

312. *The Interpretation of Electric Polarisation Coefficients.*

By FRANK R. GOSS.

RECENT investigations dealing with electric dipole moments have been of considerable value to organic chemistry—particularly with regard to problems of stereochemical structure and electronic behaviour—and it is obviously desirable that the data should be as accurate as possible. Considerable experimental uncertainty still exists where the moment is small, or where it may be presumed from other considerations to be zero. With the object of clarifying the position, an experimental and theoretical study has been made of the polarisation coefficients of benzene. In such cases the Debye formula $\mu = 0.01273\sqrt{P_0T} \times 10^{-18}$ e.s.u. is applied in the calculation of moments on the erroneous assumption that the electron polarisation is a constant; again, since the dipole moment (μ) is proportional to the square root of the experimentally determined orientation polarisation (P_0), the degree of accuracy with which P_0 must be measured becomes rapidly greater for small values of μ , so that it is difficult to obtain sufficiently exact values for those substances having moments of less than, say, 0.5×10^{-18} e.s.u.: in fact, many compounds have been assumed to possess a zero moment on uncertain experimental foundations, simply on account of their structural formulæ.

The elimination of error in the calculation of P_0 by means of the formula $P_0 = P - (P_E + P_A)$ depends, with low values of P_0 , on a more exact understanding of the nature of the total polarisation (P), the electron polarisation (P_E) and the atom polarisation (P_A).

The electron polarisation is usually regarded as the value of the Lorentz-Lorenz expression when this is calculated from the refractivity (n_∞) which the substance would have at infinite wave-length. It is not satisfactory in calculating n_∞ to take random points on the experimental polarisation curve, which Errera ("Polarisation dielectrique," 1928, p. 29) has shown to follow the equation $P_E + P_A = \sum C_E / (v_E^2 - v^2) + \sum C_A / (v_A^2 - v^2)$, where v_E

and ν_A are the resonating frequencies, and C_E and C_A are constants for a given molecular condition, *i.e.*, varying with change of temperature and pressure. Following this equation, the refractivity between ν_E and ν_A is given by an equation of the form $n^2 = k_1 + k_E/(\lambda^2 - \lambda_E^2) - k_A/(\lambda_A^2 - \lambda^2)$ (cf. *ibid.*, p. 90), where λ_E and λ_A are wave-lengths corresponding to ν_E and ν_A , k_1 is the square of the refractive index corresponding to P_E , k_E and k_A are constants related to C_E and C_A . In order to obtain k_1 from experimental values of n and λ , it is usually desirable to choose values of λ such that the last term in the equation can be neglected, and sufficiently far from the ultra-violet absorption bands for the effects of the separate bands to become merged (cf. Gifford and Lowry, *Proc. Roy. Soc.*, 1923, *A*, 104, 432). These conditions are fulfilled with sufficient accuracy for the present purpose if, in the equation $n^2 = k_1 + k_E/(\lambda^2 - \lambda_E^2)$, the constants k_1 and k_E are evaluated by substituting values of n for the α and β hydrogen lines: λ_E may be taken as the wave-length of any intense absorption band. Then from k_1 , the refractivity for infinite wave-length, the electron polarisation P_E is directly derived.

It is well known that the values obtained for P_E depend on the molecular condition of the substance, rising with temperature for the liquid, and having a somewhat higher value for the vapour. Data for liquid benzene are given by Parker and Thompson (J., 1922, 121, 1341), who observed that the polarisation increased with temperature, and from their results it is found that the polarisation for the sodium D line (P_D) rises from 26.1 to 26.3. The value of P_D calculated from the refractivity for benzene vapour, given by Wasastjerna (*Soc. Sci. Fenn. Phys.-Math.*, 1925, 2, 13, 1), is 27.2. The values (see table) for P_E were calculated by means of the above dispersion formula, λ_E being taken as 0.2605 (Kwiciński and Marchlewski, *Bull. Acad. Polonaise*, 1929, *A*, 255). They are related amongst themselves in the same way, being somewhat less than 1 c.c. lower than the corresponding values of P_D . All these figures are in accordance with the theory of optical and electrical properties developed by Raman and Krishnan (*Proc. Roy. Soc.*, 1928, *A*, 117, 589), who show that $(n^2 - 1)/(n^2 + 2) = \nu C(1 - \nu\Phi)$, where ν is the number of molecules per unit volume, C is a function of the moments induced by the incident light, and Φ involves, in addition, factors expressing the variation of the polarisation field along the principal optic axes of the molecules, when the field is anisotropic. From this formula it follows that

$$P_E = (n^2 - 1)M/(n^2 + 2)d = C/(1/N - d\Phi/M),$$

where N is the Avogadro number. An application of this formula to benzene has been made by Krishnan (*Proc. Roy. Soc.*, 1929, *A*, 126, 155), who has calculated $d\Phi$ from values of light scattering and shown that it decreases with temperature, and hence that the value of P_E for liquid benzene increases with temperature. For the vapour, which is optically isotropic and for which $\Phi = 0$, P_E should have a value independent of temperature and considerably higher than that for the liquid.

