FEBRUARY 15, 1932 PHYSICAL REVIEW VOLUME 39

A DETERMINATION OF THE TOTAL ELECTRIC POLARIZATION AND THE ELECTRIC MOMENTS OF CERTAIN ORGANIC MOLECULES

By Louis M. Heil
Mendenhall Laboratory of Physics, Ohio State University

(Received September 14, 1931)

Abstract

An investigation has been made of the effect of temperature on the dielectric constants and densities of bromobenzene and iodobenzene in dilute solution with hexane and of hexane, and of m-p-o-xylenes as pure liquids.

The values of the electric moments and the validity of the Debye law: The values obtained for the electric moments are as follows; p-xylene, 0; m-xylene, 0.34×10^{-18}; o-xylene, 0.44×10^{-18}; bromobenzene, 1.35×10^{-18}; iodobenzene, 1.25×10^{-18}. In every case it was found that the Debye law, $P=P_0+a/T$, was valid.

Variation of the electric moment with variation of the atomic weight of a substituted atom; The results of this investigation give additional evidence of the rule that, as the atomic weight of a substituted atom is increased, the electric moment of the molecule decreases.

Change of induced polarization with the temperature. Evidence has been deduced which suggests that the induced polarization may be a function of the temperature and that this effect may neutralize or diminish the effect of a small dipole.

Introduction

The total polarization of a molecule is generally assumed to consist of three parts; (1) the electronic polarization, which is ascribed to the oscillatory motion of the electrons in the atom under the action of the alternating field of the exciting radiation, (2) the atomic polarization, produced by the vibration of the atoms or ions under the action of the alternating field, (3) the dipole polarization, which is ascribed to an electrically unbalanced molecule which is free to oscillate as a whole.

According to the Debye theory the total polarization P is,

$$P = P_e + P_a + P_d \tag{1}$$

where P_e is the electronic polarization; P_a the atomic polarization; P_d the dipole polarization. $P_d=(4/9)\pi Nu^2/kT$ where N is Avogadro's number; u the electric moment of the molecule; k the Boltzmann constant per molecule. The value of the total polarization can be obtained, after a measurement of the dielectric constant and density of a substance at a certain temperature, from the Clausius-Mossotti relation,

$$P = \frac{e-1}{e+2}\times\frac{M}{d}\,. \tag{2}$$

This total polarization P may be measured at any temperature T by a method like that used by Smith,[1] Stranathan,[2] or Williams.[3] From Cauchy's

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[1] Smyth, J.A.C.S. **50**, 536 (1928).

[2] Stranathan, Phys. Rev. **31**, 653 (1928).

[3] Williams and Krchma, J.A.C.S. **49**, 1676 (1927).

relation between the index of refraction and the wave-length, $n=A+B/\lambda^2$, it is possible to estimate the index of refraction for infinite wave-length. The electronic polarization can then be calculated from the Lorentz-Lorenz relation,

$$P_e = \frac{n^2-1}{n^2+2} \times \frac{M}{d} \cdot \qquad (3)$$

Since the total and the electronic polarizations are then known, the electric moment can be calculated provided that the atomic polarization is assumed to be zero and the electronic polarization remains constant. However, the atomic polarization is not known to be zero and the calculation of the electric moment on this basis gives values which are a little too high, the difference depending on the magnitude of the atomic polarization.

The total polarization may also be measured over as large a range of temperature as possible. Then by making use of relation (1) we get

$$P = P_0 + a/T$$

where $P_0=P_e+P_a$ and $a=(4/9)\pi N u^2/k$. By plotting the total polarization times the absolute temperature against the temperature we get a straight line whose intercept on the vertical axis is a and whose slope is P_0. In this method the electric moment of the molecule is determined independently of the electronic and atomic polarizations provided these polarizations are not functions of the temperature. The sum of the atomic and electronic polarizations is also determined and if the electronic polarization is calculated the atomic polarization can be determined.

In the case of associating substances it is necessary to make measurements on the polarizations of dilute solutions of the polar substance in a non-polar solvent. These polarizations are then plotted against the concentration and the value for zero concentration is determined by extrapolation. The non-associating substances permit their polarizations to be measured in the pure state.

