

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Polarity in Certain Hydrocarbon Vapors

BY K. B. McALPINE AND C. P. SMYTH

The measurements in the present paper were carried out in order to examine closely certain important molecules possessing little or no polarity. The dipole moments have been calculated from the dielectric constants determined for the substances in the vapor state, the familiar Debye equation being used. In this equation¹

$$P = a + b/T \quad (1)$$

the polarization $P = \frac{\epsilon - 1}{\epsilon + 2} V$, where ϵ is the dielectric constant and V the molar volume. For an ideal gas, $V = RT/p'$, so that the polarization may be written

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{RT}{p'} \quad (2)$$

The actual pressure p of a gas under observation may be corrected to the pressure p' , which it would exert if it were in the ideal condition and occupying the volume V , by means of the equation

$$p' = p \left[1 + \frac{p}{RT} \left(\frac{a}{RT} - b \right) \right] \quad (3)$$

This equation is derived simply from the van der Waals equation, a and b being the constants of this latter equation, different from the a and b of the Debye equation. Putting in numerical values

$$P = 62,371 \left(\frac{\epsilon - 1}{\epsilon + 2} \right) \frac{T}{p'} \quad (4)$$

where p' is expressed in millimeters.

Experimental Method

As the apparatus employed in measuring the dielectric constants was similar in many respects to that used by Zahn,² no detailed explanation of the symbolic diagram of it in Fig. 1 is given. Two circuits, I and II, were maintained in a condition of sustained oscillation by electron tubes, the wave length used being about 500 meters, corresponding to a frequency of 6×10^6 . The individual frequencies were adjusted so that a beat note of 1000 cycles was produced, which could be picked up by a detector-amplifier system and compared with the 1000 cycle note emitted by a Leeds and Northrup hummer. The reference beat note, relative to which all adjustments in the measuring condenser system were made, was the frequency of the hummer, the identity of the beat note between the oscillators and the note emitted by the hummer being indicated by the absence of throbbing in the ear phones. The two oscillatory circuits were shielded by enclosure in large, wooden boxes covered with galvanized iron. Precise adjustment of the frequency of circuit II was made by turning a grounded brass disk D in such a way as to vary its distance from the circuit, changes of a small fraction of a cycle per second being thus securable. All adjustments of the condensers and switches were made from the outside by means of glass rods passing through the boxes.

(1) Cf. Smyth and Morgan, *THIS JOURNAL*, **50**, 1547 (1928).

(2) Zahn, *Phys. Rev.*, **24**, 400 (1924).

The gas condenser C in Fig. 1 consisted of two concentric cylinders, of pure copper tubing, 0.3 cm. thick and 13.4 cm. long, the outer grounded cylinder having an external

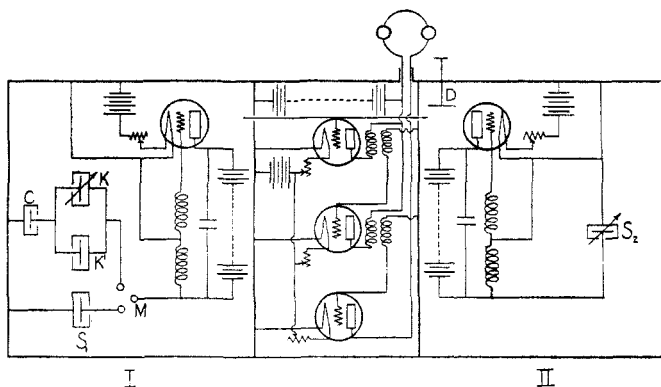


Fig. 1.—Diagram of circuits.

diameter of 6.1 cm. and a separation from the inner of 0.07 cm. The cylinders were, at first, gold-plated, but, as the plate developed imperfections at the higher temperatures used, it was ground off and the pure copper surface employed. When not in use, the

