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The Variation of Dielectric Constant with Temperature. II. Electric Moments of the Ethylene Halides

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Both the free and hindered rotation of atoms or groups of atoms about single chemical linkages may be studied with the Debye relation between the molar polarization, P, and the reciprocal of the absolute temperature, $1/T$. The quantitative treatment by one of us for the simplest case of a free rotation has been compared with the more recent and more general expressions of Eyring and of Zahn. For the case in which the relation between P and $1/T$ is nonlinear the use of Meyer's equation has been suggested for the calculation of the electric moment of the molecule. An apparatus has been described for measuring the dielectric constant of a vapor as a function of temperature. This apparatus includes a comparatively cheap vapor condenser of Monel metal, a means of obtaining vapor at any desired pressure up to that characteristic of 100°C, and a method of measuring vapor pressure in an all-glass apparatus. An experimental procedure has been designed to minimize as far as possible the systematic errors due to simplifying assumptions in the capacity equations of the measuring circuit. The results of dielectric constant and density measurements on ethylene chloride and ethylene bromide have been recorded. The experimental values for the total polarizations of these compounds have been plotted against the reciprocals of the absolute temperature. These results have been utilized for the calculation of the several electric moments by the usual methods based on the linear equation of Debye and by the application of Meyer's equation. All of the methods for the calculation of electric moments were found to give results approaching each other at higher temperatures but tending to deviate more and more at lower temperatures. It has also been possible to calculate the characteristic moments of the $C-Cl$ bond and the $C-Br$ bond from the experimental data. The characteristic moments of the bonds were found to bear the same ratio to each other as the moments of the methyl compounds. It has been further shown that Meyer's equation is applicable to the results for vapors and for solutions now existent in the literature. The indications are that the difference between the experimental results for vapors and for solutions may be due to changes in internal structure produced in the molecule by the solvent.

Introduction

DURING the last two decades dielectric theory has played an important role in the development of ideas concerning the electrical constitution of matter. Quantum theory has clarified the view of intra-atomic matter, while the older kinetic and thermodynamic theories have been concerned with intermolecular action of comparatively large aggregates. In the field between, where the interest lies in the relative positions and interactions of atoms and groups of atoms within the molecule, dielectric theory has found important and unique application.

The interpretation of the temperature effect on the mean electric moment $\bar{m}$ of a molecule in an external field F was presented by P. Debye in the year 1912 through the familiar equation:[1]

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[1] Debye, Phys. Zeits. **13**, 97 (1912); See also *Polar Molecules*, Chemical Catalog Co., New York (1929).

$$\bar{m} = (\alpha_0 + \mu^2/3kT)F. \tag{1}$$

In this equation α_0 is the polarization due to deformation, μ is the permanent moment of the molecule, k is the Boltzmann constant (1.37×10^{-16}), and T is the absolute temperature.

The general formula for the polarizability is, therefore,

$$\alpha = \alpha_0 + \mu^2/3kT.$$

Experimental verification of this equation has followed its combination with the Clausius-Mosotti relation, written for the molar polarization P, as follows:

$$\frac{\epsilon - 1}{\epsilon + 2}\cdot\frac{M}{\rho} = P = \frac{4\pi N}{3}\alpha = \frac{4\pi N}{3}\left(\alpha_0 + \frac{\mu^2}{3kT}\right) \tag{2}$$

or

$$P = A + B/T. \tag{2'}$$

Here ϵ is the dielectric constant, M is the molecular weight, ρ is the density, N is the Avagadro constant (6.06×10^{23}), $A = 4\pi N\alpha_0/3$ (molar polarization due to deformation), and $B = 4\pi N\mu^2/9k$ (molar polarization due to the permanent moment of the molecule). The experimental determination of ϵ and ρ for a compound over a series of temperatures permits the calculation of the relation between the total polarization P and $1/T$. This affords a direct check on the linearity of the Debye relationship. It also distinguishes between nonpolar and polar molecules, and in the case of the latter, provides a means of calculating the permanent moment μ from the constant B. Such experimental studies have amply verified the fundamental correctness of the above equations.

From such results the electric moment μ has been obtained by one of the following methods:

(1) The constant B, and thus μ, can be obtained from the slope of the linear plot of P *vs.* $1/T$.

(2) Multiplying Eq. (2′) through by T gives:

$$PT = AT + B. \tag{2''}$$

The quantity B can now be obtained from the intercept, at $T = 0$, of the plot of PT *vs.* T. This method does not differ essentially from the first.

(3) In Eq. (2′) the deformation polarization A can be approximated from refractivity data. Ten percent may be added to the molecular refractivity in order to allow for the contribution of the atoms. The ratio B/T is then obtained as the difference between P and A. This method must be used when data at only one temperature are available. Its use, in conjunction with the value of B given above, depends as much upon the linear form of the Eq. (2′) as does either of the other two methods.

INTRA-MOLECULAR ROTATION

The possibility of rotation about some valence bonds has long been suspected. We will confine our attention in this article to what are probably the simplest molecules in which this phenomenon is exemplified, namely, the ethylene halides. In these compounds rotation about the C–C bond would be expected from the purely chemical evidence that it has been impossible to separate cis and trans isomers. The fact that these molecules have finite dipole moments has been established by numerous investigators. The most important results for ethylene chloride and ethylene bromide have been brought together in Table I. If the trans form alone were present there would result a zero moment. The finite moment found experimentally may be due to one of three possibilities: (1) Molecules of only the cis form may be present. (2) There may be a mixture of molecules of the cis and trans form. (3) The moment may represent an average of the moments of a number of molecules having effectively different dissymmetries due to the relative rotation of the two polar groups about the C–C linkage. The first of these is excluded because the cis form is the one having the higher potential energy (due to repulsion between like polar groups) and would thus hardly be formed in preference to the trans form. There is also evidence against this possibility in the fact that the moments in Table I are much lower than those of the corresponding cis forms of the acetylene dihalides. The second possibility, and indeed the first as well, would be at variance with all the evidence, both chemical and physical, for the rotation about such valence bonds. Evidence of a variation of moment with temperature further strengthens the supposition of such a rotation.

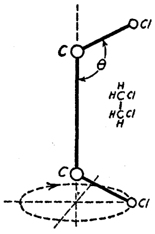

Fig. 1.