Raman and Krishnan (*loc. cit.*) have shown further that the sum of the electron and atom polarisations of a liquid can be expressed by an analogous formula

$$P_E + P_A = (\epsilon - 1)M/(\epsilon + 2)d = X/(1/N - d\psi/M).$$

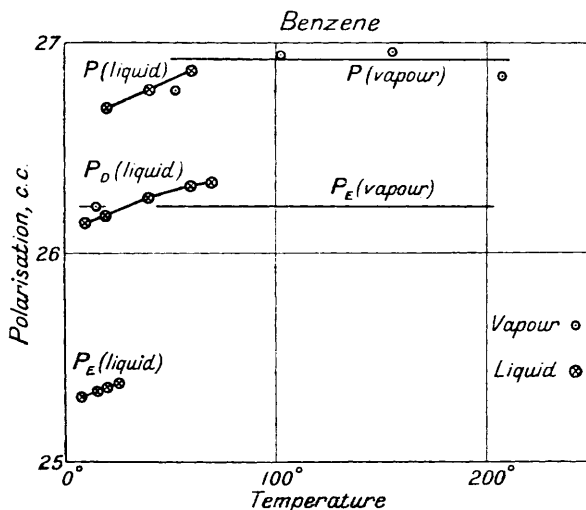
There should consequently be an analogous increase in the total polarisation of a non-polar liquid with temperature; whereas for the vapour the polarisation should be independent of the temperature and slightly higher than the value for the liquid. The increase of the polarisation with temperature for liquid benzene is well established, and figures are given in Table I based on measurements made in the course of this investigation, McAlpine and Smyth (*J. Amer. Chem. Soc.*, 1933, 55, 453) having shown that no change occurs in the polarisation of benzene vapour over a wide range of temperature.

From the graph of these data (see Fig. 1), it is clear that the temperature coefficient for the total polarisation (P) for liquid benzene is, within the limits of experimental error, identical with that for the electron polarisation as represented by the P_E (liquid) and P_D (liquid) curves, and hence it follows that for liquid benzene as well as for the vapour, P_A is constant, and the dipole moment zero.

t.	Liquid.									Vapour.				
	$d^{1,2}$	n_D	n_p	k_E	k_1	P_E	n_D^6	P_D	ϵ^7	P	P_E^{10}	n_D^9	P_D^3	P
8.5°	0.8900	1.5038 ²	1.6208 ³	0.0162	2.2169	25.314								
10.0	0.8884						1.5068	26.142						
15.0	0.8830	1.4997 ³	1.5164 ³	0.0158	2.2054	25.342					26.22	1.001821	27.20	
20.0	0.8776	1.4966 ⁴	1.5133 ⁴	0.0158	2.1962	25.359	1.5002	26.173	2.2862	26.694				
25.0	0.8722	1.4933 ⁵	1.5098 ⁵	0.0156	2.1869	25.373								
40.0	0.8560						1.4876	26.259	2.2473	26.781				
52.8														26.77 ¹⁰
60.0	0.8344						1.4743	26.309	2.2082	26.862				26.94 ¹⁰
70.0	0.8236						1.4675	26.326						26.96 ¹⁰
102.0														26.84 ¹⁰
155.6														
207.0														

¹ Timmermans and Martin, *J. Chim. physique*, 1926, 23, 733. ⁶ Parker and Thompson, *loc. cit.*
² Perkin, J., 1900, 77, 273. ⁷ This paper.
³ Gifford and Lowry, *loc. cit.* ⁸ Morgan and Lowry, *loc. cit.*
⁴ Wegmann, *Z. physikal. Chem.*, 1888, 2, 218. ⁹ Wasastjerna, *loc. cit.*
⁵ Hubbard, *ibid.*, 1910, 74, 228. ¹⁰ McAlpine and Smyth, *loc. cit.*

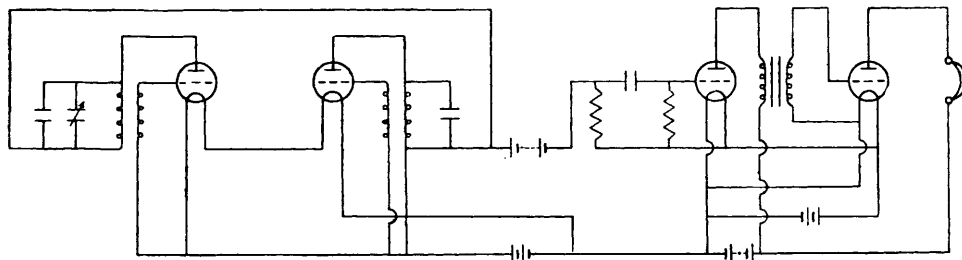
FIG. 1.



EXPERIMENTAL.

To obtain the data upon which the foregoing values for the polarisation of liquid benzene are based, dielectric constants have been measured by a simple heterodyne method based on that of Whiddington (*Proc. Camb. Phil. Soc.*, 1921, 20, 445; cf. Whiddington and Long, *Phil. Mag.*, 1925, 49, 113).

