221. *The Dipole Moments of Vapours. Part II.*

By L. G. GROVES and S. SUGDEN.

IN continuation of the work described in Part I (J., 1934, 1094), measurements have been made of the dielectric constants of six more substances in the vapour state over a range of temperature. The dipole moments deduced from these measurements are recorded (in Debye units; e.s.u. × 10^{-18}) in Table I.

All the substances so far examined by us give a linear relation between the measured polarisation and the reciprocal of the absolute temperature; extrapolation gives a value of P_{A+E} which is nearly equal to the optical polarisation. The atom polarisation must therefore be small, but its exact determination by this method is difficult when the substances examined have a considerable moment, since a small error in the slope of the curve has a very large effect on the extrapolated value of P_{A+E}. The chief interest in measurements of this kind lies in the values of the dipole moments; we have therefore preferred to assume that P_A is 5% of P_E (cf. Sugden, *Trans. Faraday Soc.*, 1934, **30**, 734) when P_E is calculated from the refractive index for the Na–D line. This gives a consistent basis for the calculation of the diple moments and causes a negligible error when the moment is greater than 1·0 D. The values marked with an asterisk in Table I have been recalculated in this way from the observations recorded in Part I.

TABLE I.

Dipole Moments of Vapours.

Substance.	μ.	Substance.	μ.
Water	1·84±0·01	Ethyl benzoate	1·95±0·02
Deuterium oxide	1·84±0·01	Acetophenone	3·00±0·01
Benzene	0	Nitrobenzene *	4·24±0·02
Chlorobenzene *	1·73±0·01	Benzonitrile *	4·37±0·02
Bromobenzene	1·71±0·01	*n*-Valeronitrile	4·09±0·01

Our value for the dipole moment of water agrees excellently with that of Sänger, Steiger, and Gächter (*Helv. Phys. Acta*, 1932, **5**, 200), *viz.*, 1·842±0·008. It will be seen that deuterium oxide has a dipole moment which is indistinguishable from that of water. The moments of the other substances examined are in all cases higher than the values deduced from measurements in solution. The behaviour of solutions will be discussed in a later paper, in which new measurements on solutions of some of the substances referred to in Table I will be reported.

A number of measurements of the dipole moments of vapours have now accumulated, and it is possible to discuss in a preliminary fashion the validity of two general relations which have been found for dipole moments in solution. The first of these concerns the behaviour of a homologous series RX, where R is an alkyl radical and X a group possessing a considerable dipole moment. For such compounds, measurements in solution show that the moments are nearly constant except when R is H or CH_3 (cf. Cowley and Partington, this vol., p. 607). The available data for dipole moments measured in the state of vapour are collected in Table II; it will be seen that the same general conclusion can be drawn from these data, although it is evident that many more observations are needed.

TABLE II.

Dipole Moments in Homologous Series.

Fluorides.		*Chlorides.*		*Bromides.*	
HF	—	HCl	1·03 [1]	HBr	0·78 [1]
CH_3F	1·81 [4]	CH_3Cl	1·87,[2] 1·86,[3] 1·86,[4] (1·69) [5]	CH_3Br	1·82,[5] 1·79 [6]
C_2H_5F	1·92 [4]	C_2H_5Cl	2·06,[2] 2·02,[3] 2·04,[3] (2·11) [5]	C_2H_5Br	2·09,[5] 2·02,[4] (1·78)[6]
		n-C_3H_7Cl	2·04 [3]	*n*-C_3H_7Br	2·11,[5] (1·79) [6]
Limit	1·92	Limit	2·04	Limit	2·08

Cyanides.		*Nitro-compounds.*		*Methyl ketones.*	
HCN	2·93 [7]	$CH_3·NO_2$	3·78,[5] 3·42 [7]	$CH_3·CO·CH_3$	2·97,[5] 2·84,[9] 2·85 [10]
$CH_3·CN$	3·94 [5]	$C_2H_5·NO_2$	4·03 [5]	$C_2H_5·CO·CH_3$	2·77 [11]
$C_2H_5·CN$	4·05 [5]	Limit	4·03	Limit	2·8 approx.
n-$C_4H_9·CN$	4·09 [12]				
Limit	4·07				

References.—[1] Zahn, *Physical Rev.*, 1926, **27**, 455. [2] Fuchs, *Z. physikal. Chem.*, 1930, **63**, 824. [3] Sänger, Steiger, and Gächter, *loc. cit.* [4] Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 499. [5] Højendahl, Thesis, Copenhagen, 1928. [6] Mahanti, *Physikal. Z.*, 1930, **31**, 548. [7] Smyth and McAlpine, *J. Amer. Chem. Soc.*, 1934, **56**, 1697. [8] *Idem, J. Chem. Physics*, 1935, **3**, 55. [9] Stuart, *Z. Physik*, 1928, **51**, 490. [10] Zahn, *Physikal. Z.*, 1932, **33**, 686. [11] *Idem, Physical Rev.*, 1930, **35**, 848. [12] Groves and Sugden, this paper.

The second generalisation concerns the comparison of the group moments of aliphatic and aromatic compounds. From dipole moments measured in solution, Sutton (*Proc. Roy. Soc.*, 1931, **131**, 668) has shown that the difference between the moments ArX–AlkX is related to the directing influence of the group X in benzene substitution. The sign of the moment is defined by allotting a positive sign to a dipole which has the positive end more distant from the Ar or Alk group. With this convention, the difference ArX–AlkX is positive for groups which have an *o,p*-directing influence and negative for those which are *m*-directing.