TABLE I. *Electric moments of ethylene chloride and ethylene bromide.*

Substance	In solution in:			As
	benzene $\mu\times10^{18}$	hexane $\mu\times10^{18}$	heptane $\mu\times10^{18}$	vapor $\mu\times10^{18}$
Ethylene chloride	1.83[2] 1.86[3] 1.75[4]	1.26–1.42[2]	1.16–1.42[6]	1.56[7] 1.01[8] 1.12–1.54[9]
Ethylene bromide	1.46–1.55[5] 1.4[4]		0.79–1.05[5]	0.94–1.10[10]

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[2] Meyer, Zeits. f. phys. Chem. **B8,** 27 (1930).
[3] Gross, Phys. Zeits. **30,** 504 (1929).
[4] Williams, Zeits. f. phys. Chem. **138,** 75 (1928).
[5] Smyth, J. Am. Chem. Soc. **53,** 2988 (1931).
[6] Smyth, J. Am. Chem. Soc. **53,** 4242 (1931).
[7] Ghosh, Mahanti and Sen Gupta, Zeits. f. Physik **54,** 711 (1929).
[8] Sänger, Phys. Zeits. **32,** 21 (1931).
[9] Zahn, Phys. Rev. **38,** 52 (1931).
[10] Zahn, Phys. Rev. **40,** 291 (1932).

In general there may be two types of rotation depending upon the energy state of the molecule. It will be recognized from the model in Fig. 1 that the cis configuration corresponds to a position of maximum potential energy of repulsion between the two moments, while the trans configuration corresponds to a position of minimum potential energy. In fact the resultant moment for the whole molecule would be largest for the cis form and zero for the trans form. This has been confirmed in the cis and trans forms of rigid double bond linkages. Calculations of Eucken and Meyer[11] have shown that free rotation occurs when the potential energy between the two halves of the molecule does not exceed $(1/10)kT$. However, if this potential energy exceeds $(1/10)kT$ there results a rotary oscillation about the position of minimum potential energy, which case we will call "hindered rotation" after the above authors. Obviously, in terms of the resultant moment of the molecule, there will be no sharp division between the two cases. When the rotation is hindered or oscillatory the amplitude of the oscillations will increase as the temperature is raised and the energy of the oscillations increases. The resultant moment of a molecule of this type will increase with the amplitude of the oscillations because the time average of the relative positions of the two polar groups will be further and further from the trans position. This is the theoretical basis for expecting the moment of the molecule to vary with temperature and thus produce a nonlinear relation between the total polarization and the reciprocal of temperature.

In the Debye theory the moment μ was assumed to be constant with respect to temperature. Consequently Eq. (2′) cannot be applied to the general case of intra-molecular rotation. However, in the limiting case of free rotation the moment will be constant as the temperature varies as long as the rotation remains free and unhindered. This case has been treated vectorially by Williams.[12] The resultant mean moment for the molecule, which is the one that would be obtained experimentally from Eq. (2′) if free rotation were actually the case, is given by:

$$\mu = 2^{1/2}\mu_1 \sin\theta \tag{3}$$

where μ_1 is the characteristic moment of the polar linkage and θ is the valence angle.

In applying Eq. (3) to the ethylene halides, using characteristic moments of 2.0 for C–Cl, 1.86 for C–Br, and 1.65 for C–I, Williams[12] found values of θ to be 38° for the chloride, 32° for the bromide, and 33° for the iodide. With tetrahedral carbon valences, the angle should be 180°–110° or 70°. We now know that the mutual repulsion of the two groups would not be likely to cause such a decrease in the angle, hence the natural conclusion is that the assumption of free rotation is not justified in these cases.

Eyring,[13] using the matrix algebra, has developed a general equation for the average resultant moment of a molecule having free rotation about certain bonds in terms of the individual permanent moments, the angles between

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[11] Eucken and Meyer, Phys. Zeits. **30**, 397 (1929).

[12] Williams, Zeits. f. phys. Chem. [A] **138**, 75 (1928).

[13] Eyring, Phys. Rev. **39**, 746 (1932).

the valence bonds, the rotation angles, and the energy. From this equation he has obtained several equations for simpler cases. Smyth,[14] in conjunction with Eyring, has applied these equations to a number of organic compounds, comparing the calculated moments with the experimentally determined moments as a qualitative measure of the degree of freedom of the rotation. For the purpose of this discussion it will be sufficient to show that Eyring's equation reduces to the Williams equation above if applied to the simple case of free rotation about one single valence bond.

Eyring's equation for a paraffin chain of $n+1$ carbon atoms, with a free rotation about each C–C linkage, is:

$$\mu = \mu_1[2n + 2(n-1)\cos\theta + 2(n-2)\cos^2\theta + \cdots + 2\cos^{n-1}\theta]^{1/2} \tag{4}$$

where μ_1 is the characteristic moment of the C-X linkage and θ is the valence angle (110°). For the simplest molecules $n+1=2$, and the equation reduces to:

$$\mu = \mu_1[2 - 2\cos^2\theta]^{1/2}. \tag{5}$$

Eq. (5) is identical with that used by Smyth for ethylene bromide and is also identical with the Williams Eq. (3), thus:

$$\begin{aligned}\mu &= \mu_1 2^{1/2}(1-\cos^2\theta)^{1/2}\\ &= \mu_1 2^{1/2}\sin\theta.\end{aligned} \tag{3}$$

Zahn[15] has used similar methods in discussing a number of special cases.

It has been pointed out above that the resultant moment μ would be expected to vary with temperature for the case of hindered rotation, and that consequently the polarization would no longer be a linear function of $1/T$. The theoretical treatment of this case thus requires a new derivation of the relation between P, μ, and T, which takes the hindered rotation into consideration. Meyer[2] was the first to do this quantitatively from the classical theoretical standpoint. Meyer's equation is

$$\left.\begin{aligned}P &= 4\pi N/3\{\alpha_0 + [2(\mu_1\sin\theta)^2/3kT](1-X)\}\\ X &= \frac{\alpha/kT + \beta/(kT)^2 + \gamma/(kT)^3 + \cdots}{m + n/kT + o/(kT)^2 + p/(kT)^3 + \cdots}\end{aligned}\right\} \tag{6}$$

where N is the Avagadro constant, k is the Boltzmann constant, α_0 is the molecular deformation polarization, μ_1 is the characteristic moment of the C-X linkage, θ is the valence angle, T is the absolute temperature, and $\alpha,\beta,\gamma,m,n,o,p$ are constants associated with the structure of the molecule.

