687. *A Comparison of the Apparent Dipole Moments of the Brominated Methanes dissolved in Benzene with the True Values determined as Gases.*

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New measurements provide the following values for CH_3Br, CH_2Br_2, and $CHBr_3$, respectively: $\mu_{\mathrm{gas}} = 1{\cdot}82, 1{\cdot}42, 0{\cdot}99$, and $\mu_{C_6H_6} = 1{\cdot}61, 1{\cdot}41, 1{\cdot}02$ D. The $\mu_{C_6H_6}/\mu_{\mathrm{gas}}$ ratios drawn from these figures fit the equations listed previously by Buckingham and Le Fèvre (*J.*, 1952, 1932) as Nos. 2, 3, and 4 better than they do No. 1.

This paper records measurements parallel to those on the chlorinated methanes (Barclay and Le Fèvre, *J.*, 1950, 556) with a view to supplement information concerning small solute molecules (Buckingham and Le Fèvre, *J.*, 1952, 1932; Harris, Le Fèvre, and Sullivan, *J.*, 1953, 1622; Buckingham, Harris, and Le Fèvre, *J.*, 1953, 1626). The results now obtained are summarised in Table 1 under the headings, and with the symbols, used before (see above references).

Table 1. *Polarisations at 25°, and dipole moments.*

	CH_3Br	CH_2Br_2	$CHBr_3$		CH_3Br	CH_2Br_2	$CHBr_3$
${}_{\mathrm{T}}P_{\mathrm{gas}}$ (c.c.)	82·5	64·3	49·8	$({}_{\mathrm{T}}P_{\infty})_{C_6H_6}$	67·7	63·4	50·9
${}_{\mathrm{D}}P$ (c.c.)	14·7	22·9	29·6	${}_{\mathrm{D}}P$ (c.c.)	14·7	22·9	29·6
${}_{\mathrm{O}}P_{\mathrm{gas}}$ (c.c.)	67·8	41·4	20·2	$({}_{\mathrm{O}}P_{\infty})_{C_6H_6}$	53·0	40·5	21·3
μ_{gas} (D)	1·82	1·42	0·99	$\mu_{C_6H_6}$ (D)	1·61	1·41	1·02

EXPERIMENTAL

Materials.—A B.P.C. sample of methyl bromide was dried by passage through phosphoric oxide, condensed, and redistilled before use, the middle fraction only being taken. Methylene dibromide (*ex* B.D.H.), after being dried ($CaCl_2$), had b. p. 97·2°/755·6 mm. The bromoform, initially a B.P.C. specimen, was dried ($CaCl_2$) and fractionated; b. p. 144·7—145·0°/760 mm. The solvent was prepared by partially freezing " AnalaR " benzene and storing the remelted solid over clean sodium wire.

Measurements on Gases.—The circuit shown as Fig. 3 of the paper by Le Fèvre, Ross, and Smythe (*J.*, 1950, **276**) and the cell assembly illustrated by Le Fèvre, Mulley, and Smythe (*J.*, 1950, **290**) were employed with methyl bromide. For the other two bromo-compounds, requiring higher temperatures, equipment depicted as Figs. 1 and 2 by Le Fèvre, Ross, and Smythe was used, together with the oven and glass-diaphragm gauge mentioned by Freeman, Le Fèvre, and Maramba (*J.*, 1952, 1649). In all cases polarisations were estimated relatively to P_{CO_2} (taken as temperature invariant and equal to 7·341 c.c.; cf. Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374) *via* the equation:

$$P_{\text{gas}} = 7{\cdot}341\,(\delta C/p)^{\text{gas}}_{p=0}/(\delta C/p)^{CO_2}_{p=0}$$

Experimental procedures and methods of calculation were as described by Le Fèvre and Russell (*loc. cit.*). Essential observations are listed in Table 2.

