

## The Problem of Atomic Polarization

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## The Problem of Atomic Polarization

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New values of atomic polarizations are obtained from the temperature variation of the dielectric constants of gases. Although the values are of a greater magnitude than those calculated for simple molecules from infrared intensity measurements, they show that the improbably

high values previously found for several alkyl halides are incorrect. If the molecule is not very large, its atomic polarization is a relatively small quantity unless dipole rotation may occur within the molecule as indicated by the dielectric constant of the substance in the solid state.

### INTRODUCTION

IN an earlier paper<sup>1</sup> the writer collected the available data on atomic polarization and attempted to investigate such relations as might be found among them, a summary of this treatment being published subsequently.<sup>2</sup> At that time Van Vleck<sup>3</sup> had calculated from infrared intensity measurements that the vibrational or atomic polarization was negligibly small for HCl, HBr, CO, CO<sub>2</sub>, NH<sub>3</sub> and CH<sub>4</sub> and attributed to experimental error the small but not inconsiderable values found for them, indicating, however, that this did not necessarily mean that other kinds of molecules might not possess significant atomic polarizations. In a recent treatment of these simple molecules,<sup>4</sup> he expresses scepticism as to "whether any information about the order of magnitude of the atomic polarization can be deduced from existing absorption data" and submits as "perhaps the best appraisal . . . that the effect of the atomic polarization on the dielectric constant is negligible in stable diatomic molecules, but not necessarily in molecules with more than two atoms." Smallwood<sup>5</sup> has recently attempted to calculate atomic polarizations but has obtained values much smaller than the observed. Thus far we have failed to account in a

general quantitative fashion for the atomic polarization. The present paper offers new and, for the most part, more accurate data on atomic polarization, which will be used to answer certain newly arisen questions and to eliminate certain incomprehensibly large values from among the earlier data.

### CALCULATION OF RESULTS

It will be remembered that the atomic polarization  $P_A$  is obtained by subtracting the electronic polarization  $P_E$  and the orientation or dipole polarization  $P_M$  from the total polarization  $P = (\epsilon - 1)M/(\epsilon + 2)d$ , in which  $\epsilon$  is the dielectric constant,  $M$ , the molecular weight, and  $d$ , the density, that is,  $P_A = P - P_E - P_M$ . If  $P_M$  can be eliminated by fixing the dipoles in the solid state,  $P_A$  may be obtained by subtracting from  $P$  the value of  $P_E$  calculated by extrapolating the molar refraction to infinite wave-length. Some of the difficulties of this method have already been discussed and others which have been made evident by recent work on solids will be treated presently. Since, in the Debye equation,  $P = a + b/T$ ,  $a = P_E + P_A$ ,  $P_A$  can, perhaps best, be determined from  $a$ , which is obtained from the temperature variation of  $P$ . When the previous tabulation of values of  $P_A$  was made, few accurate measurements of the temperature variation of the dielectric constants of gases were available and the extreme inaccuracy of some was not fully recognized. Moreover, as the present work will show, the apparent temperature variation of the polarization in solution is sometimes misleading. As previously pointed out, the values of  $P_A$  are,

<sup>1</sup> C. P. Smyth, J. Am. Chem. Soc. **51**, 2051 (1929).

<sup>2</sup> C. P. Smyth, *Dielectric Constant and Molecular Structure*, p. 163, The Chemical Catalog Company, Inc., New York, 1931.

<sup>3</sup> J. H. Van Vleck, Phys. Rev. **30**, 31 (1927).

<sup>4</sup> J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, p. 51, Oxford University Press, Oxford, 1932.

<sup>5</sup> H. M. Smallwood, Zeits. f. physik. Chemie [B] **19**, 242 (1932).

at best, inaccurate, since they are determined as small differences between relatively large quantities, all the errors of experiment and method being thus accumulated in them. The values in Table I, assembled by Dr. Kenneth B. McAlpine, have been calculated from the temperature variation of the dielectric constants of the sub-

TABLE I.

