303. *The Apparent Dipole Moments of Water and Hydrogen Sulphide Dissolved in Benzene.*

By C. L. ANGYAL and R. J. W. LE FÈVRE.

Equation (*a*) of the preceding papers has been used to estimate the apparent moments of water and hydrogen sulphide dissolved in benzene. Results are reconcilable with those obtained by direct observation.

IN connection with points raised in the two preceding papers we here comment on the applicability of equation (*a*) (preceding papers) to the cases of water and hydrogen sulphide. Through experimental causes, the moments of these materials are more easily studied in the gaseous than the dissolved states.

Water.—For this substance the following determinations of μ_{gas} are recorded :

1·87	Jona, *Physikal Z.*, 1919, **20**, 14; cf. Zahn, *Phys. Review*, 1926, **27**, 329.
1·82—1·77	Stuart, *Z. Physik*, 1928, **51**, 490.
$1{\cdot}84_7$	Sänger and Steiger, *Helv. Phys. Acta*, 1928, **1**, 369.
$1{\cdot}84_2$	Sänger, *Physikal Z.*, 1930, **31**, 306; cf. also Sänger, Steiger, and Gächter, *Helv. Phys. Acta*, 1932, **5**, 200.
1·83	Stranathan (*Phys. Review*, 1934, **45**, 741.
1·84	Groves and Sugden, *J.*, 1935, 971.
1·831	Stranathan, *Phys. Review*, 1935, **48**, 538.
1·844	Hurdis and Smyth, *J. Amer. Chem. Soc.*, 1942, **64**, 2829.

The 1935 measurements by Stranathan involved 14 temperatures, being in this respect more extensive than any of the others. The Debye equation derived from them is $P = 4{\cdot}03 + 20710/T$, whence $\mu = 1{\cdot}843$ if the various constants listed by Birge (*Reports Progr. Physics*, 1941, **8**, 126) are used. The distortion polarisation, ${}_{\text{D}}P$, is thus about 1·09 times the $[R_L]_{\text{D}}$ (3·71 c.c.).

Since the molecular volume, V, of liquid water at 25° is 18·069 c.c. ("International Critical Tables," Vol. III, p. 25), $(n^2_{\text{Eff}})^{\text{H}_2\text{O}}$ follows, *via* $(V + 2{}_{\text{D}}P)/(V - {}_{\text{D}}P)$, as 1·86. For comparison, $(n^2_{\text{D}})^{25}$ is 1·7756 (*op. cit.*, Vol. VII, p. 13). The ratio, $(n^2_{\text{Eff}})^{\text{C}_6\text{H}_6}/(n^2_{\text{Eff}})^{\text{H}_2\text{O}}$, is therefore $2{\cdot}30/1{\cdot}86 = 1{\cdot}24$.

A scale drawing, based upon an O–H separation of $0{\cdot}958_4$ Å and an H–O–H angle of 104° 27′ (cf. Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," van Nostrand Co., 1945, p. 489) gave $A : B : C$ as $2{\cdot}73 : 3{\cdot}35 : 2{\cdot}44$, and $\exp x^2$ as 0·875.

Accordingly, by equation (*a*) (preceding papers), the apparent dipole moment of water in benzene is predicted as $0{\cdot}944\mu_{gas} = 0{\cdot}944 \times 1{\cdot}84 = 1{\cdot}74$ D.

Actual determinations in this solvent have been reported to show moments of 1·70—1·83 D:

1·70	Williams, *Physikal. Z.*, 1928, **29**, 204, 683.
1·72	*Idem, J. Amer. Chem. Soc.*, 1930, **52**, 1838.
1·76	Müller, *Physikal. Z.*, 1934, **35**, 1009.
1·83	Schupp and Mecke, *Z. Elektrochem.*, 1948, **52**, 54.

Williams worked with the saturated solution, the concentration of which he inferred from extant solubility data (Hill, *J. Amer. Chem. Soc.*, 1933, **45**, 1143). Müller, and Schupp and Mecke, examined a number of mixtures, made up by weight, having graded strengths.