TABLE 2. *Polarisation–temperature relations.*

T, °K	$(\delta C/p)^{\text{gas}}_{p=0}$	P, c.c. (obs.)	P, c.c. (calc.)	p, range in cm.	No. of obsns.	T, °K	$(\delta C/p)^{\text{gas}}_{p=0}$	P, c.c. (obs.)	P, c.c. (calc.)	p, range in cm.	No. of obsns.
Methyl bromide *											
294·7	88·29	83·33	83·25	19—47	11	374·0	57·13	68·58	68·71	27—51	10
339·0	68·27	74·22	74·29	17—47	10	404·8	49·78	64·72	64·60	21—52	12
350·5	64·36	72·36	72·34	18—50	10	455·6	40·31	59·06	59·04	16—59	10
Methylene dibromide †											
362·9	40·36	57·07	56·89	10—20	10	448·7	28·59	50·09	50·39	9—43	12
378·8	37·60	55·52	55·46	16—30	11	488·0	25·18	48·04	48·17	9—31	11
397·0	34·90	54·03	53·97	13—39	10	523·6	22·87	46·84	46·46	11—57	12
419·0	31·86	52·08	52·34	13—36	11						
Bromoform †											
394·2	29·31	45·06	44·87	4—10	11	452·4	24·16	42·69	42·90	7—26	8
426·5	26·50	44·11	43·72	11—30	9	466·2	22·98	41·86	42·52	5—32	12
434·1	25·59	43·37	43·47	13—35	13	494·0	21·96	42·41	41·79	5—52	11
436·5	25·30	43·11	43·39	5—24	12	507·0	20·94	41·52	41·48	6—29	12

* Standardising equation: $(\delta C/p)^{CO_2}_{p=0} = (2307{\cdot}4/T) - 0{\cdot}054$.

† Standardising equation: $(\delta C/p)^{CO_2}_{p=0} = (1901/T) - 0{\cdot}047$.

In each of the three cases the observed polarisations (P, obs.) were fitted by the method of least squares to " Debye " equations of the form $P = A + B/T$; the figures under P, calc. have been computed from the constants A and B so obtained. If for a given set P, obs. − P, calc. = Δ, then the standard errors in A and B may be estimated by the formulæ cited for this purpose by Harris, Le Fèvre, and Sullivan (*loc. cit.*). Thus our results appear as follows:

$$CH_3Br: \; P = (14{\cdot}7 \pm 0{\cdot}4) + (20{,}205 \pm 113)/T; \; \mu_{\text{gas}} = 1{\cdot}821 \pm 0{\cdot}005\,\text{D}.$$
$$CH_2Br_2: \; P = (22{\cdot}9 \pm 0{\cdot}8_4) + (12{,}330 \pm 352)/T; \; \mu_{\text{gas}} = 1{\cdot}42 \pm 0{\cdot}02\,\text{D}.$$
$$CHBr_3: \; P = (29{\cdot}6 \pm 2{\cdot}0) + (6005 \pm 286)/T; \; \mu_{\text{gas}} = 0{\cdot}99 \pm 0{\cdot}2\,\text{D}.$$

In Table 3 these values are compared with those recorded previously.

Measurements on Solutions in Benzene.—These have been made at 25° by the usual procedures (Le Fèvre, " Dipole Moments," Methuen, 2nd Edn., 1948, pp. 31—42), the apparatus described by Le Fèvre and Ross (*J.*, 1950, 283) and by Calderbank and Le Fèvre (*J.*, 1948, 1949) being used. The methyl bromide was dissolved in benzene as was sulphur dioxide by Le Fèvre and Ross, and similar methods were adopted for transferring the solutions to the cell or pyknometer. Calculations and symbols used have been explained previously (Le Fèvre, *Trans. Faraday Soc.*, 1950, **46**, 1, and footnote to Buckingham and Le Fèvre, *J.*, 1952, 1932); however, in the case of methylene dibromide it seemed necessary to assume that both $\varepsilon_{12} - \varepsilon_1$ and

TABLE 3. *Comparison between present and previous measurements.*

μ (D)	Results as :	No. of temps. studied	Author(s) and ref.
			Methyl bromide
1·82	$P = 14{\cdot}7 + 20{,}205/T$	6	Present work
1·82	—	—	(Calc. from Pohrt, *Ann. Physik*, 1913, **42**, 569, by Höjendahl, *Physikal. Z.*, 1929, **30**, 392)
1·79	Individual polarisations	5	Mahanti, *ibid.*, 1930, **31**, 546
1·78	$P = 15{\cdot}40 \pm 19{,}580/T$	5	Smyth and McAlpine, *J. Chem. Physics.*, 1934, **2**, 499
1·75	Individual polarisations	5	Mahanti, *Phil. Mag.*, 1935, **20**, 274
1·79	Individual polarisations	4	Groves and Sugden, *J.*, 1937, 158
$1{\cdot}79_7$	Stark splitting	—	Shulman, Dailey, and Townes, *Phys. Rev.*, 1950, **78**, 145
			Methylene dibromide
1·42	$P = 22{\cdot}9 \pm 12{,}330/T$	7	Present work
1·43	$P = 23{\cdot}51 \pm 12{,}445/T$	5	Maryott, Hobbs, and Gross, *J. Amer. Chem. Soc.*, 1941, **63**, 659
			Bromoform
0·99	$P = 29{\cdot}6 \pm 6005/T$	8	Present work