FIG. 2.

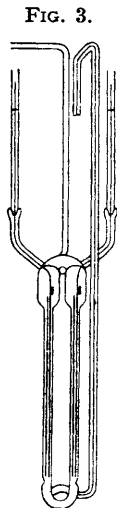


Measurement of Dielectric Constants.—The measuring apparatus consisted of two oscillating circuits connected in series (Fig. 2), each containing a Marconi DEH210 triode valve, a variable condenser of maximum capacity 1000 μ F, and a loosely coupled coil consisting of copper wire

wound round a cylindrical ebonite former, and having an inductance in the plate circuit sufficient to give oscillations with a wave-length of about 1500 m.

One of the condensers was an ordinary variable instrument which was kept in a constant position throughout each set of readings, and the other was a "Laboratory Standard Air Condenser" supplied by Messrs. H. W. Sullivan, Ltd. It was fitted with a microscope, enabling the instrument to be read to $0.03 \mu\mu\text{F}$, and with a rigid extension arm of aluminium tubing having an ebonite handle which made it possible to operate the condenser from a distance of 6 ft., and to set it to the nearest $0.03 \mu\mu\text{F}$.

The experimental condenser (Fig. 3) consisted of two concentric cylinders of "Firth Staybrite" steel, 1 mm. thick, with a gap of 1 mm. between them, and rigidly connected by Bakelite screws cut off flush with the inner and outer surfaces of the cylinders. These were enclosed in a hollow cylindrical vessel having double walls of Jena glass, and provided with two inlet tubes, through one of which the liquid to be measured was transferred from a receiver protected by calcium chloride drying tubes, by reducing the pressure in the other. Platinum wires, fused into glass mercury cup terminals which were ground on to two further inlet tubes in the experimental condenser, provided contact with the steel plates; each wire being bound by a "Firth Staybrite" screw to a lug on one of the plates. Contact between the mercury cups of the experimental condenser and the terminals of the standard variable condenser was made by two lengths of No. 18 Glazite tinned copper wire which rested on ebonite mercury cup contact breakers, so designed that, although stray capacities were eliminated, a minimum movement of the connecting wires took place.



The experimental condenser was immersed in a chlorobenzene bath contained in a 4-litre vacuum vessel surrounded by an earthed shield. The bath temperatures were measured with thermometers which had been compared with N.P.L. standards, and they never varied more than 0.2° during each set of readings. Uniformity of temperature throughout the bath liquid, which circulated both inside the inner and outside the outer plates, was secured by a stream of air bubbles. Care was also taken to maintain the surface of the chlorobenzene at a standard level to avoid changes in the earth capacities of the plates.

The apparatus as a whole was contained in an earthed shield, and separate sets of accumulators were provided for the oscillating and the amplifying valves.

When the capacity in one of the two oscillators was varied, the resulting heterodyne note was passed through a simple two-valve low-frequency amplification stage with an earphone detector. The null point of the two oscillators was determined by taking the mean position between the two lowest notes audible in the earphone. The use of the lowest audible notes, which are sharply defined and of constant frequency, was both quicker and more accurate than that of matching two notes against a standard by the method of beats, and speed was of the highest importance because of the risk of error through evaporation of the liquids.

Calibration of Apparatus.—The standard variable condenser was calibrated with a small fixed condenser. A comparison of the values for the dielectric constants of benzene and carbon tetrachloride (see below) given by the respective capacities of the experimental condenser in dry air and in the liquid concerned, with the best absolute values recorded in the literature (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, 123, 685; Morgan and Lowry, *J. Physical Chem.*, 1930, 34, 2417 *et seq.*), showed that the effects of mutual and earth capacities, and of inductances arising from the leads and the distancing screws of the experimental condenser, have either been cancelled out, or are negligible with respect to the large air capacity of the condenser.

	Dielectric constants.*		
	20°.	40°.	60°.
Benzene	2.2862	2.2472	2.2082
Carbon tetrachloride.....	2.2409	2.1999	2.1589

* Values of ϵ are reduced to vacuum as unity.

Purification of Materials.—"B.D.H. Extra pure" benzene was frozen and drained twice, dried over phosphoric oxide for 2 days, and fractionally distilled. It had a constant b. p. and was shown to be free from thiophen; m. p. 5.3° .

Carbon tetrachloride of "A.R." quality, supplied by B.D.H., was fractionally distilled, and

the middle portion collected. It was dried over calcium chloride and again fractionally distilled. The middle fraction had a b. p. range of less than 0.1° .

I wish to express my appreciation of much help and encouragement from Professor C. K. Ingold, F.R.S., and my indebtedness to the Royal Society and Imperial Chemical Industries Ltd. for substantial grants, and to the Talbot-Stead Tube Co. Ltd. for the gift of the steel condenser plates.

THE UNIVERSITY, LEEDS.

[*Received, August 1st, 1933.*]