It was the purpose of this investigation to determine the electric moments and an estimate of the atomic polarization of a number of organic molecules. The molecules studied were, bromobenzene and iodobenzene in dilute solution with hexane, and p-xylene, m-xylene, and o-xylene as pure liquids. The bromobenzene and iodobenzene were chosen to complete the monohalogen substituted group since chlorobenzene has carefully been worked out by Smyth.[4] The molecules p-xylene, o-xylene and m-xylene were investigated to determine their electric moments by the method of temperature variation in order to find the effect of the position of the substituted radical. The molecules p-xylene, o-xylene and m-xylene are non-associating and can be investigated in the pure state.

EXPERIMENTAL

The method for determining the dielectric constants of the liquids and solutions is indicated in Fig. 1. The apparatus consisted essentially of a substitution bridge, a 476 kilocycle oscillator and a detector.

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[4] Smyth and Morgan, J.A.C.S. **50**, 1547 (1928).

The oscillator.

The oscillator O consisted of one oscillatory circuit whose output was amplified by two tubes in parallel. The output of these tubes was in turn inductively coupled to the bridge. The oscillatory circuit was maintained at a fixed frequency by means of a quartz crystal giving a frequency of 476 kilocycles.

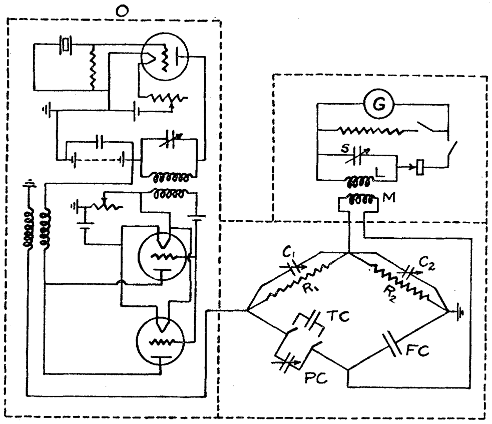

Fig. 1. A diagram of the circuit.

The bridge.

The bridge consisted of two 1000 ohm resistances forming R_1 and R_2 one path of the bridge with a variable capacity C_1 and C_2 across each resistance. In the other path of the bridge there was a parallel set of condensers, consisting of the test condenser TC and a precision condenser PC, in series with a fixed capacity of 1400 mmf.

The detector.

The detector circuit consisted of a coil L inductively coupled to a coil M across the bridge. A condenser S connected in parallel with the coil L was adjusted to give parallel resonance for the frequency of 476 kilocycles. The point of balance was determined by means of a high sensitivity galvanometer and a carborundum crystal.

The test condenser.

The test condenser consisted of three concentric brass cylinders of diameters 3.0, 3.2, and 3.4 cm. The length of the outer two was 15 cm and of the inner 13 cm. The outer two were connected together by means of a circular brass ring soldering them at the top and bottom. The upper part of the outer cylinders was cut away so that there could be a free circulation of the cooling liquid around the condenser. The connection to the inner plate was made through a brass tube with a glass capillary as an insulator. The condenser was immersed in a cooling bath consisting of solid carbon dioxide and alcohol in a Dewar flask. The solutions were cooled to the lowest desired temperature for the initial measurement and then the temperature was increased by means of a heating coil immersed in the bath. The temperatures were measured by means of a copper-constantin thermo-couple and a White potentiometer.

Measurement of densities.

The densities of the solutions and liquids were measured by means of a pycnometer similar to that used by Isnardi.[5] It was made of Pyrex and had a volume of 15 cubic centimeters.

The purity of substances.

Petroleum hexane from Eastman Kodak Company was used entirely for the non-polar solvent. Smyth has shown that in this type of work, there is no error in using the petroleum hexane in place of the pure normal hexane. The brombenzene, iodobenzene and the xylenes were chemically pure Eastman Kodak substances and no further effort was made for purification.

Method of procedure.

