

60. *Sulphur Dioxide. Its Apparent Dipole Moment as a Solute and as a Pure Liquid compared with the True Value as a Gas.*

By R. J. W. LE FÈVRE and I. G. ROSS.

Measurements at 25°, and calculations by the Debye–Clausius–Mosotti formulæ, provide moments of 1.6₁ D. (in benzene), 1.6₂ D. (in carbon tetrachloride), *ca.* 1.4 D. (in chloroform), and 1.1₆ D. (as pure liquid).

Sulphur dioxide is the simplest molecule with a negative Kerr constant whose apparent dipole moments as liquid, or in solution, have been compared with the true value (*i.e.*, 1.6₂ D., see preceding paper) as measured in the gaseous state.

The ratios found for $\mu_{\text{liq.}} : \mu_{\text{gas}}$ or $\mu_{\text{soln.}} : \mu_{\text{gas}}$ disagree with forecasts based on various previous formulæ or “rules” for the effects of media on μ_{apparent} . Theories utilising the conception of hindered molecular rotation in liquid systems are also unsatisfactory in their present forms. A recent treatment of the $\mu_{\text{soln.}} : \mu_{\text{gas}}$ aspect of the problem by Ross and Sack, however requires a small *diminution* in μ_{apparent} on dissolution in benzene or carbon tetrachloride. The experimental indications are that the direction of change is as predicted.

For the purpose indicated in paragraph (a) of the opening of the previous paper, we required dielectric polarisation data for sulphur dioxide, both as a pure liquid, and as a solute in a non-polar solvent. The literature, however, contained only a few ϵ and d points for the former

state, and none for the latter. We have therefore made appropriate measurements on sulphur dioxide-benzene and sulphur dioxide-carbon tetrachloride systems. These are now recorded, together with the details of our redetermination of ϵ_{SO_2} .

Solutions of Sulphur Dioxide.—These were made up by dissolving the gas in a weighed amount of solvent and observing the increase of weight.

For benzene, in which sulphur dioxide is extremely soluble, the solution was prepared by attaching the flask to the outlet tube *C* of the gas apparatus (see Fig. 3, preceding paper), and controlling the vaporisation of purified liquid sulphur dioxide so as to maintain a gas pressure of about $1\frac{1}{2}$ atmospheres. The flask was cooled to *ca.* 5° and shaken occasionally, absorption taking place readily, about 2 hours sufficing to make up a solution of adequate concentration. By not passing the gas *through* the liquids the possibility of solvent loss (which would result in an underestimate of the weight fraction) was avoided.

For carbon tetrachloride, with which this process would have been tedious, owing to the lower solubility, a small quantity of liquid sulphur dioxide was collected in a test tube attached to the ground glass cone on *C*. When the gas pressure had reached atmospheric, the tube was detached and the contents introduced into the weighed benzene, the flask being closed with a rubber stopper, and reweighed.

The density measurements were made with a Sprengel pycnometer of about 10 ml. capacity, with capillary side-arms. The liquid was moved by pressure of dry air, rather than by suction, which caused liberation of gas. Even so, evolution of vapour did occur at times during adjustment in the thermostat, and the accuracy of the measurements, while adequate, is less than that made with non-volatile solutes. The dielectric constant determinations were made with the resonance apparatus described by Calderbank and Le Fèvre (*J.*, 1948, 1949). The cell was filled and emptied by air pressure. The results are given in Table I, the symbols being those customarily used by us (cf. *J.*, 1937, 1805).

TABLE I.

Sulphur dioxide in benzene.						Sulphur dioxide in carbon tetrachloride.		
$10^6 w_1$.	$(d_{12})_{25}^{25}$.	$(\epsilon_{12})_{25}^{25}$.	β .	$\alpha\epsilon_2$.	τP_{12} *	$10^6 w_1$.	$(\epsilon_{12})_{25}^{25}$.	$\alpha\epsilon_2$.
0	0.87378	2.2725	—	—	—	0	2.2261	—
14396	0.87821	2.3508	0.351	—	—	7438	2.2805	7.32
29537	0.88179	2.3853	0.354	4.35	58.8	7834	2.2835	7.29
34459	0.88462	2.4241	0.360	4.40	64.6	8972	2.2884	6.95
40972	0.88690	2.4515	0.366	4.37	63.8	12178	2.3127	7.11
59644	0.89252	2.5409	0.360	4.50	64.1	24634	2.3994	7.04
73010	0.89705	2.6117	0.364	4.61	64.6	31909	2.4354	6.56

* Calculated by Sugden's equation (*Trans. Faraday Soc.*, 1934, **30**, 720).