Eq. (6) expresses the nonlinear relationship between P and $1/T$ for the simple case of hindered rotation in the ethylene halides. Meyer pointed out that at high temperatures the term X becomes negligible and Eq. (6) reduces to

$$P = 4\pi N/3\{\alpha_0 + [2(\mu_1\sin\theta)^2/3kT]\}. \tag{7}$$

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[14] Smyth, J. Am. Chem. Soc. **54,** 2261 (1932).

[15] Zahn, Phys. Zeits. **33,** 400 (1932).

Comparing this with the Debye Eq. (2) it is seen that:

$$\mu = 2^{1/2}\mu_1 \sin\theta \tag{3}$$

which is the equation for free rotation previously developed.[12] Thus, at high temperatures Meyer's Eq. (6) is in accord with theory for the case of free rotation.

For the case of free rotation the resultant moment μ can be calculated from the experimental results by using the linear Debye equation in the three ways mentioned above. However, in order to calculate μ from experimental results when the rotation is hindered it is necessary to apply Eq. (6). This is a point which other experimenters either do not seem to have recognized or have thought unnecessary. At least we have been unable to find evidence of its use for the calculation in nonlinear cases.

On dividing the denominator of the function X of Eq. (6) into the numerator the function becomes:

$$\begin{aligned} X &= (\alpha/m)(kT)^{-1} + [(\beta m - \alpha n)/m^2](kT)^{-2} + \cdots \\ &= C(1/T) + D(1/T)^2 + \cdots \end{aligned} \tag{8}$$

where

$$C = \alpha/mk;\ D = (\beta m - \alpha n)/m^2k^2.$$

The expression for P in Eq. (6) then becomes:

$$\begin{aligned} P &= \frac{4\pi N}{3}\alpha_0 + \frac{4\pi N}{9k}2(\mu_1 \sin\theta)^2[(1/T) - C(1/T)^2 - D(1/T)^3 - \cdots] \\ &= A + B'[(1/T) - C(1/T)^2 - D(1/T)^3 - \cdots] \end{aligned} \tag{9}$$

where

$$A = (4\pi N/3)\alpha_0;\ B' = (4\pi N/9k)2(\mu_1 \sin\theta)^2.$$

In Eq. (9) the difference $P-A$ must be the polarization due to the resultant moment μ of the molecule at any temperature T. It is reasonable to suppose that the same relation holds between the resultant moment and the polarization caused by it as holds in the ordinary case where there is no intramolecular rotation. Then we can write from the ordinary Debye equation:

$$\begin{aligned} P &= A + (4\pi N/9kT)\mu^2 \\ \mu^2 &= (9kT/4\pi N)(P - A). \end{aligned} \tag{2}$$

Substituting for the value of $P-A$ in Eq. (9) we obtain the expression

$$\mu^2 = (9kT/4\pi N)B'[(1/T) - C(1/T)^2 - D(1/T)^3 - \cdots].$$

Putting in the value of B' and simplifying we find

$$\mu^2 = 2(\mu_1 \sin\theta)^2[1 - C(1/T) - D(1/T)^2 - \cdots]. \tag{10}$$

For the actual calculation of μ it is more convenient to retain the constant B', thus:

$$\mu^2 = (9k/4\pi N)B'[1 - C(1/T) - D(1/T)^2 - \cdots]. \tag{10'}$$

Now from the experimental plot of the total polarization P against $1/T$ the constants in Eq. (9) can be determined, and from these, substituted in Eq. (10′), the resultant moment μ can be calculated for any temperature.

EXPERIMENTAL

According to the results existent in the literature at the present time there is still some question as to whether or not ethylene chloride and ethylene bromide actually have nonlinear relationships between their total polarizations and the reciprocals of the temperature. Smyth,[5,6] studying solutions in heptane, and Meyer,[2] working with solutions in hexane, obtain a curvature in their plots of P against $1/T$. However, the results of these investigators for the corresponding solutions in benzene are inconclusive. It should be emphasized that experiments with solutions alone can hardly be sufficient to decide a question of this sort because of ignorance of the effect of the solvent. The experiments of Zahn[9] on the vapor of ethylene chloride show a nonlinear relationship while Ghosh and his associates[7] obtain a linear relation, and Sänger's results[8] are inconclusive.* Very recently Zahn[10] has reported data for ethylene bromide vapor. It is difficult to draw any conclusion from these data of Zahn when his total polarizations are plotted against the reciprocals of temperature. In view of this situation it was decided to complete the work, begun early in 1930, with the ethylene chloride and ethylene bromide vapors.

The object of the experimental part was, therefore, to obtain values of the total polarization P over as wide a temperature range as possible. The apparatus and method were designed for vapors having an appreciable vapor pressure in the neighborhood of 100°C. The determination of ϵ requires capacity measurements on a condenser in a vacuum and in an atmosphere of the vapor. The density term in the Clausius-Mosotti relation requires a knowledge of the pressure of the vapor and the temperature. To satisfy these requirements the apparatus must contain: (a) A condenser in a chamber holding the vapor; (b) apparatus for admitting and exhausting the vapor; (c) a means of determining the pressure of the vapor in the chamber; (d) a means of controlling and measuring the temperature of the condenser chamber; (e) apparatus for measuring the capacity of the condenser.

(a) The condenser was of the concentric cylinder type. Four cylinders of Monel metal (cold drawn, seamless, annealed tubing) were polished inside and outside and mounted concentrically as shown in Fig. 2. Four mica spacers were used in each end to keep the cylinders in position. The dimensions and spacings are listed below the figure. In cutting the outside cylinder to length three lugs were left on each end. These were shaped as indicated in the figure and used to support the condenser in a vertical position in a large Pyrex tube. Part of the Pyrex chamber is shown by dashed lines in the figure. Alternate cylinders were electrically connected through short lugs left projecting from their ends when they were cut to length. These lugs were simply spot-welded together. Leads to the outside were small tungsten wires, spot-welded

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* In a recent communication to us Sänger has stated that a redetermination of several of his experimental points has brought his results to a practical agreement with those of Zahn.

to the Monel lugs, passing out through gas tight Pyrex-tungsten seals. The lead from the outside and second inner cylinders was taken off at the bottom and grounded as indicated, while the lead from the first and third inner cylinders was taken off at the top and served to connect the condenser to the capacity measuring apparatus.

(b) The condenser and chamber were mounted vertically as shown in Fig. 3. The entrance tube was at the top and led out through the three-way stopcock marked *A*. One of the tubes from this stopcock led directly to the tube *D* containing the liquid under investigation. The third outlet from stopcock *A* led to the evacuating system through stopcocks *B* and *C*. Stopcock *B* led to a "Hi-Vac" oil pump and stopcock *C* led through the trap shown, and a calcium chloride tube, to a water aspirator.