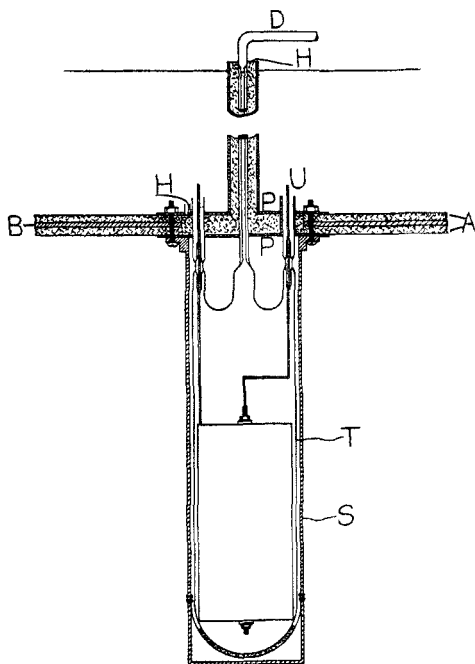


Fig. 2.—Gas condenser and shield.

apparatus was kept filled with nitrogen to prevent gradual oxidation of the copper. The ends of the inner cylinders were fastened with silver solder and a copper rod holding it in place was insulated from the outer cylinder by quartz rings. The outer cylinder was wrapped with a thin sheet of mica, around which was wound a platinum resistance thermometer. The leads from the thermometer coil and those from the condenser were silver-soldered to tungsten wires, which were sealed through four tubes at the top of the thick-walled 65 mm Pyrex tube T enclosing the condenser (Fig. 2). Two of these tubes and the 2 mm. capillary D leading to the vacuum system are shown in Fig. 2. The tube T was mounted in a cylindrical electrostatic shield S, closed at the bottom to prevent oil from coming up around the lead tubes. To prevent convection currents within the shield at high temperatures, it was found necessary to provide the top of the shield with a coil H, heated by

direct current, which was completely shielded from the ungrounded lead U of the condenser by means of grounded brass plates P. S was bolted securely to a cover consisting of two sheets of 6.4 mm. asbestos A, reinforced by a grounded sheet of 3.2 mm.

brass B. The whole was then mounted in a large shielded box into which a large oil heating bath or toluene cooling bath could be inserted without introducing capacity effects. To prevent radiation from the oil-bath from reaching the rest of the oscillatory circuit, the condenser box was situated outside the main generator box, the lead from the condenser being brought through an opening in the latter box and supported by a notched sheet of mica fastened over the opening.

Because of small changes in the distributed capacity and inductance of the oscillatory circuits resulting from changes in the room temperature, the filament heating current, and the plate voltage, the beat note between the oscillators showed a slow and often irregular drift in frequency. In order, therefore, to provide a reference capacity which could be considered as constant during the period of a run, a 1000 $\mu\text{mf.}$ variable air condenser S_1 (Fig. 1) was set in an electrostatic shield immersed in an oil-bath and so connected that the turn of a mercury switch M substituted it in circuit I in the place of the gas condenser system. The beat note could then be brought back to 1000 cycles by adjustment of D in circuit II.

For the manipulation of the gases, a system of reservoirs, traps, and purification tubes was used in connection with a mercury vapor pump. The gas pressure was read on a large mercury manometer provided with a steel scale. Liquids were vaporized in the apparatus from a U-tube which served as a pressure gage in the manner described by Zahn.³

The gas cell C was connected in series with the two parallel capacities K and K' , K being a General Radio Company Type 222 variable precision condenser of 1500 $\mu\text{mf.}$ capacity. The capacity C of the gas condenser when evacuated is made up of a geometrical capacity C_0 , which becomes ϵC_0 when gas is admitted, and a fixed capacity L dependent upon the leads and insulators. When gas is admitted to C , the increase in its capacity ΔC must be balanced by a change ΔK in K in order to hold the frequency constant. The dielectric constant ϵ of the gas is then given by the expression

$$\epsilon - 1 = \frac{C^2}{C_0} \frac{(-\Delta K)}{(K + K' + C)\Delta K + (K + K')^2} \quad (5)$$

in which the value of ΔK is negative.³

The precision condenser K was very carefully calibrated in position in the apparatus by a method similar to that previously described by one of the writers.⁴ The condenser scale divisions, of which there were 2500, were used as convenient units of capacity. The probable error in ΔK was 0.3 scale division. At first, K' consisted of three mica condensers of 1200, 2400 and 4800 $\mu\text{mf.}$ capacity in parallel, but as these condensers showed a slight, irregular variation in capacity with the passage of time they were replaced by two variable air condensers, which showed no change with time. The capacity of these two condensers, which were used at their maximum value, was determined by a careful step-by-step calibration as $K' = 7097 \pm 2$ scale divisions on the precision condenser.

