9.4		1.14	1.50	1.2	
Allyl bromide	7.0		1.13	1.01	0.81	
Propyl bromide	7.2		1.0	1.33	.95	
t-Butyl bromide	8.6?		1.10	1.18	1.10	
Isoamyl bromide	6.1		.90		0.83	
Tertiary amyl bromide	9.1?		1.10		1.19	
Bromobenzene	5.4		0.78	0.90	0.75	
m-Bromoaniline	13?		.173		1.65	
o-Bromotoluene	5.3?		.69		0.74	
1-Bromonaphthalene	5.1		.73		.73	
Ethylene bromide	4.8	6.3	.56	.88	.69	.98
1,2,3-Tribromopropane	6.4?		.74		.85	
Methyl iodide	7.1		1.20		.95	
Ethyl iodide	7.4		1.12		.99	
t-Butyl iodide	6.3?		1.11		.85	
Isoamyl iodide	5.6?		0.83		.78	
t-Amyl iodide	6.9?		1.20		.93	
Methylene iodide	5.5		0.73	1.55	.76	
Nitromethane	39.4		3.82	5.81	4.73	
Nitroethane	30.0?		3.26	4.76	3.63	
Nitrobenzene	36.1		3.05	3.74	4.36	
o-Nitrotoluene	27.4		2.78		3.34	
m-Nitrotoluene	23.8		3.43		2.92	
Methylamine	<10.5		0.68	1.02	<1.35	
Ethylamine	6.3?		.75	0.51	0.85	
Diethylamine	3.7	5.5	.40	.53	.55	.76
Ethylenediamine	16?		1.49		2.0	
Nitrosodimethylamine	54		4.79		6.46	
Formamide	>84		5.84		>10	
Methyl alcohol	33.7		1.26	1.78	4.07	
Ethyl alcohol	25.07		1.28	1.49	3.05	
Propyl alcohol	21.8		1.03		2.66	
Isopropyl alcohol	26		1.15	0.98	3.15	
n-Butyl alcohol	17.8		0.85	.99	2.20	
s-Butyl alcohol	15.5		.95		1.93	
t-Butyl alcohol	11.4		.87		1.45	
Amyl alcohol	15.8		.81		1.97	
Isoamyl alcohol	15.3		0.79	0.95	1.92	
Dimethylethylcarbinol	11.7		.82	.94	1.49	
Heptyl alcohol	6.7		.69		0.91	
Cyclohexanol	15		.88	1.01	1.88	
Benzyl alcohol	13		.96		1.65	
Glycol	41.2		1.17	2.29	4.95	
Propionaldehyde	18.9	14.4	1.92		2.31	1.81
Butyraldehyde	13.4		1.69		1.68	
Benzaldehyde	18		1.87		2.23	
Furfuraldehyde	41.9		3.58		5.04	
Paraldehyde	14.5		0.89		1.82	
Acetone	21.5		2.32	2.62	2.60	
Methyl ethyl ketone	18.5		2.06		2.25	
Methyl propyl ketone	16.8		1.75		2.09	
Mesityl oxide	15.4		1.70		1.93	
Cyclohexanone	18.2		1.75	2.15	2.26	
Methyl t-butyl ketone	12.6		1.59		1.60	
n-Dipropyl ketone	12.6		1.37		1.60	
Methyl hexyl ketone	10.4		1.10		1.34	
Acetophenone	18.6		1.83		2.42	
Menthone	9.6?		1.30	1.37	1.24	
Benzophenone	13.3		1.38	1.47	1.68	
Acetyl acetone	23.1	25.9	2.12	1.87	2.83	3.16
Diethyl ketone	17.3		1.75		2.15	
Acetic anhydride	20.5		1.59	1.99	2.50	
o-Cresol	5.8		0.74		0.80	
m-Cresol	5		.84		.71	
p-Cresol	5.6		.87		.78	
Pyridine	12.5		1.46	1.64	1.59	
Aniline	7.25		0.91		0.97	
Methylaniline	6		.86		.82	
o-Toluidine	6.4		.84		.87	
m-Toluidine	6.0		.75		.82	
Quinoline	9.		1.20		1.17	
Phenylhydrazine	7.2		1.04		0.96	
Methyl phenylhydrazine, *asym.*	7.3?		0.95		.98	
Azoxyphenetole	6.8		0.84		.92	