We find that the six solutions listed in the paper by Müller and the five in that by Schupp and Mecke form a consistent set when brought to the common basis that $\varepsilon^{20}_{C_6H_6} = 2{\cdot}2825$ and $(d_4^{20})_{C_6H_6} = 0{\cdot}87909$. Thus, with compositions expressed as weight fractions, the ten solutions with $100w_1$ between 0·01141 and 0·05780 show $\alpha\varepsilon_2$ values of 21·0, 19·9, 21·7, 20·7, 20·1, $19{\cdot}7_5$, 19·7, $20{\cdot}0_5$, 20·3, and 20·2 (mean value, 20·3); we neglect the weakest mixture, of $100w_1 = 0{\cdot}0028$, the $\alpha\varepsilon_2$ of which is 25·0. From Müller's experiments it is evident that the average βd_2 is *ca.* $0{\cdot}8_7$, whence $(1 - \beta)$ is only 0·01.

The total polarisation of water at infinite dilution in benzene at 20° is therefore (cf. *Trans. Faraday Soc.*, 1950, **46**, 1) $18{\cdot}0(0{\cdot}341 \times 0{\cdot}01 + 0{\cdot}186 \times 20{\cdot}3) = 68{\cdot}0$ c.c. This, with a distortion polarisation of 4·0 c.c., yields a moment of 1·75 D, in fair agreement with the predicted value of 1·74 D.

If instead of "effective" refractive indexes we use the n_D^2 figures appropriate to water and benzene, equation (*a*) still gives a satisfactory forecast for $\mu_{C_6H_6}$. Since other workers have examined water also in dioxan and ether we include these solvents in the following table:

Solvent	$(\varepsilon_2)^{25}$	$(n_2^2)^{25}_D$	$\mu_{soln.}$ (calc.)	$\mu_{soln.}$ (found)
Benzene	2·2725	2·2417 [1]	1·73	1·75
Dioxan	2·306 [2]	2·0171 [3]	1·77	1·90 [4], 1·89 [5]
Ether	4·250 [1]	1·8295 [1]	1·76	1·71 [4]

[1] *J.*, 1950, 556. [2] *J.*, 1935, 957. [3] *J. Amer. Chem. Soc.*, 1937, **59**, 1344. [4] Linton and Maas, *Canad. J. Res.*, 1932, **7**, 81. [5] Weith, Hobbs, and Gross, *J. Amer. Chem. Soc.*, 1948, **70**, 805.

It is seen that we fail to predict a "positive" solvent effect for dioxan, while the degree of diminution of μ_{gas} for ether is insufficient. The latter, however, is a polar liquid and we have previously noted (*J.*, 1950, 556) that equation (*a*) is inadequate in such cases. Moreover, for both solvents there are possibilities of hydrogen-bonding with the solute which cannot exist in water–benzene mixtures. The factors affecting the apparent moment of water may not therefore be the same throughout the three media listed.

Hydrogen Sulphide.—Two determinations only of μ_{gas} are in the literature:

1·10	Braunmühl, *Physikal. Z.*, 1927, **28**, 141.
0·94	Zahn and Miles, *Phys. Review*, 1928, **32**, 497.

Because of the poor concordance we have re-examined the polarisation–reciprocal temperature relation for this substance.

The apparatus used was that depicted as Figs. 2, 3, and 4 of *J.*, 1950, 276, together with the vapour jacketing arrangement shown in *J.*, 1950, 290. The cell was calibrated with carbon

Polarisations of gaseous hydrogen sulphide.

t (C)	$10^6/T$ (K)	$(\delta C/p)^{H_2S}_{p=0}$	P_{H_2S} (c.c.)	P_{H_2S} (calc.)	*p* range (cm. Hg)	No. of observations
62·5°	2981°	24·63	26·5	26·3	30—62	11
77·0	2857	22·77	25·6	25·7	30—65	15
81·0	2825	22·61	25·7	25·6	30—67	16
100·0	2681	20·27	24·3	24·9	32—67	14
111·0	2604	20·18	24·9	24·5	31—65	9
132·0	2469	18·42	24·0	23·8	30—67	15
159·0	2315	16·61	23·1	23·1	35—67	15

whence, by least squares, $P = 11{\cdot}88 + 4843{\cdot}7/T$, and $\mu = 0{\cdot}89_2$ D.

dioxide, the temperature-invariant polarisation of which was taken as 7·341 c.c. (cf. Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374). Since standardising observations showed $(\delta C/p)^{CO_2}_{p=0} = 2307{\cdot}4/T - 0{\cdot}054$, the polarisations in the third column of the annexed table are obtained for each temperature by $P_{H_2S} = 7{\cdot}341\ (\delta C/p)^{H_2S}_{p=0}/(\delta C/p)^{CO_2}_{p=0}$.