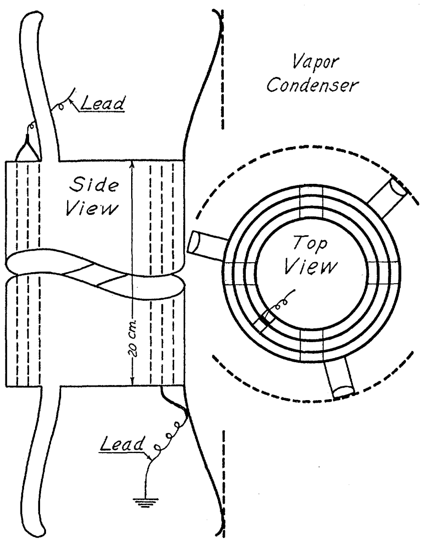

Fig. 2.

Cylinder	Outside Diam.	Spacing
Outside	4.76 cm	
1st inner	4.13	1.95 mm
2nd inner	3.65	1.50
3rd inner	3.18	1.50

Sufficient liquid for a whole series of determinations was placed in the tube *D* before it was sealed to the apparatus. The liquid was then cooled to a point where it solidified and the tube *D* was sealed to the apparatus through the small connecting tube. While the liquid was still frozen the stopcocks were turned so as to connect tube *D* through stopcock *B* to a source of carbon dioxide and the vacuum pump. In this way the space above the material was thoroughly flushed out several times with dry carbon dioxide, the carbon dioxide entering through stopcock *B* from auxiliary tubes not shown in the figure. Tube *D* was finally evacuated and then closed by means of stopcock *A*. By surrounding tube *D* with hot water contained in the vacuum flask the liquid could be heated to give any desired vapor pressure up to that characteristic of 100°C.

In the meantime the rest of the apparatus was flushed out with dry carbon dioxide and evacuated. This was possible because the three-way stopcock *A* was mounted in such a way that the condenser chamber could be connected to the vacuum system while tube *D* was closed.

With the condenser chamber and connecting tubes evacuated stopcock *B* was closed and then stopcock *A* was turned to allow the vapor to flow from tube *D* into the condenser chamber until the desired pressure of vapor was obtained. Stopcock *A* was then set in an intermediate position so as to close both *D* and the condenser chamber. Condensation of vapor in the tube leading from stopcock *A* to the condenser chamber was prevented by means of the heating coil shown in the figure. Of course, the chamber itself was always kept at a temperature higher than that of the liquid in tube *D*.

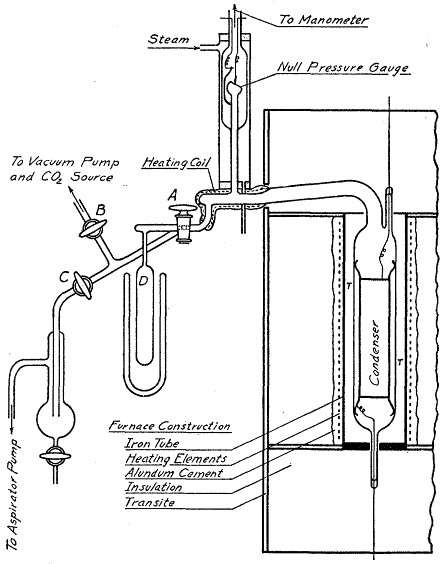

Fig. 3.

After the measurements of temperature, pressure, and capacity (to be described later) the system was evacuated, keeping tube *D* closed as before. In evacuating the vapor, as much as possible was pulled out by the aspirator pump through stopcock *C*. Stopcock *C* was then closed and the system finally evacuated by the oil pump through stopcock *B*. In actual determinations the condenser chamber was flushed out several times with the vapor itself before it was finally admitted for the measurements. For the vapors of ethylene chloride and ethylene bromide stopcock *A* was lubricated with a paste made of P_2O_5, SiO_2, and phosphoric acid. Stopcocks *B* and *C* were lubricated with ordinary vacuum stopcock lubricant of the rubberized type.

(c) Pressure measurements were made by means of a null gauge of the glass diaphragm type described by Daniels.[16] This gauge, with the glass diaphragm and the platinum wires leading from it, is shown in Fig. 3. The vapor side of the gauge was connected directly with the large tube leading to the condenser chamber. Steam was passed around the gauge to prevent condensation of vapor inside. The other side of the gauge was connected to a mercury manometer for reading the pressure. A system of stopcocks leading both to the atmosphere and to the vacuum system allowed adjustment of the pressure to the null point.

A gauge of this type always has an additive correction factor which must be determined in order to convert manometer readings at the null point into actual pressures. This correction factor was obtained when there was no vapor in the apparatus by connecting the gauge and manometer system to the inside system through stopcock *B*, allowing carbon dioxide to flow into both systems to any desired pressure, (measured now on the manometer) and then closing stopcock *B* and adjusting the pressure in the gauge and manometer system to the null point. The difference between the actual pressure and the pressure at the null point would then be the correction. The gauge was checked in this way after every two or three hours of operation. With a gauge of this type no vapors come into contact with the mercury manometer, the manometer can be operated at room temperature, and no mercury vapor enters the inside of the apparatus.

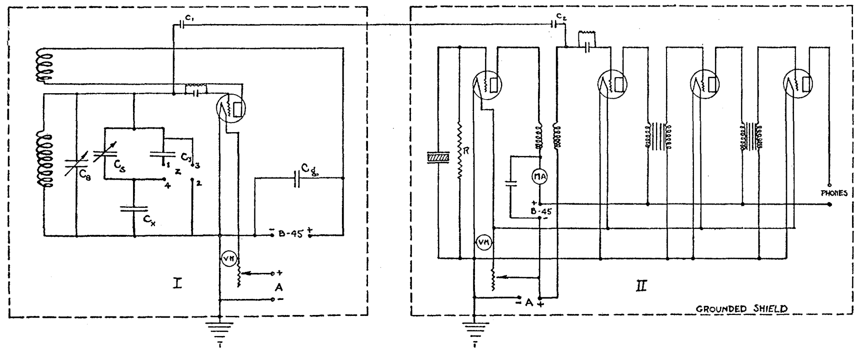

Fig. 4.