The results of the comparison are given in Table I and are shown graphically in Fig. 1, where the dielectric constant ϵ is plotted against p, the ideal value of the polarization per cc. The full curve at the left, which corresponds to the Clausius–Mosotti relation $p = (\epsilon - 1)/(\epsilon + 2)$
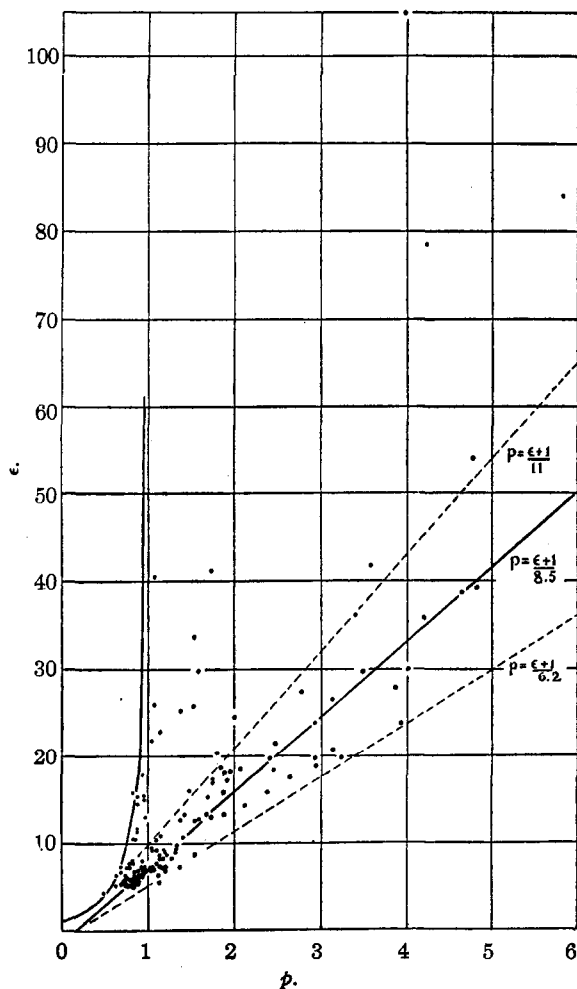

Fig. 1.

and is asymptotic to $p = 1$, is included for reference. It may be seen from the figure that the majority of the points are consistent with a linear increase of the dielectric constant with p described by the expression

$$p = (\epsilon + 1)/8.5 \qquad (1)$$

corresponding to the full straight line. The figures 1 and 8.5 are of course only estimates (compare the dotted straight lines corresponding to a different choice of coördinates). The same thing is seen rather better by comparing columns 3 and 4 in Table I. For the most part the agreement between the two columns is fairly good.

On the other hand, hydrocyanic acid, formic acid, formamide, water, most of the alcohols, and a few other substances have dielectric constants much greater than corresponds to this empirical relation. Most of these will be recognized as liquids which are generally supposed to be strongly associated due to the formation of hydrogen bonds. Kumler has pointed out[6] that such liquids show abnormalities in regard to boiling point and dielctric constant, and it is not surprising that they should be exceptional in the present case. It would simply mean that the actual polarizations for the liquid state are quite different from the ideal values calculated from the moments taken from the literature.

In Fig. 2, values of the polarization per gram, calculated from the relation $p' = (\epsilon + 1)/8.5\rho$, ρ denoting density, are plotted against the reciprocal of the absolute temperature for a number of liquids for which data are available. The result should in each case be a straight line whose intercept on the axis of ordinates gives the sum of the atomic and electronic polarizations per cc. and whose slope gives the electric moment in accordance with the relation

$$\mu = 0.0127 \sqrt{M \frac{dp'}{d1/T}} \times 10^{-18} \text{e. s. u.} \qquad (2)$$

where M is the molecular weight. The straight lines of the figure are in each case so drawn as to fit the data and at the same time give the correct intercept on the axis of ordinates (in accordance with optical or other data). Except for acetone and nitrobenzene, the nine liquids are in moderately good accordance with expectations. If we calculate the moments from the slopes of the lines as drawn we obtain the following values

Substance	μ cal. $\times 10^{18}$	μ literature $\times 10^{18}$
Chloroform	1.22	1.10–1.15
o-Toluidine	1.63	1.44–1.65
Ethylene chloride	1.96	1.12–1.75
Pyridine	2.24	2.11–2.21
Benzyl cyanide	3.27	3.47–3.56
Acetone	2.85	2.61–2.97
Nitrobenzene	4.29	3.66–4.08
Nitromethane	3.40	3.02–3.78
Water	2.77	1.88

The moments calculated in this way are in good agreement with the values from the literature, except for water, which, as was pointed out above, is in all probability much associated.