The bridge was first brought to a balance by adjusting the precision condenser and the condensers shunting the resistances. (The shunting condensers

TABLE I. *Interpolated values of the dielectric constants and densities* ($d^{t}_{4^\circ}$) *of solutions of bromobenzene and iodobenzene in hexane.*

	Bromobenzene					Iodobenzene				
Mol. fract.	0.04	0.08	0.12	0.16	0.20	0.02	0.04	0.06	0.08	0.10
t°C.										
−60	2.152 0.7652	2.295 0.7969	2.437 0.8283	2.580 0.8603	2.722 0.8923	2.080 0.7560	2.149 0.7785	2.217 0.8010	2.288 0.8235	2.356 0.8460
−50	2.132 0.7561	2.270 0.7877	2.408 0.8190	2.546 0.8509	2.683 0.8828	2.068 0.7471	2.130 0.7693	2.397 0.7920	2.263 0.8144	2.330 0.8368
−40	2.113 0.7471	2.246 0.7785	2.379 0.8098	2.512 0.8415	2.644 0.8732	2.046 0.7383	2.110 0.7601	2.175 0.7830	2.240 0.8055	2.303 0.8276
−30	2.094 0.7382	2.222 0.7693	2.350 0.8004	2.478 0.8320	2.606 0.8638	2.028 0.7289	2.090 0.7509	2.153 0.7740	2.216 0.7961	2.277 0.8183
−20	2.075 0.7290	2.198 0.7600	2.322 0.9711	2.445 0.8227	2.568 0.8543	2.010 0.7200	2.072 0.7419	2.133 0.7649	2.194 0.7869	2.253 0.8090
−10	2.056 0.7200	2.174 0.7510	2.294 0.7819	2.412 0.8133	2.530 0.8447	1.992 0.7105	2.053 0.7330	2.112 0.7557	2.170 0.7777	2.229 0.7996
0	2.037 0.7112	2.150 0.7418	2.265 0.7727	2.379 0.8039	2.492 0.8352	1.957 0.7015	2.033 0.7240	2.090 0.7465	2.147 0.7684	2.402 0.7902
10	2.018 0.7020	2.126 0.7327	2.237 0.7635	2.345 0.7946	2.454 0.8258	1.959 0.6928	2.015 0.7151	2.070 0.7372	2.123 0.7591	2.177 0.7808
20	1.999 0.6931	2.102 0.7235	2.208 0.7542	2.312 0.7850	2.416 0.8162	1.943 0.6838	1.998 0.7062	2.047 0.7280	2.100 0.7497	2.153 0.7714
30	1.980 0.6842	2.078 0.7143	2.180 0.7450	2.279 0.7757	2.378 0.8066	1.928 0.6749	1.978 0.6972	2.027 0.7187	2.077 0.7403	2.128 0.7617
40	1.961 0.6752	2.054 0.7051	2.151 0.7356	2.245 0.7663	2.339 0.7970	1.912 0.6666	1.960 0.6882	2.009 0.7095	2.057 0.7308	2.106 0.7523
50	1.942 0.6662	2.030 0.6960	2.122 0.7262	2.211 0.7568	2.300 0.7875	1.896 0.6576	1.944 0.6792	1.992 0.7002	2.038 0.7214	2.085 0.7427
60	1.923 0.6578	2.006 0.6868	2.093 0.7168	2.177 0.7473	2.261 0.7780	1.881 0.6488	1.927 0.6700	1.973 0.6910	2.016 0.7120	2.061 0.7330

Infinite dilution polarizations of C_6H_5Br and C_6H_5I

	−60	−50	−40	−30	−20	−10	0	10	20	30	40	50	60
C_6H_5I	98.7	96.8	95.3	93.8	92.5	91.2	89.9	88.1	86.5	84.5	82.6	81.3	80.0
C_6H_5Br	100.0	99.0	97.7	96.2	94.4	92.8	91.3	90.0	88.9	87.7	86.2	85.0	84.0

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[5] Isnardi, Zeits. f. Physik 9, 153 (1922).

were necessary since the resistances could not be made entirely non-inductive and non-capacitive and since there are always stray capacity effects.) After this balance was obtained, the test condenser containing the substance whose dielectric constant was to be determined was connected in parallel with the precision condenser. A new balance was then determined by adjusting *only* the precision condenser. The change in the setting of the precision gave the capacity of the test condenser. The correction for the leads and the spacers of the test condenser was determined by filling the condenser with benzene, $e = 2.273$ at 25°C.[4,6,7] The capacity of the test condenser after the correction was made was found to be 217.1 mmf. On account of the low conductance of the substances under investigation, it was never necessary to make any adjustment of the shunting condensers to secure a balance. The probable error in the determination of the dielectric constants was about 0.2 percent.

