contraction of density globes is a linear function of the pressure difference to which the bulb is submitted.

Brussels, Belgium

[Contribution from the Department of Chemistry of Princeton University]

THE DIELECTRIC POLARIZATION OF LIQUIDS. V. THE ATOMIC POLARIZATION

By C. P. Smyth

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In previous communications[1] the total polarization, P, of a substance has been divided into three parts, P_E, the electronic polarization, P_A, the atomic polarization and P_M, the orientation polarization due to the permanent moments of the molecules. This series of papers is concerned mainly with the conclusions to be derived from the values of P_M for liquids, but, as P_M is commonly obtained from the total polarization, P, by subtracting P_E and P_A, it is evident that no treatment of the problem can be complete without consideration of the two latter quantities. As P_E is discussed in another paper,[2] the present treatment will be confined to the significance of P_A, especially in its relation to molecular structure.

The polarization is commonly obtained from dielectric constants measured at frequencies up to 3,000,000 cycles or wave lengths down to 100 meters. For much higher frequencies or shorter wave lengths, the orientation of the dipoles in an applied field often becomes less and P_M diminishes, being negligible for frequencies in the infra-red region. In the range of visible light the frequency of the alternating field is so great that, for the most part, the electrons only are affected by it, the polarization being P_E alone. P_E is thus determined as the molar refraction for visible light. In the absence of anomalous dispersion, the small variation of P_E with wave length may be calculated by a simple dispersion formula such as that of Cauchy or Sellmeier[3] and the value of P_E obtained for the comparatively low frequencies, virtually infinite wave length, at which the dielectric constant is measured. However, the presence of oscillators with frequencies in the infra-red region causes anomalous dispersion and, in consequence, polarizations greater than the values obtained by extrapolation with the simple formulas. Actually these oscillators are displaced in the electric field, forming electric doublets and thus contributing to the polarization of the medium. Although some of these oscillators may be electrons, the majority are atoms, ions or radicals and, for this reason, their contribution

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[1] (a) Smyth, Morgan and Boyce, This Journal, **50**, 1536 (1928); (b) Smyth and Morgan, *ibid.*, **50**, 1547 (1928); (c) Smyth and Stoops, *ibid.*, **50**, 1883 (1928).

[2] Smyth, Engel and Wilson, This Journal, **51**, 1736 (1929).

[3] See Errera, "Polarisation Diélectrique," Les Presses Universitaires de France, Paris, 1928; also Smyth, *Phil. Mag.*, **45**, 849 (1923).

to the total polarization is termed the "atomic polarization" and designated by P_A. P_A is usually so small and difficult to determine with accuracy[4] that any attempt to subdivide it into the contributions of atoms, radicals, ions, etc., seems rather futile in the present state of our knowledge.

Since $P = P_E + P_A + P_M$ and P and P_E can always be determined, P_A is obtained by difference when P_M is known. P_M can be calculated from the temperature variation of the polarization of a gas or of dilute solutions, from which the polarization at infinite dilution can be obtained. From measurements of dielectric constant[1b,5] in the solid state at temperatures sufficiently low and frequencies sufficiently high to prevent all orientation of the dipoles in the alternating field, a value can be obtained for the polarization from which P_M is eliminated, so that P_A can be obtained by subtracting P_E.[4,6]

Errera[3] has assembled a considerable number of values of P_A from the literature, calculating several not previously known. These are regrouped in Table I together with new values calculated by the writer and others taken from the literature. The values of the electric moment of the molecule, μ, are shown in order that it may be ascertained whether there is any connection between μ and P_A. For the gases, $P_E + P_A$ is determined from the temperature variation of the dielectric constant and P_A then obtained by subtracting P_E. A similar method is employed for $CHCl_3$, C_4H_9Cl, C_2H_5Br, C_4H_9Br, C_2H_5I and C_6H_5Cl, the substances being measured in solution. For the liquids without moment, P_A is determined by subtracting P_E from P, and for the majority of those with moment by subtracting P_E for the liquid from P for the solid. A small error in these calculations is caused by the fact that the value of P_E for the liquid may often be slightly different from those for the solid and the vapor, which are usually unknown. In the case of liquids for which μ is given as 0, it is sometimes impossible to distinguish between a very small value of μ and 0, which means that P_M may have a small finite value, instead of 0. This would, of course, cause a small error in P_A. As, in general, P_A is determined as a small difference between relatively large quantities, all the errors of experiment and method are accumulated in its values. A number of values obtainable from the literature, in particular several for vapors, are obviously so much in error that they are excluded from Table I, and the decimal places for many have been rounded off. The literature sources from which the values of μ and P_A have been obtained are indicated by the numbers following their values. Where no number is given after P_A, the value has been calculated by the writer from the data used in obtaining μ