The fixed capacity through the quartz insulators in the gas condenser was calculated from the dimensions and the known dielectric constant of quartz as 7.3 ± 0.7 scale divisions. The capacities of the various leads were very carefully determined by the usual methods of short-circuiting or disconnecting the condensers and of setting up imitation leads. The values expressed in scale divisions for the different capacities involved were $C = 448.6 \pm 0.7$, $L = 23.3 \pm 1.4$, $C_0 = 425.3 \pm 2.1$. An attempt made to determine C_0 and L in the manner commonly used in measurements on liquids by measuring the cell empty and again filled with pure benzene gave less accurate results and was abandoned. The value of K needed in the equation for $\epsilon - 1$ was determined

(3) Zahn, *Rev. Sci. Instr.*, **1**, 299 (1930).

(4) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, Inc., New York, 1931, p. 52.

for a number of settings on the high part of the scale by tuning the oscillators to zero beats, short-circuiting C , and changing K by an amount ΔK until the original frequency was restored. K was then calculated from the equation for series capacities. When all the errors in the calibration and capacity determination are taken into account, it appears that the probable error in the absolute value of $\epsilon - 1$ arising from these causes is 0.9%. The relative error from these causes should be less than 0.2%.

During the course of a run the temperature of the gas cell was maintained constant to 0.02° by means of the bath surrounding it. This control was necessitated by the excellent thermal insulation which, unfortunately, existed between the two cylinders of the condenser. A rapid temperature rise of as much as 0.2° caused an unequal expansion of the two cylinders with a resulting change in capacity, and the temperature change resulting from change in gas pressure made it necessary to delay a capacity reading for half an hour after the pressure change had been effected in order that the temperature might become uniform.

The difficulty of temperature equalization made it impossible to obtain an accurate value for the capacity of the evacuated condenser directly. In the most satisfactory method of obtaining it a reading was taken on the precision condenser with the gas or vapor in the condenser at 20–30 mm. pressure and another at 100–150 mm. When these two precision condenser readings were plotted against p' and a straight line drawn through the points, the intercept of the line at $p' = 0$ gave the vacuum reading. The values of $(\epsilon - 1)/(\epsilon + 2)$ were then calculated directly. When working with vapors at low temperatures, measurements were made at several pressures in order to detect possible condensation. The values of $(\epsilon - 1)/(\epsilon + 2)$ were then plotted against the corrected pressures p' . Any condensation was evidenced by a departure of the points for high pressure from the straight line through the lower points. The effect of any drift in the circuits outside the gas condenser was eliminated by repeating every run in the reverse direction.

In order to determine by actual experiment the accuracy of the measurements, a large number of determinations were made upon air carefully dried and purified by passage through a soda lime tower, and upon carbon dioxide, taken from a cylinder and repeatedly fractionated by condensation with liquid air. The values of $\epsilon - 1$ were reduced to 0° and 760 mm., the perfect gas law being employed for air and the van der Waals equation for carbon dioxide. For air, the average deviation from the mean of twenty-three measurements was 0.41%, and, for carbon dioxide, the average deviation in twenty-one measurements was 0.33%. The values have been compared with the results of fifteen other investigations, of which the two most extended and reliable gave the values shown in Table I for comparison with those of the present investigation. At the bottom of the table are the values of $n_\infty^2 - 1$, n_∞ being the index of refraction extrapolated to infinite wave length. Since, for carbon dioxide, correction has been made for infra-red absorption⁵ and since, for air, this absorption can be neg-

TABLE I
VALUES FOR AIR AND CARBON DIOXIDE

	CO ₂	($\epsilon - 1$) $\times 10^6$ Air	CO ₂ /Air
Zahn ^{2,6}	972	572	1.700
Stuart ⁷	987	582	1.696
McAlpine and Smyth	989	581	1.702
$(n_\infty^2 - 1) \times 10^6$	975 ⁸	575 ⁸	1.696

(5) Fuchs, *Z. Physik*, **46**, 519 (1928).