Atomic polarizations			
Nitric oxide	0.4 <sup>a</sup>	Methyl fluoride	2.4 <sup>c</sup>
Nitrous oxide	0.4 <sup>a</sup>	Methyl chloride	2.2 <sup>c</sup>
Carbon disulfide	0.3 <sup>f</sup>	Methyl bromide	1.2 <sup>c</sup>
Propylene	0.6 <sup>d</sup>	Methyl iodide	1.4 <sup>c</sup>
Propane	0.3 <sup>d</sup>		
Benzene	1.9 <sup>d</sup>	Ethyl chloride	1.4 <sup>c</sup>
Toluene	2.5 <sup>d</sup>	Ethyl bromide	2.9 <sup>c</sup>
<i>n</i> -Heptane	1.1 <sup>e</sup>	Ethyl iodide	1.5 <sup>c</sup>
Ethylene oxide	1.8 <sup>g</sup>	CHFCI <sub>2</sub>	0.9 <sup>b</sup>
Ethyl ether	3.9 <sup>g</sup>	CHF <sub>2</sub> Cl	3.9 <sup>b</sup>
	3.3 <sup>h</sup>	CF <sub>2</sub> Cl <sub>2</sub>	4.1 <sup>b</sup>
		CFCl <sub>3</sub>	3.0 <sup>b</sup>

<sup>a</sup> C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.* **1**, 60 (1933).

<sup>b</sup> C. P. Smyth and K. B. McAlpine, *ibid.* **1**, 190 (1933).

<sup>c</sup> C. P. Smyth and K. B. McAlpine, unpublished measurements.

<sup>d</sup> K. B. McAlpine and C. P. Smyth, *J. Am. Chem. Soc.* **55**, 453 (1933).

<sup>e</sup> C. H. Schwingel and J. W. Williams, *Phys. Rev.* **35**, 855 (1930).

<sup>f</sup> C. T. Zahn, *ibid.* **35**, 848 (1930).

<sup>g</sup> H. A. Stuart, *Zeits. f. Physik* **51**, 490 (1928).

<sup>h</sup> O. Fuchs, *ibid.* **63**, 824 (1930).

stances in the vapor state, which seems to provide the most accurate method of determination. Some recent data are omitted as being less accurate. An accurate value for ethyl ether is taken from the old tabulation for comparison with a newly determined value.

## DISCUSSION OF RESULTS

The atomic polarizations for the small molecules in Table I are small but not the negligibly small values that would probably be calculated from infrared intensity measurements. Although they are hardly larger than the possible experimental error, it is important to note that no negative values have been obtained, nor have negative values been obtained from any dependable measurements. This shows that the magnitude of

the atomic polarizations cannot be due to experimental error. In accordance with a previously noted tendency, propylene and toluene, which have small dipole moments, have larger atomic polarizations than the closely related molecules of propane and benzene, which have no moments. The values for benzene and heptane vapors differ by less than the experimental error from those previously found for the liquids.

In measurements upon solutions of polymethylene bromides,<sup>6</sup> the moments of which increase with rising temperature because of the potential energy between the two principal dipoles in each molecule, it was found that the values of  $P_A$  calculated from the apparent values obtained for the constant  $a$  of the Debye equation were very high, 60 in the case of pentamethylene bromide. As an increase of moment with rising temperature would reduce the slope of the  $P-1/T$  curve and thus give too large a value of  $a$  and of  $P_A$ , the apparent high  $P_A$  values were regarded as practically meaningless. This suggested the possibility that the surprisingly high values of the atomic polarization found for a number of alkyl halides<sup>1,7</sup> from measurements on temperature variation of the polarization might be due to an increase in moment with rising temperature. Although not highly probable, it appeared possible that there might be sufficient stretching of the carbon-halogen bond with rising temperature to cause an appreciable lengthening of the dipole with consequent increase in moment. In order to investigate this possibility, the values for the methyl and ethyl halides in Table I were acquired. The probable error in these values appears to be somewhat less than 1. As there is no regular trend in the values, it appears probable that the true values lie between 1.5 and 2.0. The values for the four substituted methanes are about twice as great, with the exception of that for CHFCI<sub>2</sub>, in which the error would seem to be abnormally large. Although these molecules have moments smaller than those of the methyl and ethyl halides, they contain three or four principal

<sup>6</sup> C. P. Smyth and S. E. Kamerling, *J. Am. Chem. Soc.* **53**, 2988 (1931).

