232. *The Dipole Moments of Vapours. Part I.*

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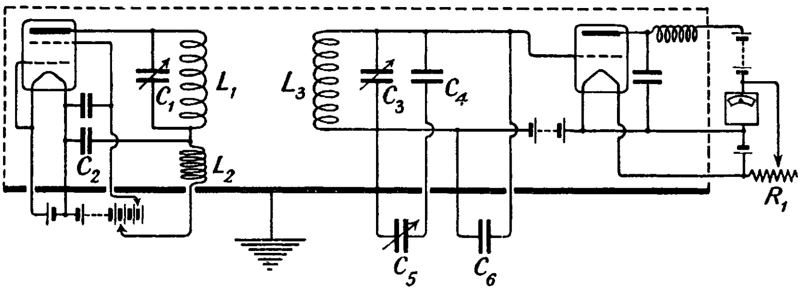
THE measurements hitherto recorded of dipole moments of vapours are nearly all confined to substances with a moment of less than 2 Debye units ($D = 10^{-18}$ e.s.u., c.g.s.). The work described below was planned to provide data over a wider range of dipole moments, since such measurements have now assumed a special interest in connexion with the interpretation of dipole moments deduced from observations in solution. The present paper describes the apparatus and method, and gives data obtained for four substances; it is intended later to provide data for a number of substances with dipole moments ranging from 0 to 4 *D*.

FIG. 1.



Apparatus and Method.—The dielectric constant of the vapour at a known temperature and pressure was measured by a resonance method, using the circuit shown in Fig. 1. The oscillator is of the Dynatron type, using a Mullard P.M. 12 screened-grid valve. This type of oscillator has been found to give greater stability of frequency and amplitude than a quartz-crystal oscillator when used under laboratory conditions. The high-frequency radiating circuit consists of the inductance L_1 and the capacity C_1; the high-frequency current was restricted to the anode-filament circuit by means of the choke and blocking condenser L_2 and C_2.

The coil L_1 and the pick-up coil L_3 were wound on specially constructed formers consisting of two ebonite rings joined at the edges by ebonite rods. This arrangement gives the minimum amount of dielectric in the field of the coil, and, by reducing energy absorption, makes the resonance curve sharper. The frequency used was approximately 1000 kc., and the field strength such as to give a resonance potential across L_3 of about 9 volts with a distance of 25 cm. between the parallel coils L_1 and L_3.

The resonance coil was tuned by the system of condensers C_3, C_4, C_5, and C_6; C_3 was an inexpensive variable condenser for rough tuning, and was maintained at a fixed capacity during a series of measurements. C_6 represents the capacity of the cell containing the vapour; the small change in capacity of C_6 when vapour was admitted to the cell or removed from it was measured by the combination C_4–C_5 of two condensers in series. C_4 was small, of the order of 10 $\mu\mu$F, whilst C_5 was a Sullivan standard variable condenser of maximum capacity 1200 $\mu\mu$F.

It is clear from simple theory that for a given state of resonance, a small change in capacity of C_6 (itself of the order of 100 $\mu\mu$F) will require a large change in C_5 to bring the circuit back to the same state of resonance. On this principle depends the accurate measurement of the small changes occurring in C_6 as a result of the introduction of vapours and gases. In order to obtain a high sensitivity on the galvanometer, conditions were adjusted to give a very sharp resonance curve. This was done by making a series of experiments with the receiving coil at varying distances from the oscillator for different values of grid bias. From a set of such measurements, the sharpest curve was obtained when the coils were separated by 25 cm., and the grid bias was $-$ 9 volts.

In making measurements, the galvanometer was used as a null instrument. The circuit was tuned by C_3 until a point, half-way up the resonance curve, was reached where, under the above conditions of grid bias, etc., the sensitivity of the apparatus was such that a 1% change in capacity of C_6 effected a 10% change in anode current. (The anode current at peak was of the order of 120—130 microamps.)