From the above data for benzene as solvent the dipole moment can be evaluated: mean $\beta = 0.359$, $\alpha\epsilon_2 = 4.21 + 5.20w_1$ whence $\tau P_\infty = 64.72$ c.c., and—since the distortion polarisation = 10.9_1 c.c. (cf. preceding paper)— $\mu = 1.61_2$.

With carbon tetrachloride as solvent, our density determinations produced somewhat scattered values (-0.21 to -0.32) for β . Recourse was therefore made, as a check, to the careful dilatometric measurements of Horiuchi (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1931, **17**, 126) on solutions of gases in certain organic liquids. Extrapolation to zero concentration of Horiuchi's figures for the coefficient of dilatation, δ , of sulphur dioxide in carbon tetrachloride gives $\delta = 2.435 \times 10^{-3}$. If the density of sulphur dioxide at N.T.P. is taken as 2.9269 g./l. (International Critical Tables, Vol. **3**, p. 3), the limiting rate of decrease in density with concentration of sulphur dioxide can be calculated; whence $\beta = -0.318$. (A similar calculation with benzene, taking $\delta = 2.138 \times 10^{-3}$, gave $\beta = +0.363$, in good agreement with our direct measurements in this medium.) We note that the densities of the two weakest sulphur dioxide-carbon tetrachloride solutions (11–16%) used by Adams and Rogers (*J. Amer. Chem. Soc.*, 1939, **61**, 112) correspond to a β of -0.22 . Nevertheless, since both $1 - \beta$ and $\alpha\epsilon_2$ increase with dilution, we have taken -0.318 and 7.32 respectively (whence $\tau P_\infty = 65.15$ c.c. and $\mu = 1.61_2$ D.) to provide a maximum estimate of the apparent moment.

Six solutions of sulphur dioxide in chloroform were also examined but were marred by unavoidable escapes of gas. The approximate values obtained for β and $\alpha\epsilon_2$ were -0.11 (± 0.01) and 8.4 (± 0.25) respectively; from these, μ is *ca.* 1.4 D.

Liquid Sulphur Dioxide.—A number of measurements of the dielectric constant of this material are on record. Coolidge (*Wied. Annalen*, 1899, **69**, 125), using Drude's second method (*ibid.*, 1897, **61**, 466), found $\epsilon = 13.75$ at 14 – 15° (frequency 300 mc./s.). Schlundt (*J. Physical Chem.*, 1901, **5**, 157, 403), with the same method, gave $\epsilon = 12.35$ at 22° , while Verain (*Ann. Physique*, 1914, **1**, 523) obtained values about half those reported by previous workers. Everschein (*Ann. Physik*, 1902, **8**, 539) used a bridge method, and covered the temperature range from 114° to 157.5° , just above the critical temperature. His results can be summarised (when $0^\circ < t^\circ < 150^\circ$) by the relation: $\epsilon_t = 15.6 - 0.078t$. Using Everschein's temperature coefficient of ϵ , we may reduce these readings to a single temperature (0°) for comparison: 14.9 (Coolidge), 15.5 (Schlundt), 14.6 (Everschein).

Coolidge and Schlundt, and presumably also Everschein (although this is not explicit in his paper), used for calibration various benzene-acetone mixtures, whose dielectric constants had been measured by Drude (*loc. cit.*). In our experience pure acetone is a most difficultly reproducible substance for use as a standard, and, in this connection, we would emphasise that the value quoted by Drude for $\epsilon_{\text{benzene}}$ at 19° (2.260) is markedly less than the value (2.2846) given by Hartshorn and Oliver (*Proc. Roy. Soc.*, 1929, **A**, **123**, 666).

Having found that the overall capacity of his cell, empty, did not vary measurably with temperature (a likely result if the effect of changes in cell dimensions due to expansion of the condenser and glass container are analysed), Eversheim used throughout the whole temperature range the value of the replaceable cell capacitance as measured at one temperature. His measurements are therefore probably all in error by a constant factor, depending on the calibration of his cell and the purity of his material.