<sup>7</sup> C. P. Smyth and H. E. Rogers, *J. Am. Chem. Soc.* **52**, 2227 (1930).

S. O. Morgan and H. H. Lowry, *J. Phys. Chem.* **34**, 2385 (1930).

dipoles instead of one. Their larger atomic polarizations are in accord with the previous observation<sup>1</sup> that the atomic polarization is greater, the greater the number of dipoles in the molecule, probably because of the bending or displacement of these dipoles within the molecule.

The value 2.2 for methyl chloride compares with the value 8.1 found by Morgan and Lowry in hexane solution, 1.3 in carbon tetrachloride solution and 8.1 in the solid state, the latter value falling to 2.0 as the temperature was lowered from  $-100^{\circ}$  to  $-190^{\circ}$ . The value 1.2 for methyl bromide compares with 21.4 in hexane solution and 2.8 for the solid at  $-100^{\circ}$ , decreasing to 0.8 at  $-120^{\circ}$ . For methyl iodide, Table I gives 1.4 as compared to values of 15.5 in hexane solution and 0 in the solid state. For ethyl bromide vapor, the value is 2.9 and for the iodide 1.5 as compared to 11 found by Smyth and Morgan<sup>8</sup> for the former in hexane solution and 12.3 by Smyth and Stoops<sup>9</sup> for the latter in heptane solution. The low values of the atomic polarizations of the vapors, which are dependable and of the same magnitude as those found for the solids, show that there is no detectable change of moment in these molecules in the temperature region studied. The high values of the atomic polarizations found in the measurements upon solutions must be regarded as incorrect.

In the measurements upon solutions each value of  $P$  used to determine the constants  $a$  and  $b$  for a substance was obtained by extrapolating to zero concentration a curve in which the polarization of the substance  $P_2$  was plotted against its mole fraction  $c_2$  in a nonpolar solvent. As the solvent reduces the forces between the polar molecules which lower the observed polarization, the value found for  $P_2$  increases with increasing dilution and the  $P_2 - c_2$  curve rises rapidly as zero concentration is approached. As rising temperature diminishes the intermolecular action, the curvature of the curves becomes less pronounced so that the extrapolation to zero concentration becomes more accurate, the higher the temperature. Since extremely dilute solutions were not used in these measurements on the alkyl

halides and since the same general method of extrapolation was employed on every curve, it is probable that the extrapolated polarization values at the lower temperatures are too low and approach the correct values only at the higher temperatures. Such polarization values would give a  $P - 1/T$  curve of too small a slope and, consequently, too large a value of  $P_A$  just as in the case of a substance, the moment of which increased with rising temperature.