[4] *Cf.* Ebert, *Z. physik. Chem.*, **113,** 1 (1924).

[5] Debye, "Handbuch der Radiologie (Marx)," Akademische Verlagsgesellschaft m. b. H., Leipzig, **1925,** Vol. VI, p. 619.

[6] Errera, *Bull. sci. acad. roy. Belg.*, [5] **12,** 327 (1926).

and the refractive indices in Landolt-Börnstein or "International Critical Tables."

TABLE I

ELECTRIC MOMENTS AND ATOMIC POLARIZATIONS

	$\mu \times 10^{18}$	P_A
HCl	1.03 (1)	1.2 (2)
HBr	0.79 (1)	0.2 (2)
HI	.38 (1)	.7 (2)
A	0 (3)	.1 (2)
N_2	0 (5)	0 (6)
NH_3	1.44 (4)	.5 (2)
O_2	0 (5)	0 (5)
CO	0.10 (6)	.1 (2)
CO_2	0 (7, 6)	0 (2)
CS_2	0.33 (6)	.9 (vapor)
SO_2	1.61 (4)	.9 (2)
CH_4	0 (8)	.8 (2)
C_2H_6	0 (9)	0 (2)
C_2H_4	0 (9)	.4 (2)
C_2H_2	0 (9)	1.9 (2)
n-C_6H_{14}	0 (10)	0.65 (10)
n-C_7H_{18}	0 (11)	.88 (11)
2,2-Dimethylpentane	0 (11)	.91 (11)
2,4-Dimethylpentane	0 (11)	.96 (11)
2-Methylhexane	0 (11)	.92 (11)
3-Methylhexane	0 (11)	.83 (11)
2,2,3-Trimethylbutane	0 (11)	.78 (11)
3,3-Dimethylpentane	0 (11)	.90 (11)
2,3-Dimethylpentane	0 (11)	.88 (11)
3-Ethylpentane	0 (11)	.76 (11)
2,2,4-Trimethylpentane	0 (11)	1.09 (11)
CH_3Cl	1.59 (24)	(4)
CH_2Cl_2	1.59 (8)	2.4
$CHCl_3$	1.05 (10)	6.2 (vapor) (12) 5.8 (liquid) (10) 6.0 (solid) (13) 3.0 (solid) (2)
CCl_4	0 (8)	3.0 (2)
$TiCl_4$	0 (14)	5.7 (2)
$SnCl_4$	0 (14)	10.6 (2)
C_2H_5Cl	1.98 (24)	(5)
C_4H_9Cl	1.89 (15)	5.4
C_2H_5Br	1.86 (10)	(11) (10)
CH_3I	1.62 (25)	(25) (vapor)
C_2H_5I	1.66 (16, 25)	(28) (vapor) 12 (liquid)
$CH_2{=}CCl_2$	1.18 (2)	2.8 (2)
cis-$CHCl{=}CHCl$	1.85 (2)	3.4 (2)
trans-$CHCl{=}CHCl$	0 (2)	3.2 (2)
cis-$CHCl{=}CHBr$	1.54 (2)	3.6 (2)
trans-$CHCl{=}CHBr$	0 (2)	3.5 (2)

TABLE I (*Concluded*)