(d) The condenser chamber was mounted inside a verticle tube electric furnace. The furnace tube was of iron and was about four inches in diameter and sixteen inches long. It was closed at the top and bottom with metal ends and was grounded, thus serving as a shield for the condenser. The heating elements were nichrome wire wound non-inductively. There were about six or seven inches of insulation surrounding the tube. The heating current was drawn from a 220 volt a.c. circuit and was controlled by several *glow-coil* resistances and two slide wire rheostats. Temperature control was obtained by merely setting the resistance in the circuit and allowing the temperature to become constant.

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[16] Daniels, J. Am. Chem. Soc. **50**, 1115 (1928).

Temperature measurements were made by means of two chromel-alumel thermocouples held against the outside of the condenser chamber at the points lettered T in Fig. 3. The cold junctions were kept in cracked ice and the voltage readings were made by means of a Leeds and Northrup Type-K potentiometer using a wall galvanometer.

(e) The dielectric constants were determined from capacity measurements made by the method of Pungs and Preuner.[17] The electrical apparatus was the same as that used and described by Schwingel and Williams,[18] and is shown in Fig. 4.

A rough control condenser C_8, a variable precision condenser C_s, a fixed mica condenser C_y of comparatively large capacity, and the vapor condenser C_x form the capacity of circuit I. The control condenser C_8 is used to adjust the capacity to any desired point on precision condenser scale, and is left fixed for any series of determinations. The total series capacity of the part of the circuit containing the vapor condenser C_x is given by:

$$1/\text{total capacity} = 1/C_x + 1/(C_y + C_s). \tag{11}$$

Let ΔC_x represent the change in the capacity of the vapor condenser C_x on the admission of a vapor and let ΔC_s represent the change in the reading on the precision condenser required to bring the circuit back to the original total capacity. Then,

$$1/\text{total capacity with vapor} = 1/\text{total capacity evacuated}.$$

From Eq. (11):

$$\frac{1}{C_x + \Delta C_x} + \frac{1}{C_y + C_s + \Delta C_s} = \frac{1}{C_x} + \frac{1}{C_y + C_s}\,. \tag{12}$$

Solving for ΔC_x:

$$\Delta C_x = \frac{C_x^2 \cdot \Delta C_s}{(C_y + C_s)^2 + (C_y + C_s + C_x)\Delta C_s}\,. \tag{13}$$

In Eq. (13) any capacity in the leads from the vapor condenser will be included in C_x. As we shall consider C_x as the true capacity between the plates of the vapor condenser it will be necessary to replace C_x in (13) by $C = C_x + X$, where X is the lead capacity. Eq. (13) then becomes:

$$\Delta C_x = \frac{C^2 \Delta C_s}{(C_y + C_s)^2 + (C_y + C_s + C)\Delta C_s}\,. \tag{13'}$$

Dielectric constant values can now be obtained from the equation

$$\epsilon - 1 = \Delta C_x / C_x. \tag{14}$$

Combining Eqs. (13′) and (14):

$$\epsilon - 1 = \frac{C^2}{(C_y + C_s)^2 + (C_y + C_s + C)\Delta C_s} \cdot \frac{\Delta C_s}{C_x}\,. \tag{15}$$

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[17] Pungs and Preuner, Phys. Zeits. **20**, 543 (1919).

[18] Schwingel and Williams, Phys. Rev. **35**, 855 (1930).

Assuming that $(C^2/C_x)=C$, and taking the reciprocal of both sides of Eq. (15):

$$\frac{1}{\epsilon-1}=\frac{(C_y+C_s)^2}{C}\cdot\frac{1}{\Delta C_s}+\frac{(C_y+C_s)}{C}+1.$$

Let the constant coefficient, $(C_y+C_s)^2/C=a^2$; then

$$(C_y+C_s)/C=a/C^{1/2}.$$

Therefore,

$$1/(\epsilon-1)=a^2(1/\Delta C_s)+a/C^{1/2}+1, \tag{16}$$

where ϵ is the dielectric constant, a is a constant of the circuit, C is the capacity of the vapor condenser and the leads, and ΔC_s is the *difference* reading on the precision condenser.

Absolute values of $\epsilon-1$ can be determined from Eq. (15) if values of the capacities C_x, X, C_y and C_s are known. In this work it was thought preferable to determine the constant a from calibrations with carbon dioxide, using Stuart's[19] value of $\epsilon-1$. Having determined a in this manner, $\epsilon-1$ for a vapor is obtained directly from Eq. (16).

The vapor condenser has been described in part a of this section. Its capacity, including lead capacity, was found to be 530 mmf. The fixed condenser C_y was found to be 2834 mmf. In this work condenser C_y was mounted inside a vacuum flask in order to decrease fluctuations due to changes in room temperature and humidity.

The first step in the actual measurement of a dielectric constant is the determination of the constant a. As has already been mentioned, carbon dioxide is admirably suited for this purpose. Stuart's[19] value of $(\epsilon-1)10^6$ for carbon dioxide is 987 at 273°K and one atmosphere. This value was converted to that corresponding to the pressure and temperature of the experiment by multiplying it by the density ratio. We then have, according to Eq. (16):

$$1/(\rho/\rho_0)(987)10^{-6}=a^2(1/\Delta C_s)+a/C^{1/2}+1,$$

where ρ is the density under experimental conditions and ρ_0 is the density under standard conditions. The quotient ρ/ρ_0 was calculated from Berthelot's equation.

The procedure followed was to make two or more determinations of the constant a in this manner at each temperature at which vapor determinations were made. After the whole temperature range of the apparatus had been covered all of the a values were averaged and the average was used to calculate the dielectric constants of the vapor at the several temperatures by Eq. (16). The vapors of the ethylene halides were run in a manner similar to carbon dioxide, readings being taken first with the apparatus evacuated, then with the vapor in the apparatus at a desired pressure, and finally after re-evacuation. In this manner the quantity ΔC_s could be determined for the several capacity balances.

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[19] Stuart, Phys. Zeits. **47**, 457 (1928).