In the case of the ten liquids studied under

(6) Kumler, THIS JOURNAL, **57**, 600 (1935).

pressure by Danforth,[7] the variation of dielectric constant with density is very nearly linear and in accordance with the empirical relation presented above, except for the two non-polar liquids, pentane and carbon disulfide, and for ethyl ether and glycerol. For the others the quantity $(\epsilon + 1)/8.5\,\rho$ varies over the whole range by no more than about 3% at most, in some cases much less. This is probably almost within the experimental error. For ether and glycerol the variation is somewhat more than 10%.
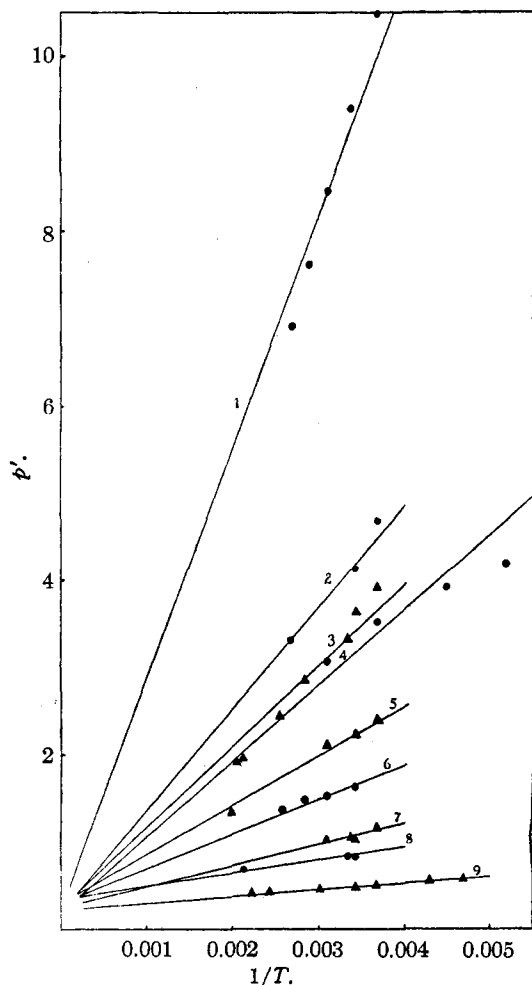
Fig. 2.—1, Water; 2, nitromethane; 3, nitrobenzene; 4, acetone; 5, benzyl cyanide; 6, pyridine; 7, ethylene chloride; 8, o-toluidine; 9, chloroform.

It is of interest to consider the meaning of the empirical relation just presented in terms of the internal field F. On the basis of the classical theory

$$F = E + (4/3)\pi I = E + pF \qquad (3)$$

(7) Danforth, Phys. Rev., 38, 1224 (1931).

where E is the electric intensity and I the electric moment per unit volume. Hence

$$F/E = 1/(1 - p) \qquad (4)$$

On the other hand, if the dielectric constant be linear in p

$$\epsilon = ap + b \qquad (5)$$

where a and b are constants.

But from the fundamental theory

$$E(\epsilon - 1) = 4\pi I = 3pF \qquad (6)$$

whence

$$\frac{F}{E} = \frac{1}{3}\left(a + \frac{b - 1}{p}\right) \qquad (7)$$

The graphs of these two expressions are shown in Fig. 3 (b is taken as -1 and a as 8.5 in accordance with what we have found). Both curves are
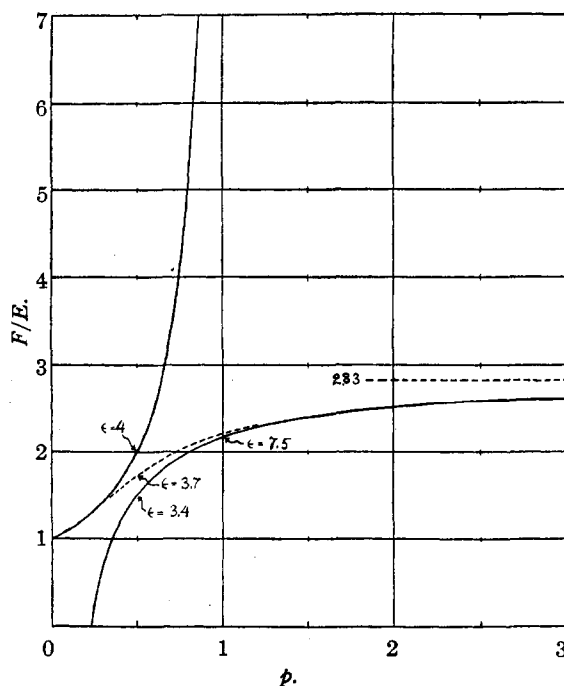