RESULTS

The experimental values, after interpolation, of the dielectric constants and densities for the low concentrations (0 to 0.2 mols) of bromobenzene and iodobenzene in hexane were found to decrease linearly with the temperature

TABLE II. *Characteristic constants of the substances, p-xylene, o-xylene, m-xylene and hexane.*

t°C	Dielectric constant	Density $d_4{}^0$	Polarization	t°C	Dielectric constant	Density $d_4{}^0$	Polarization
	p-xylene				hexane		
20	2.264	0.8611	36.51	−60	2.010	0.7332	29.58
30	2.249	0.8522	36.59	−50	1.995	0.7244	29.60
40	2.234	0.8433	36.66	−40	1.980	0.7157	29.62
50	2.219	0.8345	36.72	−30	1.966	0.7069	29.66
60	2.024	0.8257	36.79	−20	1.952	0.6982	29.70
70	2.189	0.8169	36.85	−10	1.937	0.6895	29.73
80	2.175	0.8080	36.94	0	1.923	0.6807	29.76
90	2.160	0.7990	37.02	10	1.908	0.6719	29.77
100	2.145	0.7900	37.09	20	1.893	0.6631	29.79
110	2.130	0.7810	37.16	30	1.878	0.6543	29.81
120	2.115	0.7720	37.23	40	1.864	0.6454	29.82
130	2.100	0.7630	37.30	50	1.850	0.6366	29.86
				60	1.836	0.6278	29.89
	o-xylene				m-xylene		
−20	2.701	0.9124	42.06	−40	2.482	0.9145	38.35
−10	2.674	0.9039	42.03	−30	2.462	0.9063	38.35
0	2.648	0.8955	42.00	−20	2.444	9.8978	38.39
10	2.621	0.8872	41.94	−10	2.426	0.8894	38.42
20	2.594	0.8793	41.85	0	2.406	0.8807	38.43
30	2.567	0.8706	41.80	10	2.386	0.8723	38.44
40	2.541	0.8623	41.74	20	2.367	0.8639	38.43
50	2.514	0.8541	41.65	30	2.348	0.8556	38.43
60	2.488	0.8458	41.58	40	2.329	0.8472	38.44
70	2.461	0.8376	41.47	50	2.309	0.8386	38.42
80	2.434	0.8296	41.35	60	2.290	0.8304	38.41
90	2.407	0.8216	41.22	70	2.271	0.8219	38.40
100	2.381	0.8132	41.12	80	2.251	0.8133	38.38
110	2.354	0.8048	40.99	90	2.322	0.8051	38.35
120	2.328	0.7966	40.86	100	2.212	0.7966	38.31
130	2.302	0.7866	40.71	110	2.193	0.7881	38.29
				120	2.174	0.7999	38.25

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[6] Hartshorn and Oliver, Proc. Roy. Soc. 664 (1929).

[7] Errera, Journ. de Physique 304 (1929).

and are given in Table I. The experimental values of the dielectric constants of the pure non-associating substances hexane, p-xylene, o-xylene and m-xylene are given in Table II. The relation of the dielectric constant and temperature is a linear one. The densities of the xylenes were also found to be linear functions of the temperature.

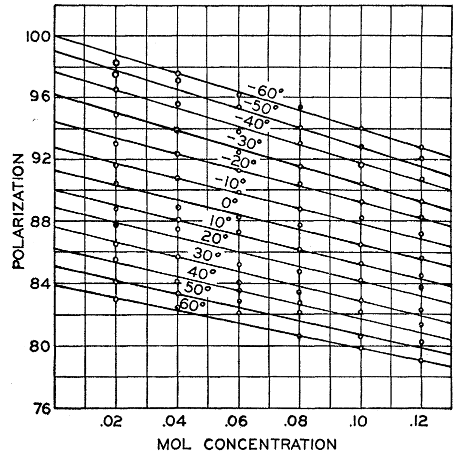

Fig. 2. The extrapolation to infinite dilution of the polarization of bromobenzene

The total polarizations of the binary mixtures, bromobenzene and iodobenzene in hexane, were calculated from the Clausius-Mossotti relation (2) using the effective molecular weight of the mixture. The polarization due to the polar component was then calculated and plotted against the concentration of the polar substance as shown in Figs. 2 and 3. These curves were extra-