A typical measurement was made in the following manner. The cell C_6 was evacuated, and the anode current adjusted by C_3 to the appropriate point on the resonance curve, maintaining a large reading on C_5. The resistance R_1 was then adjusted until the bulk of the anode current was balanced out, leaving a suitable small reading as constant reference point. Vapour or gas was then introduced into C_6, producing a small increase in capacity; this was compensated by reducing the value of C_5 until the galvanometer recorded the same value for the anode current as it did before the admission of gas.

If C_5 and C_5' be the readings of the measuring condenser before and after the admission of gas, then it is easily shown that ΔC_6, the change in the capacity of C_6, is given by

$$\Delta C_6 = C_4^2(C_5 - C_5')/[C_5C_5' + C_4(C_5 + C_5') + C_4^2].$$

Hence $\varepsilon - 1$ is given by

$$\varepsilon - 1 = \frac{\Delta C_6}{C_6} = \frac{C_4^2}{C_6} \cdot \frac{C_5 - C_5'}{C_5C_5' + C_4(C_5 + C_5') + C_4^2} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It should be noted that C_6 in equation (1) is the replaceable capacity of the cell, and does not include the stray capacities of leads, etc. The term C_4^2 in the denominator is very small and can be neglected.

Construction of Cell.—The cell consisted of two stainless-steel cylinders fixed concentrically with a gap of about 1 mm. It was sealed inside a large glass bulb immersed in an electrically heated oil-bath. Leads were taken from the inner and the outer cylinder to mercury cups on the top of the vessel. In use, the outer cylinder and the iron vessel containing the oil-bath were earthed to give as complete shielding as possible.

A very simple device proved satisfactory for fixing the steel cylinders rigidly together. Small grooves were made in the walls of the annular gap at three positions 120° apart. These grooves were a little too small to admit three short lengths of glass rod when the cylinders were concentric. Two of the rods were held in position whilst the outer cylinder was distorted in a vice till the third could be slipped into position. On releasing the outer cylinder the rods were gripped firmly. Three similar rods were inserted in the other end of the gap and gave a very rigid assembly. Owing to the larger expansion of glass than of the differential expansion of the two cylinders, it was anticipated that the cylinders would be bound more tightly together at higher temperatures. This expectation was justified since it was found that the capacity of the cell showed no change after repeated heating and cooling.

Calibration of Cell.—It will be seen from equation (1) that the dielectric constant of the cell contents can be deduced from an apparatus constant C_4^2/C_6, the initial and the final reading of the measuring condenser C_5, and an approximate knowledge of C_4 (C_4 was measured and found to be 10 $\mu\mu$F $\pm$ 0·7). The latter need not be known with great accuracy since the term in the denominator of (1) involving C_4 is small compared with the product C_5C_5'. The cell was therefore calibrated by making observations with gases of known dielectric constant. From the measurements of Bryan and Sanders (*Physical Rev.*, 1928, **32**, 202), Stuart (*Z. Physik*, 1928, **47**, 457), and Zahn (*Physical Rev.*, 1926, **27**, 455), the mean polarisation of air was taken as 4·368 c.c. and that of carbon dioxide as 7·317 c.c. It being assumed that the polarisation of these gases does not change with temperature and that the gas laws hold, the dielectric constant of the gas at a known temperature and pressure may be calculated by the relation

$$\varepsilon - 1 = Pp \times 4{\cdot}810 \times 10^{-5}/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where P is the molecular polarisation, p the pressure (in mm. of Hg), and T the absolute temperature.

One of the chief difficulties encountered in these measurements was a slow change in amplitude of the oscillation which caused a drift in the zero reading of the galvanometer. This drift slowly diminished with time, and after some hours even changed in sign. In order to eliminate errors due to this drift, the valves were run until it was small, and observations made in pairs in the order (1) cell evacuated, (2) cell filled, (3) cell evacuated. With gases, the cell could be filled and emptied in a few seconds, and with vapours all the observations could be made in **3** minutes. The results calculated from (1) and (2) will be affected by the zero drift in the opposite direction to those calculated from (2) and (3), so the mean value of the pair of results largely eliminates the error due to this cause. The data for the calibration of the cell are set out in full in Table I to indicate the magnitude of the differences between the members of each pair and the constancy of the mean values.