Fig. 3.—F/E, the ratio of the internal field to the electric intensity, as a function of the polarization per cc. (a) in accordance with the Clausius-Mosotti relation (left-hand full curve), (b) on the basis of the empirical equation 1 (right-hand full curve). The right-hand curve approaches $F/E = 2.83$ asymptotically.

hyperbolas and we must suppose that the transition from one to the other occurs somewhat as shown by the dotted line, between $p = 0.3$ and $p = 1.3$ or between $\epsilon \cong 3$ and $\epsilon \cong 10$. It is of course always possible to calculate p from ϵ if F/E is known by means of the relation

$$p = \frac{E}{F}\frac{(\epsilon - 1)}{3} \qquad (8)$$

which is general.[8]

It is of interest also to consider the moment of glycine calculated from the relation given above. On the basis of the observations in water at 25° the polarization is 3060 cc. and the moment 12.2 × 10⁻¹⁸ e. s. u. This would correspond to a dipole distance of 2.55 Å. Recent calculations

(8) It may also be worth mentioning the implication of any linear relation between polarization and dielectric constant in the case of anomalous dispersion. According to the Debye treatment, based on the Clausius–Mosotti equation, the absorption index reaches a maximum at a frequency given by

$$2\pi\nu = \frac{1}{\tau}\frac{\epsilon_0 + 2}{\epsilon_1 + 2}\sqrt{\frac{\epsilon_1}{\epsilon_0}}$$

where τ is the relaxation time, ϵ_0 the dielectric constant at low frequencies and ϵ_1 the dielectric constant at frequencies above the region of dispersion. On the other hand, if the Clausius–Mosotti relation be replaced by any linear relation, the same for both ϵ_0 and ϵ_1, this expression reduces to

$$2\pi\nu = \frac{1}{\tau}\sqrt{\frac{\epsilon_1}{\epsilon_0}}$$

(see Debye, "Polar Molecules," Chemical Catalog Co., New York City, 1929).

based on a model proposed by Kirkwood[9] give a value of 3.17 Å. for this distance, or a moment of 15.2 × 10⁻¹⁸ e. s. u.

Summary

A correlation of the dielectric constant of a large number of polar liquids with assumed values of the polarization per cc. calculated by ascribing to the molecules in the liquid state the electric moments obtained from measurements on the vapor and on dilute solutions in non-polar solvents suggests an empirical relation between polarization and dielectric constant: $p = (\epsilon + 1)/8.5$. This relation is fairly satisfactory when applied to the variation of dielectric constant with temperature and with pressure in the case of a number of polar liquids for which data are available. The meaning of such a relation in terms of the internal field in the liquid is discussed.

(9) J. G. Kirkwood, J. Chem. Phys., 2, 351 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Electric Moments of Molecules in Liquids

BY LARS ONSAGER

In its original, still generally accepted, form Debye's dipole theory[1] accounts quantitatively for the dielectric properties of gases, and qualitatively for those of liquids. In view of the extensive and consistent evidence the fundamental hypothesis of molecules possessing permanent electric moments is not in doubt.

When the theory is applied to liquids (and solids), the interaction of a molecule with its environment must be taken into account. For this purpose, Debye borrowed the theory of "internal field" which was developed by Clausius and Mosotti, one that has been applied universally and with remarkable success to aggregates of polarizable molecules. According to this theory, the "internal field" which polarizes a molecule in the dielectric equals the external field, augmented by $(4\pi/3)$ times the electric moment induced in a unit volume of the dielectric. Debye's implicit assumption is that the force-couple which tends to orient an electrically asymmetric molecule in a polarized dielectric is proportional to the same "internal field." This assumption leads to

(1) P. Debye, Physik. Z., 13, 97 (1912).

Debye's well-known formula for the dielectric constant (ϵ)

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3}\sum N\left(\alpha + \frac{\mu^2}{3kT}\right) \qquad (1)$$

where α denotes the polarizability of the molecule, μ its permanent electric moment, kT the energy of thermal agitation, and N the concentration (molecules/cc.), and the summation is extended over all species of molecules present.

Formula (1) can be tested in a number of ways. When only a single species of molecules is present, one can compute the dipole moment μ, with the aid of Eq. 1, from the observed dielectric constant, and the test is whether the dipole moments computed for the liquid state or in liquid mixtures with a non-polar component remain the same as that observed in the vapor state. A more thorough analysis of the problem shows that one should not expect the dipole moment to remain quite constant, because all real molecules have a positive polarizability α. The polarization of the dielectric in the electric field of the molecule itself gives rise to a reaction field, which tends to enhance the electrical asymmetry.