The available data for dipole moments measured in the vapour state are collected in Table III. The moments of AlkX have been taken as equal to the limits for the appropriate homologous series in Table II. It will be seen that Sutton's generalisation is confirmed by the vapour measurements, although the differences between the aromatic and the aliphatic group moments are rather smaller than those found in solution.

TABLE III.

Aliphatic and Aromatic Group Moments.

	μ.		μ.	Diff.	Directing influence.
C_6H_5F	$-1·57$ [8]	AlkF	$-1·92$	$+0·35$	*o,p*
C_6H_5Cl	$-1·70$,[8] $-1·73$ [12]	AlkCl	$-2·04$	$+0·33$	*o,p*
C_6H_5Br	$-1·71$ [12]	AlkBr	$-2·08$	$+0·37$	*o,p*
$C_6H_5·CN$	$-4·37$ [12]	Alk·CN	$-4·07$	$-0·30$	*m*
$C_6H_5·NO_2$	$-4·24$,[12] $-4·19$ [8]	Alk·NO$_2$	$-4·03$	$-0·2$	*m*
$C_6H_5·CO·CH_3$	$-3·00$ [12]	Alk·CO·CH$_3$	$-2·8$	$-0·2$	*m*

(For references, see Table II.)

EXPERIMENTAL.

Measurement of Dielectric Constants.—The apparatus described in Part I was used. Some difficulty was encountered owing to breakage of the glass bulb enclosing the cell after heating to 250°. This has been overcome by mounting the stainless-steel cylinders in an annular vessel of Pyrex glass.

Preparation of Specimens.—Conductivity water was used as " light " water; the deuterium oxide was purchased from Norsk Hydro-elektrisk Kvaelstofaktieselskab and contained 98·4% D_2O. The acetophenone used was the specimen purified by Sugden (J., 1933, 772).

Commercial specimens of bromobenzene and of ethyl benzoate were purified by repeated fractional distillation. The specimens used had respectively $D_{4°}^{20°}$ 1·4955 (Young, J., 1889, **55**, 486, gives $D_{4°}^{20°}$ 1·4953) and $D_{4°}^{25°}$ 1·0445 (Int. Crit. Tables give $D_{4°}^{25°}$ 1·0453). *n*-Valeronitrile, prepared from *n*-butyl bromide and purified by repeated distillation, had $D_{4°}^{20°}$ 0·7992: Mercx, Verholt, and Bruylants (*Bull. Soc. chim. Belg.*, 1933, **42**, 177) found $D_{4°}^{20°}$ 0·7992.

In the tables below, T is the absolute temperature, p the approximate pressure (mm.) of the vapour measured, and P the total polarisation (in c.c.) which is calculated on the assumption that the vapour obeys the gas laws. The dipole moment in the last column is calculated on the assumption that P_A is 5% of P_E (see p. 972).

Water.

$P_E = 3·7$ c.c.; $P_{A+E} = 3·9$ c.c.

T.	p.	P.	μ.
383°	114	58·1	1·83
,,	138	58·9	1·85
440	150	51·2	1·84
,,	125	51·7	1·85
458	163	49·1	1·83
,,	214	49·3	1·84
484	212	47·3	1·84
,,	222	47·5	1·85
	Mean	1·84±0·01	

Deuterium oxide.

$P_E = 3·7$ c.c.; $P_{A+E} = 3·9$ c.c.

T.	p.	P.	μ.
364°	110	61·5	1·84
,,	116	61·9	1·85
420	121	53·8	1·84
,,	129	53·6	1·84
446	180	50·7	1·84
,,	189	50·6	1·84
473	214	48·5	1·85
,,	202	48·5	1·85
	Mean	1·84±0·01	

Bromobenzene.

$P_E = 33·9$ c.c.; $P_{A+E} = 35·6$ c.c.

T.	p.	P.	μ.
374°	87	84·1	1·71
,,	90	84·1	1·71
398	103	81·4	1·72
,,	70	81·2	1·72
413	100	79·7	1·72
438	93	76·8	1·71
,,	93	77·1	1·71
443	170	76·8	1·72
483	113	73·6	1·71
,,	95	73·6	1·71
	Mean	1·71±0·01	

Ethyl benzoate.				*Acetophenone.*				n-*Valeronitrile.*			
P_E = 42·6 c.c.; P_{A+E} = 44·7 c.c.				P_E = 36·3 c.c.; P_{A+E} = 38·1 c.c.				P_E = 25·2 c.c.; P_{A+E} = 26·5 c.c.			
405	37	101·8	1·94	410	53	174·5	3·01	423	57	270·1	4·09
434	88	99·5	1·96	,,	48	173·3	3·00	,,	60	271·6	4·10
,,	70	99·5	1·96	432	96	166·7	3·00	449	60	257·7	4·10
474	120	93·3	1·93	,,	69	166·2	2·99	,,	64	256·8	4·09
,,	150	92·9	1·93	460	110	158·3	2·99	484	82	239·1	4·08
505	110	91·5	1·96	,,	75	159·3	3·01	,,	74	240·6	4·10
	106	91·6	1·96	493	69	150·4	3·00	522	83	224·8	4·10
	Mean	1·95±0·01		,,	74	150·8	3·00	,,	91	224·9	4·10
					Mean	3·00±0·01			Mean	4·09±0·01	

We are indebted to Sir Robert Robertson, K.B.E., F.R.S., for giving us facilities for carrying out this work.

BIRKBECK COLLEGE, FETTER LANE, E.C. 4.
GOVERNMENT LABORATORY, CLEMENT'S INN PASSAGE, STRAND.

[*Received, June* 12*th,* 1935.]