	$\mu \times 10^{18}$	P_A
cis-CHBr=CHBr	1.22 (2)	5.3 (2)
trans-CHBr=CHBr	0 (2)	4.8 (2)
cis-CHI=CHI	0.75 (2)	8.0 (2)
trans-CHI=CHI	0 (2)	5.6 (2)
Cyclohexane	0 (2)	0.74 (2)
Benzene	0 (17)	1.5 (2)
p-$C_6H_4(CH_3)_2$	0 (18, 19)	2.1 (2)
$C_6H_5NO_2$	3.9 (19)	8 (2)
C_6H_5Cl	1.52 (10)	3.3 (10)
o-$C_6H_4Cl_2$	2.25 (20)	5.8 (2)
m-$C_6H_4Cl_2$	1.48 (20)	4.4 (2)
p-$C_6H_4Cl_2$	0 (2, 20)	3 (2)
o-$C_6H_4Br_2$	1.67 (2)	3.8 (2)
m-$C_6H_4Br_2$	1.22 (2)	2.2 (2)
o-$C_6H_4I_2$	1.63 (2)	1.3 (2)
H_2O	1.79 (21)	5.3 (vapor) (2) 2.0 (solid) (2)
H_2S	0.93 (6)	<1.5
CH_3OH	1.64 (22)	4.9 (13)
C_2H_5OH	1.74 (22)	5 (2)
$(CH_3)_2O$	1.29 (21)	2.2 (21)
$(C_2H_5)_2O$	1.14 (21)	3.9 (21)
$(CH_3)_2SO_4$	3.27 (2)	33.4 (2)
Cane sugar	......	24.8 (23)
Citric acid	......	28.4 (23)

(1) Zahn, *Phys. Rev.*, **24,** 400 (1924); (2) Errera, "Polarisation Diélectrique," Les Presses Universitaires de France, Paris, **1928**; (3) von Braunmühl, *Physik. Z.*, **28,** 141 (1928); (4) Zahn, *Phys. Rev.*, **27,** 455 (1927); (5) Calculated from (6); (6) Zahn and Miles, *Phys. Rev.*, **32,** 497 (1928); (7) Stuart, *Z. Physik*, **47,** 457 (1928); (8) Sänger, *Physik. Z.*, **27,** 556 (1926); (9) Smyth and Zahn, THIS JOURNAL, **47,** 2501 (1925); (10) Smyth and Morgan, *ibid.*, **50,** 1547 (1928); (11) Smyth and Stoops, *ibid.*, **50,** 1883 (1928); (12) Calculated by Errera from (8); (13) Ebert, *Z. physik. Chem.*, **113,** 1 (1924); (14) Calculated from results of Errera; (15) Unpublished work of Mr. H. E. Rogers; (16) Unpublished work of Dr. W. N. Stoops; (17) Sänger, *Physik. Z.*, **27,** 165 (1926); (18) Smyth, THIS JOURNAL, **46,** 2151 (1924); (19) Williams, *Physik. Z.*, **29,** 174 (1928); (20) Smyth, Morgan and Boyce, THIS JOURNAL, **50,** 1536 (1928); (21) Stuart, *Z. Physik*, **51,** 490 (1928); (22) Stranathan, *Phys. Rev.*, **31,** 653 (1928); (23) Ebert, *Z. physik. Chem.*, **114,** 430 (1925); (24) Sircar, *Indian J. Phys.*, **12,** 197 (1928); (25) Mahanti and Sen Gupta, *ibid.*, **12,** 191 (1928).

Van Vleck[7] has calculated from infra-red intensity measurements that the vibrational polarization, which is P_A, is negligibly small for HCl, HBr, CO, CO_2, NH_3 and CH_4 and attributes to experimental error the difference found between the extrapolated refraction and the total induced polarization. He indicates, however, that this does not necessarily mean that, in other kinds of molecules, there may not be infra-red vibrational or electronic bands of such large amplitude, high effective charge or low frequency

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[7] Van Vleck, *Phys. Rev.*, **30,** 31 (1927).