We have accordingly re-measured the dielectric constant of sulphur dioxide at 0° (when the vapour pressure is only 1.53 atm.) and used the (corrected) slope of Eversheim's graph to calculate the value of 25° (vapour pressure, 3.82 atm.). By working at the lower temperature, the system could be closed with ordinary taps, instead of sealing off the inlet tubes, thus considerably lessening the chance of disturbing the cell and leads between readings.

To this end, a cell was used, consisting of two coaxial brass tubes, $\frac{1}{2}$ " and $\frac{5}{8}$ " external diameter, and 13 mm. (inner) and 15 mm. long respectively, spaced by four glass beads (diameter ca. 1 mm.), fitting into shallow sockets on the inner cylinder. The assembly hung rigidly from two stout tungsten wires which passed through the glass ("Pyrex") into mercury-filled cups, whence leads were taken to a coaxial cable connector, fixed on the wooden bridge locating the cell in a constant temperature bath. The latter was a lagged 3-l. beaker, filled with ice and water and provided with a levelling device. Adequate stirring, it was found, could be achieved by dropping a few small fragments of solid carbon dioxide into the bath.

The capacitance measurements were performed with an apparatus similar to that used for measuring the dielectric constants of sulphur dioxide solutions.

The cell was calibrated at 0°, using five liquids whose dielectric constants had been determined at this temperature by Le Fèvre (*Trans. Faraday Soc.*, 1938, **34**, 1127), together with ethylene dichloride.

It was found that for any given liquid, the value of ($C_{\text{liq.}} - C_{\text{air}}$) was reproducible to better than two scale divisions of the variable condenser connected in parallel with the cell, a liquid with $\epsilon - 1 = 2$ giving a difference of approx. 200 such divisions.

The results of this calibration are given in Table II, the cell constant being the replaceable capacitance, measured in divisions of the condenser scale.

TABLE II.
Calibration of liquid cell.

Liquid.	($C_{\text{liq.}} - C_{\text{air}}$).	$\epsilon - 1$.	Cell constant.
Carbon tetrachloride	131	1.2734	102.9
Toluene	144	1.4350	100.3
Ether	379	3.803	99.7
Chloroform	433	4.189	103.5
Ethyl bromide	933.5	9.19	102.0
Ethylene dichloride	1038.5	10.514	103.5

Acetone ($\epsilon - 1 = 20.58$) was also used, but with it the resonance curve was damped and widened. Rejecting the ether reading as improbably low, and noticing that any error in the cell constant calculated from toluene is magnified by the fact of its having a small dielectric constant, we adopted the mean value of 103 for the cell constant, with a probable error of about $\pm 1\%$. We are not justified in assuming any deviation from linearity of ($C_{\text{liq.}} - C_{\text{air}}$) with dielectric constant.

The value taken for the dielectric constant of ethylene dichloride needs further comment, in view of the recently published value (extrapolated to 0°) of 11.77 (Clay, Dekker, and Hemelryk, *Physica*, 1943, **10**, 768). The figure used in Table II is that found by Davies (*Phil. Mag.*, 1936, [vii], **21**, 1008), whose objective was to establish this liquid as a standard substance. Davies has reviewed determinations prior to his own; most of those which are subsequent, despite their claimed accuracy of 0.02%, are not supported by details of any practical re-examination of the problem of obtaining reproducibly purified specimens. The earlier figure, due to Davies, has accordingly been retained.

Sulphur dioxide, from a cylinder, was dried by repeated fractional distillation over phosphoric oxide, the gas being passed each time through phosphoric oxide-glass wool bulbs. It was finally distilled from fresh phosphoric oxide directly into the cell, which for the purpose was connected *via* its right-hand arm to the outlet tube C of the gas-handling apparatus (Fig. 3, preceding paper) by thick-walled rubber tubing, the system being made vacuum tight. When surrounded by alcohol at about -80° , the cell took 1—2 hours to fill. This accomplished, the alcohol was replaced by ice-water, and the capacitance measured when stationary conditions had been attained. The sulphur dioxide was then cautiously allowed to boil off, air (dried by passage over 5 feet of P_2O_5) passed through for about a minute, and the "air" reading taken. The differences, $C_{\text{liq.}} - C_{\text{air}}$, so obtained were constant at 1450.0, whence $\epsilon_{\text{SO}_2} = 15.0_8$ at 0°, and (using the corrected $\delta\epsilon/\delta t$ of -0.075) 13.20 at 25°.