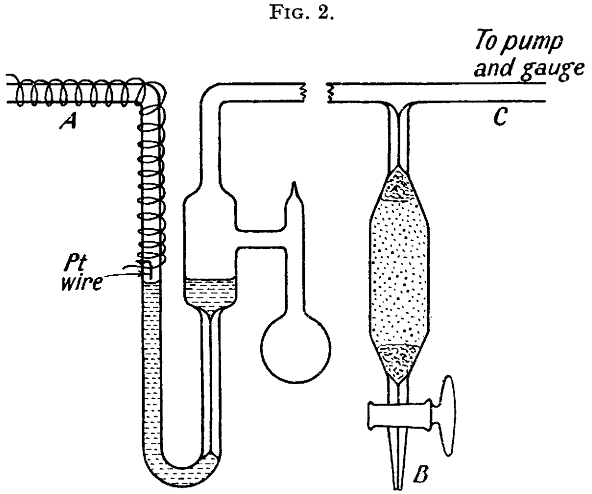
TABLE I.

Calibration of Cell.

Gas.	T.	p, mm.	$(\epsilon - 1) \times 10^4$.	C_5, $\mu\mu F$.	ΔC_5.	C_4^2/C_6.	Mean.
Air	288·6°	783	5·700	1146·0			
				704·0	442·0	1·065	1·060
				1152·7	448·7	1·055	
,,	,,	780·5	5·682	1158·7			
				711·4	447·3	1·071	1·061
				1172·7	461·3	1·050	
,,	424·9	777	3·842	1152·0			
				801·3	350·7	1·034	1·059
				1128·7	327·4	1·084	
Carbon dioxide	288·6	783	9·549	1140·0			
				554·4	585·6	1·060	1·061
				1138·7	584·3	1·061	
,,	,,	,,	,,	1140·0			
				555·0	585·0	1·060	1·062
				1135·3	580·3	1·065	
,,	427·6	777	6·395	1154·7			
				675·3	479·4	1·064	1·060
				1162·0	486·7	1·055	
	,,	781·2	6·430	1155·3			
				671·3	484·0	1·055	1·059
				1149·3	478·0	1·062	

Mean $C_4^2/C_6 = 1·060 \pm 0·001$.

FIG. 2.



The air was dried by passage over phosphoric oxide, and the carbon dioxide was taken from a cylinder of the compressed gas, which was known from analysis to contain 99·9% CO_2.

Control of Vapour.—After several trials, it was found that the most convenient method of admitting vapour to the cell was a slight modification of the apparatus of Miles (*Physical Rev.*, 1929, **34**, **964**) shown in Fig. 2. The tube A leading to the cell in the oil-bath was heated electrically with a winding of nichrome wire lagged with asbestos. A suitable quantity of liquid was introduced into the bend of the U-tube and cooled by a freezing mixture. The cell was evacuated through tube C, and a little dry air admitted through the leak B. Regular ebullition in the left-hand limb was facilitated by the platinum wire sealed into the heated limb. Air was swept out of the cell by admitting vapour and pumping it out several times, leaving a few mm. pressure of vapour in the cell. By careful manipulation of B, any desired pressure of vapour could then be rapidly introduced into the cell or rapidly removed by opening the connexion to the pump. The pressure recorded on the gauge was corrected for any difference of level of the liquid in the arms of the U-tube.

The four liquids for which data are given below were specimens which had been purified by one of us for the determination of dielectric constant in the liquid state (Sugden, J., 1933, 768).