as to cause a difference between the extrapolated refraction and the total induced polarization, thereby giving significant values for P_A. There appears to be reasonable doubt as to whether the value 1.2 of P_A for hydrogen chloride can be due in the main to experimental error, and this is true also of the value 0.9 for sulfur dioxide and especially of the value 1.9 for acetylene. However, the values for argon, nitrogen, oxygen and ethane are virtually 0, and that for ethylene, 0.37, differs from 0 by no more than the probable error. At this point one may inquire whether P_A, which is obtained usually as a small difference between relatively large quantities, really exists as a quantity of significant size or whether it appears merely as the result of the combined errors of P, P_E and P_M. The question may be answered by pointing to the fact that, except in the case of a very few results obtained from notably inaccurate measurements, experiment yields no negative values for P_A.

Since P_A is due to electrical dissymmetry caused by the displacement of atomic nuclei or groups within the molecule, one would expect it to be greater, the greater the number of the nuclei or groups in the molecule. Some evidence of such an increase is given by the paraffins in Table **I**. The possible error in P_A for methane is so large that this value has little significance and P_A for ethane is very small. The values for hexane, the nine isomers of heptane and the octane, 2,2,4-trimethylpentane, are obtained from measurements of P and P_E carried out with care upon the same samples of material. The temperature variation of P for five of these substances leads to the belief that P_M may be taken as 0 for all of them. The values of P_A thus obtained as $P-P_E$ should be more accurately comparable with one another than the others in the table. Although P_A for the heptane isomers varies somewhat with the structure, it is evident that there is an increase in passing from hexane to heptane to octane. A more striking increase of P_A with increase in the number of nuclei or groups is brought out by comparison of the value 28.4 for cane sugar with that of 5 for ethyl alcohol. Ebert[4] has calculated that each mole of water of hydration in $Na_2CO_3 \cdot 10H_2O$ contributes 4.75 to the value of P_A, each mole in $BaCl_2 \cdot 2H_2O$, 4.25, and each mole in $CuSO_4 \cdot 5H_2O$, 4.06, which shows a definite dependence of P_A upon the number of nuclei.

Since P_A depends upon the displacement of the nuclei or groups in the molecule, it should depend upon the forces binding these nuclei or groups, that is, the valence forces. Bates and Andrews[8] have used thermal data to calculate the force necessary to pull apart two atoms from their positions of equilibrium, and have obtained results which are of the same order of magnitude as the approximate values calculated by the writer[9] from molar

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[8] Bates and Andrews, *Proc. Nat. Acad. Sci.*, **14**, 124 (1928); Andrews, *Chem. Rev.*, **5**, 533 (1928).

[9] Smyth, *Phil. Mag.*, **50**, 361 (1925).

refractions for the forces necessary to displace bonding electrons from their normal locations. In many cases where the actual forces cannot be calculated from the refractions, an idea of their relative magnitudes can be obtained from the refractions calculated for the electron groups. In this way, it is indicated that the C–O and H–O bonds are probably more rigid than the C–C and C–H bonds, in spite of which the values of P_A for the alcohols and ethers are larger than those for the paraffins. Although the values of P_A obtained for water by different methods do not agree well with one another, the correct value is almost certainly higher than that for hydrogen sulfide, while the refractions indicate that the forces of linkage are stronger in the water molecule. On the other hand, the forces linking carbon to halogen are lower than the C–C and C–H forces and the values of P_A for the compounds containing halogens are higher than those for the hydrocarbons. The marked rise in P_A on passing from carbon tetrachloride to titanium tetrachloride to stannic chloride is consistent with the decrease in binding force indicated by the refractions, the refractions of the chlorides in stannic chloride being almost those of free chloride ions. The different behaviors of the acetylene dihalides and the dihalogenated benzenes cannot be explained in terms of these forces alone. It seems probable that the smaller forces required to bend rather than stretch bonds may play an important role, but our knowledge of these is at present very meager. In any event, it is evident that the forces which have been considered do not provide an adequate explanation of the differences in P_A.