From these quantities the "apparent" dipole moments according to the formulæ of Debye, ${}_0P = M[(\epsilon - 1)/(\epsilon + 2) - (n^2 - 1)/(n^2 + 2)]/d$, and Onsager, ${}_0P = M(\epsilon - n^2)(2\epsilon + n^2)/d\epsilon(n^2 + 2)^2$, can now be calculated approximately. The refractive index, n , of sulphur dioxide for the D line at 20° is 1.342 (Nasini, *Gazzetta*, 1883, **18**, 296) corresponding approximately to 1.362 at 0° (Bleekrode, *Proc. Roy. Soc.*, 1884, **37**, A, 339). Nasini (*loc. cit.*), Cailletet and Matthias (*Compt. rend.*, 1887, **104**, 1564), Lange (*Z. angew. Chem.*, 1899, **12**, 277), Stowe (*J. Amer. Chem. Soc.*, 1929, **51**, 410), Seyer and Peck (*ibid.*, 1930, **52**, 14), and Eversole, Wagner, and Bailey (*J. Physical Chem.*, 1941, **45**, 1388), quote densities for liquid sulphur dioxide which, after conversion to 0° and 25°, provide the average values 1.435 (0°) and 1.369 (25°).

By substitution, we find :

		0°.	25°.
Debye equation	$\circ P$	27.0 c.c.	27.3 c.c.
	μ	1.10 D.	1.16 D.
Onsager equation	$\circ P$	84.4 c.c.	79.4 c.c.
	μ	1.93 D.	1.96 D.

For large values of ϵ , the Debye expression is highly insensitive to small variations in this quantity. With regard to the Onsager equation, it can easily be shown that for ϵ *ca.* 15, n^2 *ca.* 2, $\Delta_{\circ P}/\circ P = -0.87 (\Delta n^2/n^2) = 1.34 (\Delta\epsilon/\epsilon) = -\Delta d/d$, and that it will therefore be affected chiefly by errors in ϵ . These we estimate generously at $\pm 1\%$, whence the uncertainty in $\circ P$ is ± 1.2 c.c., and in μ , ± 0.07 D.

Discussion.—As a preliminary, the foregoing experimental results (as calculated by the Debye equation) are summarised in convenient form as Table III.

TABLE III.

State.	Gas.	Solution in C_6H_6 .	Solution in CCl_4 .	Solution in $CHCl_3$.	Liquid.
τP_{apparent}	65.15	64.7 ₂	65.1 ₅ †	51.2	38.2
$\mu_{\text{apparent}}^2/\mu_{\text{gas}}^2$	—	0.99 ₂	1.00 †	0.74	0.50
$\delta\mu^*/\mu_{\text{gas}}$	—	-0.00 ₄	0 †	-0.136	-0.28

* $\delta\mu = \mu_{\text{liquid}}$ OR $\mu_{\text{soln.}}$ minus μ_{gas} .

† A *maximum* estimate, cf. p. 284.

Solutions of Sulphur Dioxide.—The particular relevance of sulphur dioxide as a substance for the investigation of solvent effects lies in the fact that it is a relatively simple molecule of shape not greatly different from ellipsoidal, and possessing a negative Kerr constant (K at 760 mm. for light of 5400 Å. = -9.4×10^{-15} ; Stuart and Volkmann, *Ann. Physik.*, 1933, **18**, 140). It is thus well suited for testing the rule—first devised by Goss (*Trans. Faraday Soc.*, 1934, **30**, 751) on the basis of the Raman-Krishnan theory (*Proc. Roy. Soc.*, 1928, **A**, **117**, 589) of the dielectric constant of anisotropic liquids (as applied to liquid mixtures) and subsequently advanced by Higasi (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **28**, 284) from a different viewpoint—that the sign of the solvent effect should be opposite to that of the Kerr constant of the substance. This rule was dependent upon the consideration of spheroidal molecules, or of those which could be regarded as approximately spheroids; recently, however, Ross and Sack (*Proc. Physical Soc.*, in the press), by widening the Raman-Krishnan and Higasi arguments to ellipsoidal molecules with *three unequal* axes, have shown that even on the basis of these—themselves not complete treatments—the Kerr constant rule could not have had a completely general applicability; indeed for molecules in which the resultant moment is parallel to the mid-axis of its ellipsoidal approximation—and sulphur dioxide is one such—the sign and magnitude of the Kerr constant need give no indication at all of the sign and magnitude of the solvent effect.