(6) Zahn, *Phys. Rev.*, **27**, 455 (1926).

(7) Stuart, *Z. Physik*, **47**, 457 (1928).

(8) "International Critical Tables," Vol. VII, p. 5.

lected, $n_{\infty}^2 - 1$ should, in the absence of a dipole moment, be identical with $\epsilon - 1$. The ratio of the value for carbon dioxide to that for air is given in the last column.

The results of the present investigation are approximately 1.5% higher than those of Zahn but differ by less than the small average deviation from the mean from the more recent results of Stuart. The close agreement of the ratio with Zahn's ratio shows the difference in the absolute values to be a matter of the respective calibrations, as this difference is within the limits permitted by the errors assigned to the two calibrations. The recent determination of $(\epsilon - 1) \times 10^6$ for nitrogen, 589, by Andrews⁹ is higher than Zahn's value 580 by just the same amount as the difference between the value for air in the present work and that of Zahn. It appears probable, therefore, that the values of $(\epsilon - 1) \times 10^6$ for air and carbon dioxide are slightly higher than those given for $(n_{\infty}^2 - 1) \times 10^6$.

Purification of Materials

Benzene.—Merck's c. p. crystallizable benzene was shaken repeatedly with concentrated sulfuric acid, water, dilute sodium hydroxide, and more water, dried over calcium chloride, and crystallized three times (m. p. 5.50°). It was then refluxed over phosphorus pentoxide, distilled, refluxed over sodium wire, and distilled again; b. p. 80.2°; n_D^{25} 1.49823.

Toluene.—Merck's c. p. toluene was washed with concentrated sulfuric acid, water, dilute sodium hydroxide solution, and again with water, shaken with pure mercury, filtered, and dried first with calcium chloride, then with phosphorus pentoxide, and, finally, by refluxing over molten sodium and subsequent distillation; b. p. 110.5°; n_D^{20} 1.4955. A second portion treated in the same way, except for the omission of the refluxing over sodium, had the same constants. A third portion was treated like the first except that between the drying with calcium chloride and that with phosphorus pentoxide, it was crystallized in an ether-bath maintained at -105-110°; b. p. 110.5-6°; n_D^{20} 1.49564. This was distilled directly from the sodium into the gas system of the apparatus for the dielectric constant measurements.

Propane and Propylene.—Gases of high purity from the Linde Air Products Company were passed through phosphorus pentoxide into the gas system of the apparatus, where they were repeatedly fractionally distilled.

Experimental Results

When $(\epsilon - 1)/(\epsilon + 2)$ is plotted against p' , which is obtained by use of equation (3), the values of the van der Waals constants being taken from Landolt-Börnstein, the slope of the resulting straight line is used to calculate the polarization, since, from equation (4), it follows that

$$P = 62,371 T \Delta \frac{\epsilon - 1}{\epsilon + 2} / \Delta p' \quad (6)$$

A line was obtained at a given temperature by determining points from pressures of 10-30 mm. up to 800-1100 mm., then down to low pressure again to make sure that no change had occurred during the course of the run. Several such runs were made at each temperature and a value of P obtained from the line for each run. The average value at each tempera-

(9) Andrews, *Physics*, 1, 366 (1931).

TABLE II
MEAN VALUES OF P AND PT

T , °K.	P	PT	T , °K.	P	PT
	Benzene			Toluene	
325.9	26.87	8,757	357.3	34.86	12,455
375.1	27.13	10,176	378.9	34.62	13,118
428.8	27.04	11,594	431.8	34.46	14,880
480.1	26.99	12,940	481.7	34.20	16,474
	Propane			Propylene	
226.7	16.00	3628	245.5	18.76	4606
246.5	16.19	3992	246.1	18.79	4623
293.3	16.11	4726	272.2	18.45	5021
352.4	16.02	5647	303.8	18.18	5523
413.3	16.04	6627	352.2	17.77	6258
485.9	16.07	7810	406.8	17.59	7154
			476.2	17.29	8233

ture given in Table II was used to calculate the values of PT , which, in Fig. 3, are plotted against T . The method of least squares was used to