The molecular polarisations were calculated by equation (2), which assumes that the vapour obeys the gas laws. To ensure that deviations from these laws did not introduce appreciable errors, small pressures of vapour were employed; usually 50 mm. for the more polar vapours, and never more than 200 mm. It is estimated that the error due to neglect of gas-law corrections is less than 1 part in 500.

DISCUSSION OF RESULTS.

The data obtained are collected in Table II. Col. 3 gives for each temperature the individual values of the molecular polarisation, each obtained from a pair of measurements to eliminate zero drift. For the three polar substances an equation of the Debye form $P = P_D + 6173\mu^2/T$ (where μ is measured in Debye units) was fitted to the data by the method of zero sum, and the values of P calculated by this equation are given in col. 4. Since interest attaches chiefly to the values of the moments, these were calculated for each temperature by using the value of P_{A+E} given by the best-fitting Debye equation, and are recorded in the last column.

The data for benzene are in satisfactory agreement with those of McAlpine and Smyth (*J. Amer. Chem. Soc.*, 1933, **55**, 453), who find $P = 26·87$. For chlorobenzene, Smyth (Faraday Soc. Discussion, April 1934) quotes $\mu = 1·70D$ from unpublished observations of McAlpine. No data have been found in the literature for comparison with the observations on nitrobenzene and benzonitrile. The moments found for the vapour are considerably larger than those obtained in non-polar solvents by the usual methods, *viz.*, $\mu = ca.\ 4·0D$.

TABLE II.

Polarisation of Vapours.

T.	P, obs.	Mean.	P, calc.	μ.
	Benzene.			
346·0°	26·2, 26·3	26·2	—	0
382·6	26·2, 26·5	26·3	—	,,
449·3	26·1, 25·9	26·0	—	,,
522·0	26·4, 26·2	26·3	—	,,
	Chlorobenzene.			
359·5	83·8, 83·9, 83·8	83·8	83·5	1·69
383·0	80·8, 80·6	80·7	80·5	1·69
417·0	75·9, 77·0	76·5	76·8	1·68
443·0	72·8, 74·7, 73·8	73·8	74·4	1·68
476·0	71·3, 72·8, 73·3	72·5	71·6	1·70
495·0	70·0	70·0	70·2	1·68
	Mean $\mu = 1·69 \pm 0·01$.			
	Nitrobenzene.			
402·0°	310·0, 309·6	309·8	310·2	4·22
414·0	303·0, 300·9, 304·2	302·7	302·3	4·23
433·0	290·2, 291·2	290·7	290·7	4·23
453·0	280·2, 278·5	279·4	279·4	4·22
496·0	262·2	262·2	258·4	4·26
523·0	242·4, 243·4	242·9	246·9	4·19
	Mean $\mu = 4·23 \pm 0·01$.			
	Benzonitrile.			
383·0	337·6, 335·7	336·6	341·6	4·35
401·0	328·9, 325·5	327·2	327·7	4·38
426·0	317·5, 314·1	315·8	310·4	4·43
452·0	294·5, 295·7	295·1	294·5	4·39
475·0	276·4, 280·9, 278·6	278·6	281·6	4·36
498·0	271·1, 275·7	273·4	270·0	4·42
525·0	257·5, 256·7	257·1	257·7	4·38
	Mean $\mu = 4·39 \pm 0·02$.			

The constants for the substances examined are collected in Table III. It will be seen that the values of P_A obtained are small and of the order of magnitude found for other

TABLE III.

Dipole Moments and Atomic Polarisations.

Substance.	μ.	P_{A+E}.	P_E.	P_A.
Benzene	0	26·2	25·1	1·1
Chlorobenzene	1·69 ± 0·01	34·9	31·0	3·9
Nitrobenzene	4·23 ± 0·01	36·2	32·0	4·2
Benzonitrile	4·39 ± 0·02	31·4	31·6	—

substances. Owing to the form of the Debye equation, small errors in the determination have a large effect upon the value found for P_A. The value of P_{A+E} found for benzonitrile is probably too low.

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