By extending Onsager's approach (*J. Amer. Chem. Soc.*, 1936, **58**, 1486) to the static dielectric constant of liquids and solutions (again, the original was derived for spherical molecules only) to ellipsoidal molecules of uniform polarisability, Ross and Sack obtain a new expression for the solvent effect, in which the sign of $\delta\mu$ depends not only on the shape of the solute molecule but also on its refractive index and on the dielectric constant of the solvent medium. We merely note here, quoting from their paper, and applying their calculation also to the carbon tetrachloride solution, that while the generalised Higasi theory, even in an amended form [which tends to reduce $\delta\mu/\mu$ by a factor of $(\epsilon + 2)/3\epsilon$], requires a $\delta\mu/\mu = +0.011$ in both benzene and carbon tetrachloride, the Ross-Sack equation leads to $\delta\mu/\mu = -0.016$ (in benzene) and -0.012 (in carbon tetrachloride). Thus, while it is not correct quantitatively, the new equation is qualitatively so in successfully covering the small decrease in apparent moment, noted (cf. Table III) with the former solvent, and inferred for the latter.

We conclude therefore, from both the theoretical considerations of Ross and Sack and the experimental evidence presented here for sulphur dioxide, that values of the Kerr constant can no longer be regarded as a satisfactory basis for predictions concerning the solvent effect.

Liquid Sulphur Dioxide.—It is now generally recognised that the assumptions made in the derivation of the Debye equation are too drastic to allow it to be used to calculate the dipole moments of molecules from measurements of the pure liquid substances; the data in the last column of Table III concerning liquid sulphur dioxide illustrate this.

Onsager's expression (cf. p. 285) for spherical isotropic molecules has been found to be of more general applicability. It has been critically tested on 31 pure liquids by Böttcher

(*Physica*, 1939, 6, 59), who finds it to give values of μ_{apparent} in good accord with μ_{gas} . Wilson (*Chem. Reviews*, 1939, 25, 377), however, has pointed out that in view of Onsager's neglect of association effects and of molecular anisotropy, this agreement is probably fortuitous. He also suggests that instead of using for n the extrapolated value of the refractive index at infinite wave-length, the effective refractive index, defined by: $(n_{\text{eff}}^2 - 1)/(n_{\text{eff}}^2 + 2) = 4\pi N\alpha/3 = d(\text{E}P + \text{A}P)/M$ should be taken, where $(\text{E}P + \text{A}P)$ is the observed distortion polarisation (preferably from gas measurements).

Wilson has adapted Onsager's theory to cover the anisotropy of the molecular units forming a liquid: if n_2 is the effective refractive index corresponding to the polarisability α_2 along the dipole axis (defined by an equation similar to that just written), and if n is the average effective refractive index, then $M(\epsilon - n^2)/d\epsilon(2\epsilon + n^2) = 4\pi N\mu^2(n_2^2 + 2)^2/9kT(2\epsilon + n_2^2)^2$ and n_2 can be estimated from Kerr constant-polarisability data. The results of these several calculations applied to sulphur dioxide at 25° are as follows:

Data used: $\text{E}P + \text{A}P = 10.9$; $d = 1.369$, $\epsilon = 13.20$, $n_{\text{eff}}^2 = 1.911$, $n_2^2 = 1.769$.

Onsager's equation (using n_{eff}^2): ${}_0P_{\text{liq.}} = 74.07$. ${}_0P_{\text{liq.}}/{}_0P_{\text{gas}} = 1.365$.

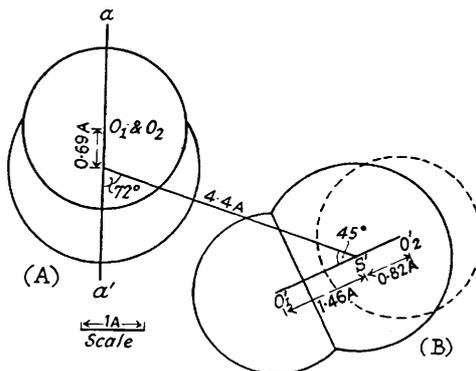
Wilson's equation: ${}_0P_{\text{liq.}} = 78.31$, ${}_0P_{\text{liq.}}/{}_0P_{\text{gas}} = 1.444$.