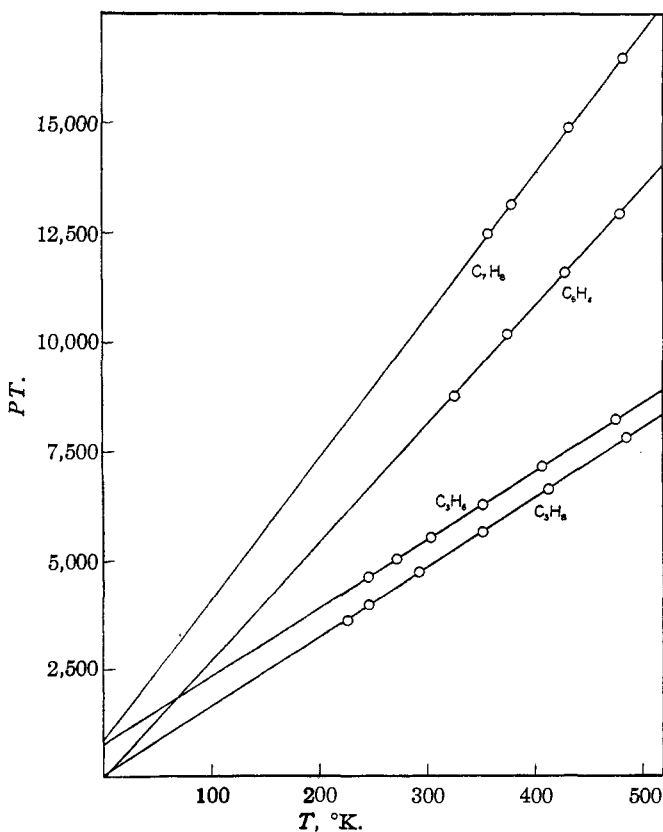


Fig. 3.— PT - T curves.

calculate the values of the constants in equation (1), which are given in Table III. The value of the refraction for infinite wave length, P_E , was obtained by extrapolation from the dispersion data for liquids in Landolt-Börnstein and the values given for the atomic polarization calculated as $P_A = a - P_E$. The electric moment μ was calculated from b as $\mu = 0.0127 \times 10^{-18} \sqrt{b}$, the probable error in the two virtually zero values being 0.05×10^{-18} , and in the other values 0.02×10^{-18} .

TABLE III
VALUES OF FUNDAMENTAL CONSTANTS

Substance	a	P_E	P_A	b	$\mu \times 10^{18}$
C_6H_6	27.0	25.1	1.9	-18	0
C_7H_8	32.5	29.8	2.7	841	0.37
C_8H_{10}	16.0	15.7	0.3	18	0
C_9H_{12}	15.7	15.1	.6	745	0.35

After the submission of these results for publication, a new method for the elimination of error due to deviation from the ideal gas laws was adopted in later work to be described elsewhere. Polarizations calculated by means of the ideal gas law are plotted against the pressure and the curve thus obtained is extrapolated to zero pressure to obtain a polarization value unaffected by deviations from the ideal gas law. In propane and propylene, the deviations are so small that the different method of calculation leaves the results in Table II unaltered. For benzene, the polarization values are lowered about 0.5% by the new method of calculation and, for toluene, about 1.2%. The changes in the constants calculated from these polarizations are shown below to be negligible or almost so.

BENZENE			TOLUENE		
$T, ^\circ K.$	P		$T, ^\circ K.$	P	
325.9	26.77	$a = 27.0$	357.3	34.46	$a = 32.3$
375.1	26.94	$b = -55$	378.9	34.18	$b = 740$
428.8	26.96	$\mu = 0$	431.8	34.02	$\mu = 0.35 \times 10^{-18}$
480.1	26.84	$P_A = 1.9$	481.7	33.84	$P_A = 2.5$

Discussion of Results

The mean value, 27.01, of the polarization of benzene vapor, which is independent of temperature, is slightly higher than the values for the liquid, 26.62 at 10° and 26.78 at 60° ,¹⁰ which increase slightly with rising temperature, and lower than the value for the solid, 28.5 at 0° , found by Morgan and Lowry. The absence of variation with temperature in the polarizations of benzene and of propane is in contrast to the small but definite increase observed in liquid benzene and in marked contrast to the uniform increase observed in all the liquid paraffins which have been studied over a wide range of temperature.¹¹ This difference in behavior between the liquid and the vapor is important since it shows that the increase in polarization with rising temperature in the liquid cannot be due to any direct intramolecular effect of temperature, for such an effect would be

(10) Morgan and Lowry, *J. Phys. Chem.*, **34**, 2385 (1930); Smyth and Stoops, *THIS JOURNAL*, **51**, 3312 (1929); Smyth and Walls, *ibid.*, **54**, 1854 (1932).