It is possible that the small molecules like hydrogen chloride and sulfur dioxide, which have electric moments, have larger values of P_A than the small molecules without moments, but this is uncertain because of the small values of P_A and the large errors. It is certain, however, that many small molecules with moments have values of P_A smaller than those of large molecules without moments. The values of P_A for the chlorine-substituted methanes are not sufficiently accurate to permit of definite conclusions. One may say, however, that CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4 and also C_2H_5Cl and C_4H_9Cl have values of P_A of about the same size, considerably larger than those for the paraffins. It would appear that the presence of electric doublets in the molecule, even if they oppose and cancel one another to give zero moment to the molecule as in carbon tetrachloride, is conducive to higher values of P_A. The doublets are presumably larger in titanium tetrachloride and still larger in stannic chloride, although as they are symmetrically located in the molecules, the total moments are zero. The value of P_A for liquid ethyl bromide is very uncertain, and the negative value, -5, calculated for the vapor from the measurements of Mahanti and Sen Gupta and not included in Table I shows only the uncertainty of the measurements.[10] The values calculated for the vapors of methyl and ethyl

[10] Mahanti and Sen Gupta, *Indian J. Phys.*, **12**, 191 (1928).

iodide from the measurements of the same investigators and shown in the table in parentheses merely indicate that P_A is probably large for these substances, being thus far in agreement with the high value for liquid ethyl iodide, which is more accurately determined. The reason for the abnormally high values for these substances and also for dimethyl sulfate, determined by a different method, is not apparent. It may be in part experimental error and in part the large doublets and small binding forces. There is evidently need of measurements upon the alkyl halides in the solid state.

Among the acetylene dihalides the *cis*-compound, which has a considerable moment, always has a value of P_A larger than that of the corresponding *trans*-compound, which has no moment, although P_A increases when chlorine is replaced by bromine and bromine by iodine, while the moment of the *cis*-compound decreases. Among the dihalogen-substituted benzenes the value of P_A decreases from the ortho to the meta to the para compounds, as the moment becomes smaller, and also decreases on passing from the chlorine to the bromine to the iodine compounds, in contrast to the increase among the acetylene dihalides. P_A for cyclohexane is about the same as that for the heptanes and differs from that for *n*-hexane by no more than the possible error. The value for benzene is a little larger and *p*-xylene, which contains two small opposed doublets where the methyl groups are attached, has a still larger P_A, but the difference between it and that for benzene lies within the possible error. When a considerable doublet is present, as in chlorobenzene, P_A is appreciably increased, and the large doublet in nitrobenzene causes a large value of P_A.

It may be concluded that P_A is not generally an additive quantity but that it tends to be greater, the greater the number of atomic nuclei or groups in the molecule; probably, also, the smaller the forces binding these nuclei or groups, the greater the number of the electric doublets in the molecule and the more unsymmetrical the arrangement of these doublets in the molecule. However, unknown factors make it difficult to explain many of the differences found between different types of molecules.

Small changes in P_E have been found to accompany change of state and change of temperature,[2] but similar changes in P_A would have to be very large to be apparent, because of the relatively large errors involved. Thus, for chloroform the values obtained from the work of two different investigators for the solid differ from one another far more than do those for the vapor and the liquid and one of those for the solid. For water the best value for the solid is much lower than the value for the vapor, but other values for the solid not listed are close to that for the vapor. One can conclude only that the variation of P_A with temperature and change of state is less than the error usually occurring in the determination of its value.