Kirkwood's equation (see below); $g = 1.399$.

It will be observed that Onsager's equation (even when n_{eff}^2 is used in place of n^2), as well as Wilson's extension of it, lead to predicted values of the orientation polarisation approximately 40% too high.

An explanation of the increased apparent moment of sulphur dioxide in the liquid state, as indicated by these equations, may be found in the results of an X-ray examination of liquid sulphur dioxide at room temperature by Bastiansen and Finbak (*Tids. Kjem. Bergvesen. Met.*, 1945, 4, 2). Their figures for the shape of the sulphur dioxide molecule in the condensed phase agree exactly with the figures of Pauling and Brockway (*J. Amer. Chem. Soc.*, 1935, 57, 2684) for the gas. They give also intermolecular distances and angles which describe a quasi-crystalline structure with 4-fold (tetrahedral) co-ordination of sulphur dioxide molecules about a central molecule. Unfortunately, these authors do not show the relative disposition of any two complete adjacent molecules, but we may determine this by applying the reasonable principle that, of the four molecules B, C, D, and E, surrounding a central molecule A, two, say B and C, must be disposed with respect to A, as is A with respect to D and E, since A is one of the four molecules adjacent to each of the latter. Then it is found that on the figures of Bastiansen and Finbak only one type of mutual orientation is possible. This is shown in the figure; the dotted O atom is the one whose position we infer; it lies either above or below the plane of the figure; the two O atoms of the central sulphur dioxide molecule A lie in the plane through aa' perpendicular to the plane of the figure. A second molecule B can occupy the positions similar to those of B on the other side of aa' , and D and E, the locations of whose S atoms only are given by Bastiansen and Finbak, are in front of and behind, respectively, and above, A, disposed in the same way as A is to B. If we calculate the field due to each of the four dipolar molecules at A (assuming the intervening dielectric to be uniform, *i.e.*, no refraction of the lines of force) it is found that in each case there is a component parallel to and in the same sense as the dipole of A; the components perpendicular to this will cancel on the average, in view of the choice of positions available for each of B, C, D, E. Thus there is a polarising field producing an additional moment which, combined vectorially with the original moment, must increase it; to attempt to calculate precisely this short-range dipolar action would involve too many assumptions, but the general conclusion, that it will reinforce rather than detract from the original moment, still holds.

Finally, Onsager's equation has been further modified by Kirkwood (*J. Chem. Physics*, 1939, 7, 911; *Ann. N.Y. Acad. Sci.*, 1940, 40, 315), who has allowed, in principle, for a mutual action of any kind between the molecules, although—since this action cannot yet be evaluated in precise terms—the equation he derives is not amenable to direct test. Kirkwood finds $M(\epsilon - 1)(2\epsilon + 1)/9\epsilon d = \text{E}P + \text{A}P + 4\pi N\mu\bar{\mu}/9kT = \text{E}P + \text{A}P + 4\pi N\mu^2g/9kT$. Here μ is the



dipole moment of the molecule in the absence of an applied field, and is evaluated sufficiently accurately by the relation due to Onsager (*loc. cit.*): $\mu = \frac{2\epsilon + 1}{2\epsilon + n^2} \cdot \frac{n^2 + 2}{3} \cdot \mu_0$; $\bar{\mu}$ is the total moment of a molecule and its neighbours in the region surrounding it, in which the local dielectric constant differs effectively from the overall macroscopic value.

The "correlation parameter," g , is a measure of the degree and strength of association of the molecules in the liquid. For water and alcohols, which have strong intermolecular hydrogen bonding, Oster and Kirwood (*J. Chem. Physics*, 1943, 11, 175) have attempted to evaluate g theoretically (but even then on questionable assumptions; Frenkel, "Kinetic Theory of Liquids," Oxford, 1946). For sulphur dioxide, which has no such strong bonding, this is not possible.

However, g is accessible from experimental data, and the value obtained (see above) shows that sulphur dioxide falls in the same class as liquids such as ammonia, ether, acetone, and nitrobenzene, for all of which g is in the range 1.1 to 1.7; we conclude therefore that sulphur dioxide shows especially marked association.