$d_{12} - d_1$ were represented by $aw_2 + bw_2^2$, and to obtain the " best possible " figures for a, *i.e.*, $(\alpha\varepsilon_1)_{w=0}$ and $(\beta d_1)_{w=0}$, by the method of least squares (cf. Harris, Le Fèvre, and Sullivan, *J.*, 1953, 1622). Table 4 sets out the measurements; the values of μ shown have been computed with the help of the distortion polarisations ascertained during the present work.

TABLE 4. *Dielectric constants and densities of solutions in benzene at 25°.*

10^5w_2	ε_{12}	$\alpha\varepsilon_1$	$(d_4^{25})_{12}$	β	10^5w_2	ε_{12}	$\alpha\varepsilon_1$	$(d_4^{25})_{12}$	β
0	2·2725	—	0·87378	—					
				Methyl bromide					
23,282	2·3387	2·84	0·88288	0·447	40,543	2·3839	2·75	0·88980	0·452
33,397	2·3655	2·78	0·88682	0·447	69,156	2·4624	2·89	0·90048	0·442
39,520	2·3819	2·77	0·88940	0·452	83,759	2·5008	2·73	0·90610	0·442

Whence mean $\alpha\varepsilon_1 = 2{\cdot}79$; mean $\beta = 0{\cdot}447$; ${}_\infty P_2 = 67{\cdot}7 \pm 1{\cdot}25$ c.c.; $\mu_{C_6H_6} = 1{\cdot}61 \pm 0{\cdot}03$ D.

10^5w_2	ε_{12}	$\alpha\varepsilon_1$	$(d_4^{25})_{12}$	β	10^5w_2	ε_{12}	$\alpha\varepsilon_1$	$(d_4^{25})_{12}$	β
				Methylene bromide					
20,952	2·2999	1·322	0·88570	0·656	55,668	2·3461	1·322	0·90615	0·665
40,378	2·3256	1·315	0·89708	0·660	65,802	2·3590	1·335	0·91161	0·668
40,616	2·3260	1·317	0·89716	0·659	73,825	2·3724	1·349	0·91757	0·678

Whence $\alpha\varepsilon_1 = 1{\cdot}28_2 + 0{\cdot}85_6w_2$; $\beta = 0{\cdot}637 + 0{\cdot}539w_2$; ${}_\infty P_2 = 63{\cdot}4 \pm 0{\cdot}6$ c.c.; $\mu_{C_6H_6} = 1{\cdot}41 \pm 0{\cdot}02_5$ D.

10^5w_2	ε_{12}	$\alpha\varepsilon_1$	$(d_4^{25})_{12}$	β	10^5w_2	ε_{12}	$\alpha\varepsilon_1$	$(d_4^{25})_{12}$	β
				Bromoform					
16,209	2·2812	0·537	0·88374	0·703	41,117	2·2949	0·549	0·89951	0·716
18,952	2·2827	0·538	0·88542	0·703	48,205	2·2988	0·546	0·90409	0·720
31,292	2·2891	0·531	0·89355	0·723	54,404	2·3016	0·535	0·90835	0·727
32,423	2·2898	0·534	0·89443	0·729	60,042	2·3048	0·538	0·91188	0·726
37,157	2·2922	0·530	0·89728	0·724	72,981	2·3121	0·543	0·92059	0·734

Whence mean $\alpha\varepsilon_1 = 0{\cdot}538$; $\beta = 0{\cdot}706 + 0{\cdot}366w_2$; ${}_\infty P_2 = 50{\cdot}91 \pm 0{\cdot}54$ c.c.; $\mu_{C_6H_6} = 1{\cdot}02 \pm 0{\cdot}06$ D.

The moments now recorded are compared in Table 5 with others previously reported by Müller and Sack (*Physikal. Z.*, 1930, **31**, 815) and Le Fèvre and Russell (*J.*, 1936, 491).