In the majority of the determinations of the electric moments of the molecules of substances in the liquid condition, P_A has been neglected entirely and P_M obtained as the difference between P and P_E. As the electric moment is calculated from the square root of P_M, the inclusion of P_A in the value of P_M usually increases the value of μ by little more than the possible error when P_M is large. Thus, inclusion of P_A with P_M in the calculation increases the value of μ for C_6H_5Cl by 0.05×10^{-18} and for o-$C_6H_4Cl_2$ by 0.06×10^{-18}. Williams and his collaborators[11] working at only one temperature have been compelled to disregard P_A and, instead of obtaining P_E by extrapolation to infinite wave length, have subtracted the molar refraction for the sodium D-line from P and calculated μ from the difference. As the molar refraction for the D-line is slightly larger than P_E for infinite wave length, this procedure reduces the error caused by the failure to subtract P_A. When P_M is small or zero, disregard of P_A may introduce a relatively large error into the value calculated for the moment. If, for p-$C_6H_4Cl_2$, the value of $P_A = 3.4$ is added to that of $P_M = 0$, the moment calculated from the sum, 3.4, is 0.45×10^{-18}, instead of zero, as given by the correct value $P_M = 0$. In certain calculations of the moment made by the writer, Table I, ref. 18, μ was calculated from the difference between P and P_E. In this way values of 0.20×10^{-18}, 0.23×10^{-18} and 0.48×10^{-18} were obtained for benzene, p-xylene and carbon tetrachloride, respectively, for which Table I shows zero values of μ and not inconsiderable values of P_A. It was recognized at the time that values of μ less than 0.4×10^{-18} were, in many cases, indistinguishable from zero by the method of calculation employed, but the calculation for p-$C_6H_4Cl_2$ given above shows that neglect of P_A may give a value of μ larger than 0.4×10^{-18} when it is really zero and, for an electrically symmetrical molecule possessing a larger value of P_A, like *trans*-CHI=CHI, the error in μ would be larger. It is evident that the value 0.13×10^{-18} for the chlorine molecule calculated by the author in the same paper merely shows the moment to be small, if not actually zero, and that the value 0.58×10^{-18} for the bromine molecule is probably high because of the neglect of P_A. The small difference between this and the value 0.40×10^{-18} recently found by Anderson[12] indicates that P_A is small for bromine.

It is evident that if the moment is high and the molecule is small and contains only one or two electric doublets, P_A may be disregarded in the calculation of μ without, as a rule, introducing serious error in the result. If, however, the moment is small and the molecule is large and contains several electric doublets, it is unsafe to neglect P_A in the calculation of the moment.

Summary

Values for the atomic polarization of a large number of substances have been calculated or taken from the literature.

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[11] Williams, *Physik. Z.*, **29**, 174 (1928).

[12] Anderson, *Proc. Phys. Soc.*, **40**, 62 (1928).

The binding forces calculated by Bates and Andrews from thermal data and by the writer from refractions are found inadequate to account for the differences between the displacements of the different nuclei and groups in the molecules.

The atomic polarization is not generally an additive quantity, but tends to be greater, the greater the number of atomic nuclei or groups in the molecule, the greater the number of electric doublets and the more unsymmetrical the arrangement of these doublets in the molecule.

In the calculation of the electric moment of a molecule, the atomic polarization may be disregarded without risk of introducing appreciable error only when the moment is high and the molecule is small and contains but one or two electric doublets.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF PRINCETON UNIVERSITY]

THE PHOTOSENSITIZED AND PHOTOCHEMICAL DECOMPOSITION OF HYDRAZINE

BY JOSEPH C. ELGIN AND HUGH S. TAYLOR

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Perhaps the most important fact now necessary for a complete understanding of the manner in which reactions are brought about by light energy is a knowledge of the action produced directly upon its absorption by the molecule. Taylor[1] has proposed, as a generalization of the facts now known, to state a Second Law of Photochemistry as follows: "The absorption of light is a quantum process involving one quantum per absorbing molecule (or atom). The photochemical yield is determined by the thermal reactions of the system produced by the light absorption." The resultants of this sequence of secondary thermal reactions are determined by ordinary physicochemical methods. The nature of the quantum process presents a more difficult problem. It has been possible in many cases from a complete kinetic study of the reaction to set up a mechanism, based on a postulated primary process, which yields satisfactory agreement with experimental observations. The postulated primary process is then assumed to be that actually occurring. For conclusive evidence as to the primary light action we must turn to that on the optical side furnished directly by molecular spectra. Thus far it has been possible to correlate satisfactorily the nature of the absorption spectrum with a definite primary action only in cases involving diatomic molecules. Those more complex give spectra showing complicated band systems which resist analysis. As a result of

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[1] Taylor, "First Report of the Committee on Photochemistry of the Division of Chemistry of the National Research Council."