(11) (a) Smyth and Stoops, *ibid.*, **50**, 1883 (1928); (b) Smyth and Dornte, *ibid.*, **52**, 3546 (1930).

apparent in the gas also. As the values of P_E for benzene and toluene are calculated directly from measurements on the liquids and those for propane and propylene as the sum of the atomic refractions obtained from measurements on liquids, it is evident that the values of P_A must be regarded as approximate. The most accurate measurements on the refraction of benzene vapor,¹² when extrapolated to infinite wave length, give a value 26.22 for P_E , which gives $P_A = 0.8$, possibly more accurate than the value in Table III and lower than the values 1.5–1.9 obtained as the difference between the solid and the liquid. Similar use of the refractive index determined for propylene by Trautz and Winkler¹³ gives $P_A = 1.0$, higher than the value in Table III. The discrepancies among the results of different investigators of the refraction of vapors make it doubtful whether the P_A values obtained by using the values of the vapor refractions are more accurate than those in Table III, which are certainly comparable with one another.

Krchma and Williams¹⁴ and Williams and Ogg¹⁵ measured benzene in three different solvents, obtaining for the polarization in carbon tetrachloride, 26.7, in carbon disulfide, 28.5, and in hexane, 27.8, and, from these values, using $P_E = 25.8$ and neglecting P_A , values of 0.06×10^{-18} , 0.09×10^{-18} , and 0.08×10^{-18} for the moment of the benzene molecule. An error occurred in these calculations for recalculation from the same data gives 0.21×10^{-18} , 0.39×10^{-18} , and 0.31×10^{-18} , values slightly higher than the figure 0.2×10^{-18} , calculated previously by one of the writers as a value indistinguishable from zero by the method employed.¹⁶ Although it has been generally assumed that the moment of the benzene molecule is zero,¹⁷ it is reassuring to obtain definite experimental evidence that it is within 0.05×10^{-18} of zero. The negative value, -18 , of b in Table III has no significance nor has the positive value 18 for propane, both showing merely that the value of the moment is within 0.05×10^{-18} of zero.

The propane molecule may be pictured as a tetrahedral carbon atom with hydrogens on two apices and methyl groups on two. Two planes of symmetry perpendicular to one another may be drawn through the central carbon atom, but, when a third plane perpendicular to these two is drawn, it is apparent that the two hydrogens are on one side of it and the two methyl groups on the other. Because of the tetrahedral angle, any moment in a C–H bond of one of the methyl groups has a component in the direction of the C–C line equal to one-third of its value. The three C–H bonds of the group have, therefore, a resultant moment equal to that of a single C–H bond. The moments in the C–H bonds of the methyl groups

(12) Wasastjerna, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, **2**, No. 13, 1 (1925).

(13) Trautz and Winkler, *J. prakt. Chem.*, **104**, 44 (1922).

(14) Krchma and Williams, *THIS JOURNAL*, **49**, 2408 (1927).

(15) Williams and Ogg, *ibid.*, **50**, 94 (1928).

(16) Smyth, *ibid.*, **46**, 2151 (1924).