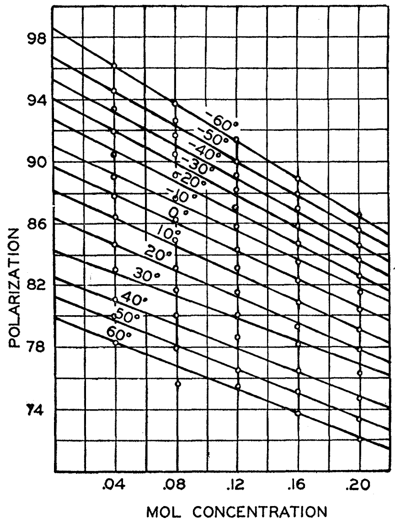

Fig. 3. The extrapolation to infinite dilution of the polarization of iodobenzene.

polated to zero concentration (infinite dilution) and the values P_{2_∞} determined. The polarization increases to a maximum at zero concentration. These extrapolated values of the polarizations are the ones that should satisfy the Debye relation (1).

The total polarizations of the m-o-p-xylenes can be determined from measurements made in the pure state since for these substances Williams has shown that the polarizations of the polar molecule in solution with a non-polar substance is directly proportional to the concentration and they are therefore non-associating.[3]

DISCUSSION OF RESULTS

Comparison with other data.

Table III gives a comparison of the results obtained on the density and dielectric constants with the corresponding results of other observers.

TABLE III.

Substance	Temperature	Density $d^t_{4^0}$	Dielectric constant	Observers
Hexane	60°C	0.6473	1.843	Smyth and Morgan[4]
Hexane	60°C	0.6430	1.856	Morgan and Lowry[9]
Hexane	60°C	0.6278	1.836	Author
p-xylene	25°C	0.8567	2.265	Williams[3]
p-xylene	17°C		2.259	I.C.T.
p-xylene	25°C	0.8545		I.C.T.
p-xylene	25°C	0.8549	2.257	Author
o-xylene	25°C	0.8764	2.507	Williams[3]
o-xylene	25°C	0.8754	2.58	I.C.T.
o-xylene	25°C	0.8749	2.580	Author
m-xylene	20°C		2.392	Isnardi[5]
m-xylene	20°C		2.374	I.C.T
m-xylene	20°C	0.8639	2.367	Author
m-xylene	20°C	0.8642		Landolt-Bornstein

Table IV gives the values of the electric moments and the atomic polarizations of the substances investigated. The value of the moment of bromobenzene has been determined by various observers,[8,10,11,12,13] who have ob-

TABLE IV.

	Electric moment $\times 10^{18}$	Atomic polarization
Hexane C_6H_{14}	0	0.6
p-xylene C_8H_{10}	0 (assumed)	2.3
m-xylene C_8H_{10}	0.34	4.0
o-xylene C_8H_{10}	0.44	4.5
Bromobenzene C_6H_5Br	1.35	13.9
Iodobenzene C_6H_5I	1.25	18.3

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[8] Williams and Allgier, J.A.C.S. **49**, 2416 (1927).
[9] Morgan and Lowry, Journ. of Phys. Chem. **34**, 2385 (1930).
[10] Das and Roy, Ind. Journ. of Phys. **15**, 441 (1930).
[11] Hojendahl, Phys. Zeits. **30**, 391 (1928).
[12] Bergmann, Engel, Sandor, Zeits. f. Phys. Chem. **10** Abt. B p. 106.
[13] Muller and Sack, Phys. Zeits. **31**, 518 (1930).

tained values ranging from 1.49×10^{-18} to 1.56×10^{-18}. All these observations, except that of Das and Roy, were made by the single temperature method. Das and Roy studied bromobenzene in dilute solution with carbon tetrachloride over a temperature range from 10°C to 60°C. Their extrapolated values of the polarization agree with those of the author the difference in the value of the moment determined is due to a lower value of the polarization at temperatures lower than those studied by Das and Roy. The value obtained for the moment of iodobenzene agrees with that obtained by other observers, 1.25×10^{-18} by Walden and Werner,[14] and 1.30×10^{-18} by Bergmann Engel and Sandor,[12] who used the single temperature method.

Effect of different substituents.

The effect of substituting chlorine, bromine and iodine in three different types of molecules is shown in Table V. From this table it is seen that in

TABLE V.