The molar polarization P is calculated from the equation

$$P = [(\epsilon - 1)/3](M/\rho).$$

The quantity (M/ρ) is obtained from Berthelot's equation,

$$M/\rho = C_1(T/p) + C_2 - C_3(1/T^2).$$

The constants of this equation are given below:

$$C_1 = 760R \text{ (if } p \text{ is in mm)} = 62370$$

	Ethylene chloride	*Ethylene bromide*
$C_2 = 9RT_c/128p_c =$	61.2	48.8
$C_3 = 54RT_c^3/128p_c =$	11.60×10^7	9.8×10^7
$R = 82.07$ cc. atmos./deg.		
(Crit. temp.) $T_c{}^* =$	562.2°K	583.0°K
(Crit. press.) $p_c{}^* =$	53.06 atmos.	68.99 atmos.
*From	Nadejdine (1887)	Vespignani (1903)

SOURCES OF ERROR

Pressure

For carbon dioxide the pressures were read directly on the mercury manometer because it was not necessary to use the null gauge with a noncondensing gas. Using a reading glass the manometer reading was accurate to ±0.2 mm. For vapor pressure readings the null gauge was necessary. However, as this could be set as closely as the manometer could be read, the accuracy here was also ±0.2 mm. There should be no systematic errors in pressure readings because the null gauge was frequently checked. Of course, at both high and low temperature extremes such an error would develop, due to chemical change in the vapor in one case, and adsorption on the condenser cylinders in the other. In these cases the pressure would no longer be an indication of the amount of material between the condenser cylinders.

Temperature

Thermocouple readings on the potentiometer could be checked without difficulty to ±0.002 millivolts. This corresponds to ±0.05°K. The two thermocouples used were calibrated against a third chromel-alumel thermocouple which had just been calibrated in steam, tin, cadmium, and zinc. The calibration points were sharp and probably as accurate as the temperature values given for them in the literature. Temperatures were reported to the nearest degree because this is within the limit of accuracy of the capacity readings.

Capacity

The pertinent reading was ΔC_s, the difference between the precision condenser readings when the apparatus was evacuated and when it was filled with gas or vapor. The precision condenser could be read to ±0.1 of a scale division. As ΔC_s was reported in tenths of a scale division the reading accuracy was ± 1. There are no systematic errors in $\epsilon - 1$ due to the method of calculation, because Eq. (16) does not involve any simplifying assumptions. Of course the practice of calibration with carbon dioxide depends upon the dielectric constant of this gas remaining constant over the temperature range used. This has been attested to by numerous investigators. It is further supported by the constancy of the a calculated from the determinations on carbon dioxide.

The accuracy of the total polarization P can be estimated by an analysis of the values of the constant a^2 obtained in a series of determinations on carbon dioxide. The least accurate of these series gave a mean absolute deviation of 2 percent.

PURIFICATION OF MATERIALS

Carbon dioxide was taken from a commercial cylinder and passed through concentrated sulphuric acid and a P_2O_5 tower.

TABLE II. *Data on ethylene chloride.* Run No. 1.

Temp. °K	$(1/T)\times 10^3$	Press. (mm)	ΔC_s	$(\epsilon-1)\times 10^6$	P (cc)
297.5		52.7	314	473	55.5
297.6		55.3	337	507	56.6
297.6		57.5	348	523	56.1
297.6		54.8	331	498	56.1
297.7		49.4	292	440	55.0
297.9		47.0	287	432	56.7
297.9		49.6	302	456	56.8
297.9		52.4	319	488	57.6
297.8		48.3	293	449	57.5
Av. 298	3.36				57.0
345.8		54.2	264	399	52.8
345.9		61.3	301	454	53.1
345.5		112.6	558	830	52.9
345.6		106.4	529	787	53.0
Av. 346	2.89				53.0
395.3		332.4	1458	2070	50.8
395.2		327.6	1450	2060	51.2
395.4		329.2	1471	2080	51.4
393.0		423.1	1909	2650	50.6
393.0		324.5	1468	2080	52.0
393.3		318.2	1431	2030	51.7
Av. 394	2.54				51.3
447.8		112.2	424	635	52.7
447.9		109.1	400	600	51.0
448.3		158.0	581	863	50.6
448.4		157.9	576	855	50.2
Av. 448	2.23				51.1
495.5		80.3	264	399	51.1
495.7		89.5	294	444	50.9
Av. 496	2.02				51.0

TABLE III. *Data on ethylene chloride.* Run No .2.

Temp. °K	$(1/T)\times 10^3$	Press. (mm)	ΔC_s	$(\epsilon-1)\times 10^6$	P (cc)
588.6		171.4	522	733	52.3
587.2		161.0	484	681	51.5
587.5		164.0	437	617	45.8
Av. 588	1.70				49.9
533.2		192.8	611	854	49.0
532.2		177.5	583	815	50.7
531.6		171.1	565	791	51.0
Av. 532	1.88				50.2
495.2		171.7	608	850	50.9
495.5		170.8	606	847	50.9
Av. 495	2.02				50.9
392.9		130.8	590	826	51.4
393.8		128.6	586	814	51.6
Av. 393	2.55				51.5

TABLE IV. *Data on ethylene bromide.* Run No. 1.

Temp. °K	$(1/T)\times 10^3$	Press. (mm)	ΔC_s	$(\epsilon-1)\times 10^6$	P (cc)
298.5		11.1	75	114	64
298.6		10.8	75	114	66
298.6		11.0	90	137	77
298.6		10.0	75	114	71
298.7		10.2	78	119	72
Av. 299	3.35				70
346.6		21.8	92	140	45.4
346.6		20.4	89	137	47.9
346.7		20.0	84	128	46.2
Av. 347	2.88				46.5
401.0		19.8	74	113	47.6
401.0		54.5	205	310	47.4
Av. 401	2.50				47.5
449.2		121.4	391	587	45.2
449.3		125.6	406	609	45.2
Av. 449	2.23				45.2
490.3		87.7	314	472	54.8
490.4		93.9	336	505	54.7
Av. 490	2.04				54.8

Ethylene chloride (from the Eastman Kodak Company) was washed twice with normal NaOH and three times with water. It was then dried over fused $CaCl_2$ for several days and fractionally distilled. The vapor of the distillate was kept in contact with P_2O_5 for several days. The liquid was then distilled directly into the apparatus as described above. B.P. 82.3−82.6°C.

Ethylene bromide (from the Eastman Kodak Company) was treated in the same way as the ethylene chloride except that the distillation was carried out under reduced pressure.

TABLE V. *Data on ethylene bromide.* Run No. 2.

Temp. °K	$(1/T)\times 10^3$	Press. (mm)	ΔC_s	$(\epsilon-1)\times 10^6$	P (cc)
611.9		130.1	324	510	49.8
613.2		103.6	254	400	49.2
Av. 612	1.64				49.5
562.2		89.4	410	642	84.0
562.2		61.7	283	447	84.6
Av. 562	1.78				84.3
494.5		109.3	481	750	70.5
494.9		89.8	391	613	70.2
Av. 495	2.02				70.4
454.0		87.0	285	449	47.3
454.2		80.1	268	422	49.8
Av. 454	2.21				48.6
425.5		80.5	265	419	45.9
425.2		71.8	238	376	46.3
425.2		65.2	224	354	47.9
Av. 425	2.36				46.7
392.3		67.1	249	392	47.6
392.0		67.4	248	391	47.3
Av. 392	2.55				47.5
363.5		45.4	196	311	51.7
363.4		46.5	202	320	51.9
Av. 363	2.76				51.8

CALCULATIONS WITH ETHYLENE CHLORIDE DATA

The Debye linear equation for the polarization as a function of the temperature is, $P=23.9+B/T$, where the value $A=23.9$ for the deformation polarization is that obtained by Hitchcock[20] for the solid substance and is,

TABLE VI.