(17) See Ref. 4, p. 106.

would, consequently, cancel moments of equal size in the two C-H bonds on the central carbon and any moment in the molecule as a whole would have to arise from polarity in the C-C bonds, from inequality in the moments of the C-H bonds of the primary and secondary carbons, or from distortion of the tetrahedral structure by repulsion in such a way as to prevent compensation of the moments of the two central C-H bonds by those of the methyl C-H bonds. If propane had the maximum moment, 0.05×10^{-18} , permitted to it by the accuracy of the measurements, it would be equivalent to the effect of the displacement of a pair of electrons 0.005 Å. from a position of symmetry. Although it is likely that the propane molecule may have a very small moment, it is evidently so small that any polarity in the C-C bonds, electrical dissymmetry caused by repulsion between the different parts of the molecule or difference in electronegativity between the hydrogens on the secondary and those on the primary carbons may be regarded as undetectable by means of the electric moment. This result is in harmony with the absence of any detectable moment in the isomers of heptane and with the consequent absence of variation in the electronegativities of the alkyl radicals detectable by this means.¹¹⁸

The value obtained for the moment of toluene is in excellent agreement with the very approximate value 0.4×10^{-18} found for the liquid.^{14,16,18}

The closeness of the accurately determined value¹⁹ for α -butylene, 0.37×10^{-18} , to that for toluene in the present paper and to the 0.35×10^{-18} found for propylene are very striking. It is evident that, although the replacement of a hydrogen by a methyl group in a saturated aliphatic hydrocarbon gives rise to no moment, a similar replacement of a hydrogen attached to an unsaturated carbon gives rise to a definite electrical dissymmetry. Calculation shows that if the C-H bond has a moment of about 0.4×10^{-18} associated with it as commonly supposed,²⁰ inductive effects should give rise to moments of the magnitude found for these unsymmetrical molecules.

The writers wish to express their gratitude to Dr. C. T. Zahn for his advice on the construction of the apparatus.

Summary

An apparatus for the accurate measurement of the dielectric constants of gases and vapors has been constructed and tested by repeated measurements upon air and carbon dioxide. Values have been determined for benzene, toluene, propane and propylene and used to calculate their polarizations and electric moments.

The absence of any change in the polarizations of benzene and propane with rising temperature indicates that the increase previously observed

(18) Williams, *Physik. Z.*, **29**, 174 (1928); Williams and Krehma, *THIS JOURNAL*, **49**, 1676 (1927).

(19) Smyth and Zahn, *ibid.*, **47**, 2501 (1925).

(20) Ref. 4, p. 117.

with rising temperature in a number of liquid paraffins is due to decrease in intermolecular action.

The zero moment found for the benzene molecule agrees with the less accurate results of the measurements upon the liquid and with the symmetrical structure of the molecule. The zero moment found for propane is consistent with the absence of moment in the higher members of the series and shows that any polarity in the C-C bonds, electrical dissymmetry caused by repulsion in the molecule or difference in electronegativity between the hydrogens on the secondary and those on the primary carbons is too small for detection by means of the electric moment.

The small moments found for toluene and propylene are of the same magnitude as those which might arise from inductive effects in the molecules.

PRINCETON, NEW JERSEY

RECEIVED JUNE 6, 1932

PUBLISHED FEBRUARY 9, 1933

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Possibility of Dipole Rotation in Certain Crystalline Solids

BY S. E. KAMERLING AND C. P. SMYTH

This paper presents the results of an investigation undertaken with the object of studying a possible contribution to the dielectric constants of certain substances through the rotation of a polar group in a molecule fixed in a crystal lattice or through the rotation of the entire molecule in the lattice, the latter possibility having been suggested by the results of Errera.^{1,2} When the molecules of a substance are so fixed in the solid state that any dipoles contained by them are unable to orient at all in an externally applied electric field, the dielectric polarization of the substance consists only of the so-called optical part, $P_E + P_A$, which should be virtually independent of temperature and of frequency within the range ordinarily used in dielectric constant measurements. Any considerable variation of polarization with temperature or frequency should, therefore, be evidence of dipole orientation, that is, of rotation of polar groups or molecules in the solid. In the present measurements, a certain number of molecules are placed between the plates of a condenser by filling the condenser with liquid, which is then frozen. Consequently, as the temperature is lowered, the number of molecules between the plates is not appreciably altered by the changing density of the solid and the apparent value observed for the dielectric constant should not alter with the density. Although this apparent value of the dielectric constant evidently differs by a small but increasing amount from the true value as the temperature falls below the freezing point, it makes an excellent substitute for the polarization, which

(1) Errera, *J. phys. radium*, [6] 5, 304 (1924).

(2) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, Inc., New York, 1931, p. 38.