TABLE 5. *Apparent moments in benzene.*

Solute	Temp.	No. of solns.	μ, D *	μ, D †	Authors
CH_3Br	25°	6	1·61	—	Present
CH_2Br_2	25	6	1·41	—	,,
	25	2	1·37	1·38 (21·5)	Müller and Sack
$CHBr_3$	25	10	1·02	—	Present
	25	4	1·02	0·99 (30·5)	Müller and Sack
	25	2	1·07	1·06 (30)	Le Fèvre and Russell

* Using the ${}_DP$ from measurements on gases.

† Using the molecular refractions shown in parentheses.

Discussion.—Table 6 contains the molecular constants and values of $\mu_{C_6H_6}/\mu_{gas}$ predicted by equations (1), (2), (3), and (4) of the paper of Buckingham and Le Fèvre (*loc. cit.*), the symbols being those defined and employed by these authors. The $(n^2)^{25}_D$ figures, other than that of benzene for which $(n^2)^{25}_D = 2{\cdot}2417$, have been calculated from Vogel's refractivities (*J.*, 1948, 1842) and the densities listed in Table 7. The ξ's were determined from the *A*'s, *B*'s, and *C*'s by referring to Osborn's graphs (*Physical Rev.*, 1945, **67**, 351). When applying equation (4), *i.e.*, Ross and Sack's expression (*Proc. Phys. Soc.*, 1950, *B*, **63**, 893), $n^2_{eff.}$ values (from ${}_DP_2$ and d_2) of 2·044, 2·447, and 2·525 respectively were used; the datum for bromoform, in comparison with the value of $(n^2)^{25}_D$ for that compound, seems possibly a little low.

TABLE 6.

Substance	*A*	*B*	*C*	—	$(n^2)^{25}_D$	$\mu_{C_6H_6}/\mu_{gas}$ calc. by equation : (1)	(2)	(3)	(4)	Ratio found
CH_3Br	5·54	3·80	3·80	0·24	2·015	0·92	0·92	0·91	0·90	$0{\cdot}88_5 \pm 0{\cdot}02$
CH_2Br_2	4·30	6·56	3·60	0·36	2·376	0·99	0·98	0·98	1·04	$0{\cdot}99 \pm 0{\cdot}03$
$CHBr_3$	6·30	6·86	6·86	0·36	2·544	1·13	1·11	1·07	1·05	$1{\cdot}03 \pm 0{\cdot}08$

From Table 6 it may be seen that each of the equations (1)—(4) predicts ratios which are essentially of the correct orders; nos. (2), (3), and (4) appear on the whole preferable to (1)—a conclusion already drawn by Buckingham and Le Fèvre (*loc. cit.*).

Calculation of μ_{gas} from Measurements on Pure Liquids.—The shape factors and values of $(n^2)^{25}_D$ of Table 6 being used in conjunction with appropriate ε's and *d*'s from the literature, μ_{gas} has been estimated from $\mu_{liq.}$ *via* equations (5), (6), and (7) of Buckingham and Le Fèvre. Results are in Table 7, and it is evident that equations (5) and (6) are most satisfactory for these molecules, and superior to Onsager's equation (7).

TABLE 7. *Calculation of μ_{gas} from $\mu_{liq.}$.*

Liquid	ε	*d*	$\mu_{liq.}$	μ_{gas}, calc. by eqn. : (5)	(6)	(7)	μ_{gas}, found
CH_3Br	$9{\cdot}0_2$ [1]	1·668 [1]	1·14	1·84	1·84	1·63	1·82
CH_2Br_2	$7{\cdot}22_5$ [1, 2]	2·470 [3]	1·10	1·43	1·42	1·39	1·42
$CHBr_3$	4·398 [4]	2·878 [5]	0·91	0·97	0·98	1·01	0·99

[1] Extrapolated from Morgan and Lowry, *J. Phys. Chem.*, 1930, **34**, 2385. [2] Interpolated value from Smyth and Rogers, *J. Amer. Chem. Soc.*, 1930, **52**, 2227. [3] Perkin, *J.*, 1884, **45**, 520. [4] Le Fèvre and Le Fèvre, *J.*, 1935, 1747. [5] Sherman and Sherman, *J. Amer. Chem. Soc.*, 1928, **50**, 1119.

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