Substituent X	Electric moment $\times 10^{18}$ C_6H_5X	CH_3X	HX
Chlorine	1.52[4]	1.56[9]	1.04[15]
Bromine	1.35 (author)	1.45[9]	0.79[15]
Iodine	1.25 (author)	1.35[9]	0.38[15]

these three series of compounds, C_6H_5X, CH_3X and HX, an increase in the atomic weight of the substituted atom produces a decrease in the electric moment of the molecule. The results obtained for bromobenzene (C_6H_5Br) and iodobenzene (C_6H_5I) are thus in agreement with this effect.

The induced polarization a function of the temperature.

Table II shows an increase in the total polarization with the temperature for the case of p-xylene. Since p-xylene is a symmetrical molecule it should have no electric moment, and its polarization, the sum of the electronic and atomic polarizations, should remain constant. The increase of polarization means that the induced polarization increases with temperature. This increase of the induced polarization with the temperature, in the case of p-xylene, leads to a negative intercept as shown in Fig. 4. The intercepts for the m-xylene and o-xylene molecules correspond to moments of zero and 0.34×10^{-18} respectively. However, since p-xylene is a symmetrical molecule, if the three straight lines in Fig. 4 representing the xylenes, are shifted, so the one representing p-xylene passes ,through the origin, intercepts corresponding to 0.34×10^{-18} and 0.44×10^{-18} as values of moments are obtained for the m-xylene and o-xylene molecules respectively. These results can be interpreted in the following manner; the total polarization of p-xylene increases with the temperature since the induced polarization increases and there is no dipole polarization; in the case of m-xylene the total polarization (see Table II) remains practically constant, since the increase in the induced

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[14] Walden and Werner, Zeits. f. physik. Chemie **12,** Abt. B (1930).

[15] Zahn, Phys. Rev. **24,** 400 (1924).

polarization is just overcome by the small dipole polarization; for o-xylene this dipole polarization is still more prominent and it produces a decrease in the total polarization. Smyth[16] has found the same effect in the case of the normal non-polar paraffins, the total polarization increasing with the temperature at a rate of 1 percent per 100 degrees.

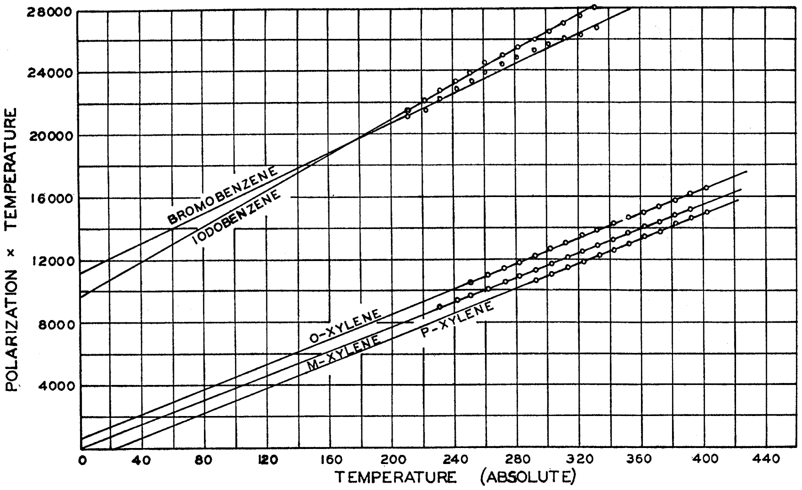

Fig. 4. Relation of polarization times temperature vs. temperature for bromobenzene, iodobenzene, p-m-o-xylenes.

SUMMARY

1. The dielectric constants and densities of dilute solutions of bromobenzene and iodobenzene in hexane have been measured. From these measurements the values of the electric moments and the atomic polarizations have been determined for the bromobenzene and iodobenzene molecules.

2. The dielectric constants and densities of pure p-xylene, m-xylene, o-xylene and hexane have been determined and the electric moments and atomic polarizations of these molecules calculated.

3. Evidence has been given to show that, as the atomic weight of a substituted atom is increased, the value of the electric moment of the molecule is decreased. It has been pointed out that the results of this investigation give additional evidence of this rule.

4. Evidence has been deduced which suggests that the induced polarization is a function of the temperature and that this effect may neutralize or mask the effect of a small dipole.

The author wishes to express his appreciation of the advice and criticism given by Dr. Alpheus Smith and Dr. C. P. Smyth during this investigation.

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[16] Smyth and Stoops, J.A.C.S. **52,** 3546 (1930).