A very pronounced case of the effect of solvent upon intermolecular action is shown by measurements upon butyl alcohol in heptane, cyclohexane and benzene solution.<sup>9</sup> In benzene solution, the moments calculated at  $10^{\circ}$  intervals from  $20^{\circ}$  to  $70^{\circ}$  deviate little from a mean value  $1.74 \times 10^{-18}$ , which is but slightly higher than the value  $1.66 \times 10^{-18}$  determined for the vapor.<sup>10</sup> In the other two solvents, the polarizations in the dilute solutions increase with increasing temperature instead of falling off as required by the Debye equation. Smallwood<sup>5</sup> calculates from these results in heptane solution an apparent moment of  $1.29 \times 10^{-18}$  at  $10^{\circ}$  rising to  $1.65 \times 10^{-18}$  at  $70^{\circ}$  and seems to imply that the difference is due to the effect of the solvent upon the actual polarization of the alcohol molecule. Since, however, it is difficult to picture the change in the moment of the alcohol molecule as occurring with sufficient ease to be affected by the difference in solvent, it seems more reasonable to adhere to the view originally advanced by Smyth and Stoops that the benzene is more effective than the heptane and cyclohexane in reducing the forces between the alcohol molecules. On this view the extrapolated polarization of the alcohol in heptane solution is much lower than the true value for the molecules isolated from one another at the low temperatures and approaches the true values with rising temperature, being approximately correct at  $70^{\circ}$ . The failure of the solvent to eliminate the effect of the forces between the polar molecules at the lower temperatures is so considerable as to be obvious in the case of the heptane solutions of butyl alcohol. A much smaller failure in the case of the solvent in the alkyl halide solutions could cause the large values observed for the atomic polarizations.

<sup>8</sup> C. P. Smyth and S. O. Morgan, J. Am. Chem. Soc. **50**, 1547 (1928).

<sup>9</sup> C. P. Smyth and W. N. Stoops, J. Am. Chem. Soc. **51**, 3312 (1929).

<sup>10</sup> J. B. Miles, Phys. Rev. **34**, 964 (1929).

## DETERMINATIONS ON SOLIDS

The highest atomic polarization seeming to possess any real significance thus far reported is the value 33.4 for dimethyl sulfate in the solid state.<sup>11</sup> Later measurements of the dielectric constant of solid dimethyl sulfate<sup>12</sup> give evidence of dipole orientation between the melting point,  $-31.4^\circ$ , and a transition at  $-68.0-71.0^\circ$ . If this is an orientation of dipoles within the molecule, as seems rather probable, the polarization arising from it must be classed as a true atomic polarization, which drops to a small value below the transition point. If, however, it arises from a limited orientation of the molecule as a whole, the atomic polarization must be estimated from the small dielectric constant below the transition point.

The high atomic polarization, 24.8, calculated by Ebert for cane sugar,<sup>13</sup> may arise from orientation of the hydroxyl group dipoles within the molecule but may be due, at least in part, to the presence of water in the material. The same may be said of Ebert's value 28.4 for citric acid containing a molecule of water of hydration, which probably contributes heavily to the value of  $P_A$ . In view of the rotation of the water molecule in

ice and the great elevation of the dielectric constant by the presence of minute quantities of ionic impurities,<sup>12</sup> large values of  $P_A$  for solids liable to contain traces of water must be viewed with scepticism. As small quantities of impurities may cause the presence of liquid in the solid for some distance below the freezing point, it is evident that, unless the substance is very pure, the atomic polarization must be determined at temperatures far below the freezing point, although the use of high frequency in the dielectric constant measurements tends to reduce the effect of impurities.<sup>12</sup> In the case of small polar molecules, like those of water and the hydrogen halides, ordinarily high frequencies and low temperatures would be useless in determining  $P_A$  because of the rotation of the molecules in the space lattice. However,  $P_A$  may be determined for these small molecules from the temperature variations of the polarizations of the gases.

## CONCLUSIONS

It may be concluded that improved methods of determining atomic polarization have demonstrated the incorrectness of the large values previously reported except, perhaps, in the case of complex molecules where dipole orientation may occur within the molecule. In the calculation of a large dipole moment, the error caused by neglect of atomic polarization is normally almost negligible.

<sup>11</sup> J. Errera, *Polarisation Diélectrique*, p. 115, Les Presses Universitaires de France, Paris, 1928.

<sup>12</sup> C. P. Smyth and C. S. Hitchcock, *J. Am. Chem. Soc.* **54**, 4631 (1932).

<sup>13</sup> L. Ebert, *Zeits. f. physik. Chemie* **114**, 430 (1925).