Temp. °K	P (cc)	B	$\mu\times 10^{18}$ e.s.u.
298	57.0	9,880	1.27
346	53.0	10,080	1.28
394	51.3	10,790	1.32
448	51.1	12,200	1.41
495	50.9	13,380	1.48
532	50.2	14,200	1.52
588	49.9	15,250	1.57

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[20] Hitchcock, Quoted by Smyth, J. Am. Chem. Soc. **53,** 4242 (1931).

furthermore, in good agreement with estimates by the optical method. The constants B calculated from the experimental points, and the corresponding moments μ are given in Table VI.

The application of Meyer's equation will now be described, again taking the deformation polarization to be 23.9. Eq. (9) then becomes

$$P = 23.9 + B'(1/T) + B'C(1/T)^2.$$

The constants in this equation can be obtained from two experimental points. These points were selected so as to give the best approximation to all the experimental results.

Points selected.

$1/T$	$(1/T)^2$	P
2.02×10^{-3}	4.08×10^{-6}	51.0
2.55	6.50	51.5

The results of the calculation are $B'=23.3\times10^3$ and $B'C=4.89\times10^6$, so that the equation for the total polarization is

$$P = 23.9 + 23{,}300(1/T) - 4{,}890{,}000(1/T)^2.$$

The equation for the moment is,

$$\mu^2 = (9k/4\pi N)[23{,}300 - 4{,}890{,}000(1/T)].$$

From this equation the values of μ in Table VII are obtained. Assuming the valence angle θ to be 70° the characteristic moment μ_1 for $C-Cl$ can be obtained from:

TABLE VII.

T	$(1/T)10^3$	$\mu\times10^{18}$ e.s.u .
298	3.36	1.05
346	2.89	1.22
394	2.54	1.33
448	2.32	1.42
495	2.02	1.48
532	1.88	1.52
588	1.70	1.56
(∞)	(0.00)	(1.94)—for free rotation

$$B' = (4\pi N/9k)2(\mu_1 \sin\theta)^2,$$

with the result that

$$\mu_{C-Cl} = 1.46 \times 10^{-18} \text{ e.s.u.}$$

CALCULATIONS WITH ETHYLENE BROMIDE DATA

The Debye linear equation in this case is, $P=29.7+B(1/T)$, where the deformation polarization is 29.7.[10] The individual experimental points, substituted in this equation give the results of Table VIII.

TABLE VIII.

Temp. °K	P (cc)	B	$\mu \times 10^{18}$ e.s.u.
347	46.5	5830	0.97
392	47.5	6980	1.05
401	47.5	7130	1.07
425	46.7	7220	1.08
449	45.2	6960	1.04

In applying Meyer's equation to the ethylene bromide data it was found that the points for the higher temperatures cannot fall on a parabola whose constant A has the value 29.7 and which represents the more reliable data at the lower temperatures. For this reason, the Meyer equation was applied only to the points corresponding to the lower temperatures in the case of ethylene bromide.

Points selected.

$(1/T)$	$(1/T)^2$	P
2.5×10^{-3}	6.25×10^{-6}	47.5
2.88	8.29	46.5

The equation for the total polarization is,

$$P = 29.7 + 15600(1/T) - 3{,}390{,}000(1/T)^2,$$

and the equation for the moment becomes,

$$\mu^2 = (9k/4\pi N)[15600 - 3{,}390{,}000(1/T)].$$

From this equation the values of (μ) in Table IX are obtained:

TABLE IX.

T	$(1/T)10^3$	$\mu \times 10^{18}$ e.s.u.
357	2.8	0.99
385	2.6	1.05
417	2.4	1.10
455	2.2	1.15
(∞)	(0.0)	(1.59)—for free rotation.

Since $B' = 15600$ and $\theta = 70°$,

$$\mu_{C-Br} = 1.20 \times 10^{-18} \text{ e.s.u.}$$

DISCUSSION OF RESULTS

The results of Zahn and Sänger for the vapors and the results of Smyth and Meyer for solutions are plotted, together with our results, in Fig. 5. The dashed curves represent the experimental curves of the various investigators while the full curves are the parabolas used in the calculation of our results. The circles represent results from vapor determinations and the squares are results from solutions. The horizontal line separates the ethylene chloride points from those for ethylene bromide. Results for both compounds are plotted on the same axes and to the same scale. The low temperature values for the vapor and the high temperature values for the solutions are probably the least accurate.

For ethylene chloride our two points at the lowest temperatures undoubtedly are high due to adsorption of vapor on the condenser cylinders. This was confirmed by purposely coating the condenser cylinders with some thermal decomposition products of the vapors by admitting vapor to the condenser chamber at 400°C. With the adsorptive properties of the surface increased in this manner the P values obtained at the low temperatures were considerably higher than those shown on the graph. The range of temperature available for the investigation of ethylene bromide was much less than that for ethylene chloride. The erratic effects at high and low temperatures are indicated by the high values of the polarization P in Tables IV and V.

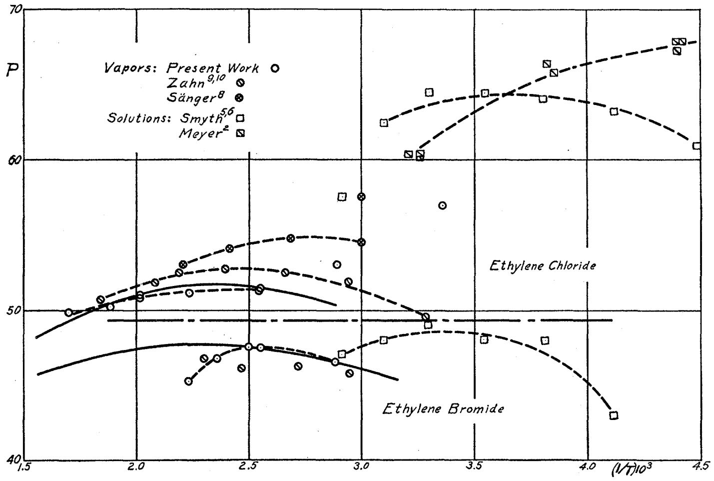

Fig. 5.