Density–temperature values for liquid hydrogen sulphide have been recorded by Steele, McIntosh, and Archibald (*Z. physikal. Chem.*, 1906, **55**, 129). Extrapolation of these gives $d^{25}_4 = 0{\cdot}825$, whence the molecular volume, V, at 25°, is 41·3 c.c. As a check on V so obtained, we may note that Bleckrode (*Proc. Roy. Soc.*, 1884, **37**, 339) found n_D to be about 1·38 at room temperatures; $(R_L)_D$ should therefore be approximately $0{\cdot}90 \times 41{\cdot}3/3{\cdot}90 = 9{\cdot}5$ c.c., in fair agreement with 10 c.c. calculated from the refractivities of hydrogen (1·1) and bivalent sulphur (7·8).

Accordingly $(n_{Eff})^2$ can be estimated from the distortion polarisation, $_DP = 11{\cdot}88$ c.c., as 2·211, so that $(n^{C_6H_6}_{Eff})^2/(n^{H_2S}_{Eff})^2$ becomes $2{\cdot}300/2{\cdot}211 = 1{\cdot}040$.

From a scale drawing, using a S–H distance of 1·334 Å and an H–S–H angle of 92° 16′ (cf. Herzberg, *op. cit.*, p. 489), the dimensions A, B, and C appear as 3·39, 3·74, and 3·08 respectively. Exp x^2 is therefore 0·867. Equation (*a*) accordingly predits $\mu_{C_6H_6}$ as $0{\cdot}974\mu_{gas}$, *i.e.*, 0·869 D.

An attempt has been made to check this forecast by direct measurement.

After preliminary trials the preparation of mixtures gravimetrically was abandoned in favour of the following procedure (adapted from Bell, *J.*, 1931, 1371): Hydrogen sulphide was bubbled gently through benzene for *ca.* 1 hour; 5·00 c.c. of the resulting solution were then added, at 30°, to a mixture of 0·1N-potassium hydroxide (40·00 c.c.), water (50 c.c.), and neutral 30% hydrogen peroxide solution (2·0 c.c.). After thorough shaking, the superfluous peroxide was destroyed by boiling, and the excess of alkali titrated with 0·1N-hydrochloric acid (methyl-red).

The dielectric constant and density of each solution were recorded as soon as possible after its production. Apparatus and methods have been noted before (*e.g. J.*, 1948, 1949). Bath-temperatures of 30° were necessitated by the season. Loss of gas (bubble formation) proved a nuisance; the following measurements alone are those during which it did not occur:

Hydrogen sulphide in benzene at 30°.

10^5w_1	ε^{30}	$\alpha\varepsilon_2$	d^{30}_4	βd_2	10^5w_1	ε^{30}	$\alpha\varepsilon_2$	d^{30}_4	βd_2
0	2·2628	—	0·86718	—	732	2·2802	2·37	0·86670	−0·065
245	2·2692	2·61	0·86708	−0·041	972	—	—	0·86653	−0·067
253	2·2682	2·14	0·86708	−0·040	1235	2·2976	2·82	0·86626	−0·074
730	—	—	0·86671	−0·064	1340	—	—	0·86616	−0·076

whence mean $\alpha\varepsilon_2 = 2{\cdot}48_5$ and mean $\beta d_2 = -0{\cdot}061$.

In view of the variations among the $\alpha\varepsilon_2$ factors, the apparently smooth diminution of βd_2 with w_1 may be misleading. Using a mean β of −0·070 with the maximum and minimum values of $\alpha\varepsilon_2$ we estimate total polarisations for hydrogen sulphide of 14·5—18·9 c.c., whence $\mu_{C_6H_6} = 0{\cdot}85$—$0{\cdot}97$ D. The predicted figure (above) is 0·87 D.

The authors gratefully acknowledge financial assistance from the Commonwealth Science Grant.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA.

[*Received, October* 6*th*, 1951.]