The dashed curves represent our interpretation of the experimental data reported by other investigators and by us. They support the theory that this type of compound should have a nonlinear relation between P and $1/T$.

For ethylene chloride the full curve on the graph, representing a parabolic relation between P and $1/T$ and calculated from our data, is a fair approximation to the experimental points. This theoretical curve has a greater curvature than the experimental curve and the maxima do not come at the same place. This is undoubtedly due to the particular selection of the deformation polarization in the calculation of the theoretical curve. A parabola could be drawn through three points on the experimental curve, and in this way the constant A in the equation could be evaluated directly from experiment. However, this procedure could hardly be expected to give an accurate measure of the deformation polarization.

The characteristic moment of (1.46×10^{-18}) for the $C-Cl$ bond, obtained from the constant B', compares well with the value of (1.5×10^{-18}), usually accepted. However, the figure (1.46×10^{-18}) is low compared to the experimental moment of methyl chloride, which is (1.86×10^{-18}) according to the tables of Smyth.[21]

Although our experimental points for ethylene bromide fall on a smooth curve it will be noticed that there is a rather sharp change in curvature at the peak. This, together with the large slope of the curve to the left of the peak, indicates that the two points for the higher temperatures may be too low. Even a straight line through these two points would give an intercept too small for the deformation polarization.

The constant B' for the parabola chosen as the representation of the data gives a characteristic moment for the C-Br bond of (1.20×10^{-18}). This seems low compared to the value of (1.5×10^{-18}) usually accepted. In this connection, however, the question arises as to why the bonds C-Cl and C-Br should both have characteristic moments of (1.5×10^{-18}) when the moments of the corresponding methyl compounds are (1.86×10^{-18}) and (1.45×10^{-18}), respectively.[21] It may be worth while to point out that the ratio of the characteristic moments obtained from ethylene chloride and ethylene bromide is very close to the ratio of the moments for the methyl compounds. Thus,

$$(\mu_1 \text{ for } C - Br)/(\mu_1 \text{ for } C - Cl) = 1.20/1.46 = 0.82$$

$$(\mu \text{ for } CH_3Br)/(\mu \text{ for } CH_3Cl) = 1.45/1.86 = 0.78.$$

The Table X contains a comparison of our moments for ethylene chloride calculated by the optical method and by the parabolic equation, with those reported by Zahn[9] for the vapor. The moments of Zahn were obtained by graphical interpolation for the temperatures listed in our table. Zahn calculated his moments by means of Eq. (2''). Since his experimental curve for the polarization P agrees very well with ours his values for the moment can be used as a comparison of the method of calculation. The results of all three columns approach each other at the higher temperatures, while at lower temperatures the first and third columns deviate from the second and from each other. The optical method is definitely the least reliable.

TABLE X. *Values of* $\mu\times10^{18}$. *(Ethylene chloride.)*

Temp. °K	Optical method	Parabolic equation	Zahn
298	1.27	1.05	1.10
346	1.28	1.22	1.25
394	1.32	1.33	1.36
448	1.41	1.42	1.44
495	1.48	1.48	1.49
532	1.52	1.52	1.53
588	1.57	1.56	
(∞)		(1.94)	

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[21] Smyth, *Dielectric Constant and Molecular Structure*, Chemical Catalog Co. (1931).

The comparison of μ values calculated for ethylene bromide vapor by the optical method, by the method of the parabola, and as reported by Zahn[10] are given in Table XI. These results cannot be used for a study of the several methods of calculation because the different columns are not based upon the same experimental points. In view of this it is surprising how well they agree.

TABLE XI. *Values of* $\mu \times 10^{18}$. *(Ethylene bromide.)*

Temp. °K	Optical method	Parabolic equation	Zahn
357	0.99	0.99	0.98
385	1.04	1.05	1.01
417	1.08	1.10	1.05
455	1.02 ?	1.15	1.13 ?
(∞)		(1.59)	

The striking thing about the results for ethylene chloride, both in solution and as vapor, is that, with the exception of a few points in individual cases, they could all be represented as a family of parabolas having a common intercept. The parabola used by us would be a typical one for the family. The difference in the various parabolas is to be found in the heights and positions of the maxima. The same thing could probably be said for the data on ethylene bromide. The difference between the results for vapor and solution appears to be the same type of difference but of a larger order of magnitude. The horizontal position of the maximum is governed by the constant C in the equation. This can be seen at once by setting the derivative with respect to $1/T$ equal to zero. It has been pointed out that the constant C is a function of structural constants of the molecule. Consequently the difference between the curves for the vapor and for solutions may be due to some structural change within the molecule when it is dissolved. The difference between the results with the vapor and with solutions for ethylene bromide is much less than in the case of ethylene chloride. This might be expected on the above basis due to the heavier bromine atoms resisting structural changes more strongly than the chlorine atoms. It is not meant to suggest here that the discrepancies between different experiments with the vapor are due to structural changes since these differences are of the order of the absolute experimental error.

CONCLUSIONS

(1) The results of the present experimental work are in accord with previous work which shows both ethylene chloride and ethylene bromide to give a nonlinear relationship between the total polarization P and the reciprocal of the absolute temperature $(1/T)$.

(2) At the lowest temperatures adsorption on the condenser cylinders tends to give high values of the total polarization and thus tends to decrease or even reverse the curvature of the P *vs.* $1/T$ relation.

(3) At the highest temperatures ethylene bromide vapor gives abnormally high values for the total polarization, due, it is supposed, to the beginning of a thermal decomposition of the material.

(4) The relation between the total polarization P and the reciprocal of absolute temperature $1/T$ for the ethylene halides can be represented by an equation of the form

$$P = A + B'(1/T) - B'C(1/T)^2.$$

This equation should be applied to such systems in which the relationship between P and $1/T$ is nonlinear.

(5) The differences between the P *vs.* $1/T$ relationships for vapor and for solution can possibly be explained as due to changes in the internal structure of the molecule in question, due to the influence of the solvent.

(6) The theoretical ideas presented permit the calculation of the characteristic moments of the C-Cl and the C-Br bonds from the experimental data. In this computation it is assumed that the angle between the line joining the centers to the two carbon atoms and the direction of the carbon to halogen bond is that required by the normal undeformed tetrahedra used to represent the spatial configuration of the molecule.