In this connection we would mention that the extraordinary mutual solubility of benzene and sulphur dioxide (amounting to complete miscibility of two substances which are chemically dissimilar) might lead to a suspicion that some sort of association of a more formal kind than the type so far considered may exist in these mixtures, although the freezing-point curve gives no indication of this. Seyer and Peck (*J. Amer. Chem. Soc.*, 1930, 52, 14), from determinations of the Eötvös constant, inferred that sulphur dioxide was associated only below 0°, and not noticeably so in mixtures. In harmony with this, we find the total polarisations (cf. Table I, p. 284) to be substantially independent of concentration. There seems, therefore, to be no evidence for the formation of sulphur dioxide-benzene complexes. Viscosity data (Adams and Rogers, *J. Amer. Chem. Soc.*, 1930, 61, 112) suggest a similar conclusion for the system sulphur dioxide-carbon tetrachloride.

Concerning the pure liquid, in addition to the remarks of Seyer and Peck, we note that Awbery and Griffiths (*Proc. Physical Soc.*, 1936, 48, 372) report sulphur dioxide as obeying Herzog and Kudar's relation (*Z. Physik*, 1933, 80, 217) between latent heat of fusion and viscosity, *i.e.*, behaving as an unassociated liquid.

The foregoing review offers nothing to support the discussion of Le Fèvre and Le Fèvre (*J.*, 1935, 1747; 1936, 487) or that of Le Fèvre and Russell (*J.*, 1936, 491), both of which assumed solute association in pairs at least. Statements made in the second 1936 paper require amendment in the light of the measurements now recorded for sulphur dioxide. Thus the sign of the Kerr constant was introduced through a structural coincidence, molecules for which K is positive or negative being classed as "type A" or "type B" respectively. Further, both these "types" were idealised (cf. diagrams on p. 1784 of the 1935 ref.) beyond usefulness where sulphur dioxide is concerned, since the mutual orientation of the sulphur dioxide molecules in the liquid, as indicated by X-ray evidence and supported by apparent moment determinations, corresponds in no way to the type of association postulated for molecules of type B, which, it was put forward, should pack together collinearly, with their dipoles parallel and in line. In particular, the predictions made by Le Fèvre and Russell (second 1936 ref. above) for cases where a solute and solvent are each of B type, are shown to be incorrect by the present findings for sulphur dioxide in chloroform and in itself.

Theories Involving Hindered Rotation in Liquids.—A number of other attempts have been made to introduce features of the structure of liquids into discussions of their dielectric properties. Stewart's idea of cybotaxis (*Rev. Mod. Physics*, 1930, 2, 116; *Physical Rev.*, 1931, ii, 37, 9), and the experimental evidence behind it, seem particularly suggestive, in that the predisposition of a liquid to contain more or less ordered arrangements over small elements of its volume springs from the anisotropic properties of the molecules concerned. Debye (*Physikal. Z.*, 1935, 36, 100, 193; *Chem. Reviews*, 1936, 19, 171) and Fowler (*Proc. Roy. Soc.*, 1935, A, 149, 1) have assumed that dipolar molecules in liquids are not free to rotate but only to execute oscillations about axes whose directions change slowly, but over short periods of time are fixed by the fields of the neighbouring molecules. Thus Debye writes for the orientation polarisation: ${}_0P = (4\pi N\mu^2/9kT)[1 - L^2(\beta)]$, where $L(\beta)$ is Langevin's function of $\beta = E/kT$. For sulphur dioxide we have ${}_0P_{\text{liq.}}/{}_0P_{\text{gas}} = 0.5 = [1 - L^2(\beta)]$, whence E , the "binding energy" = $3.4kT$; for comparison, water shows ${}_0P_{\text{liq.}}/{}_0P_{\text{gas}} = 0.193$ and $E = 11kT$, and ammonia, 0.41 and $4.4kT$ respectively. The theoretical calculation of E has not yet been accomplished. Attempts, using the molecular interactions obtained by London (*Trans. Faraday Soc.*, 1937, 33, 8) in conjunction with inter-dipole distances of $2r$, where $r^3 = 0.916 \times \text{molecular volume} \times 10^{-24}$,

yield only $E = 0.25kT$ for water and $0.1kT$ for ammonia. A more serious objection is that the factor $[1 - L^2(\beta)]$ fails to deal with cases (*e.g.*, trimethylamine) where ${}_0P_{\text{liq.}}/{}_0P_{\text{gas}}$ exceeds unity.

Kincaid and Eyring (*J. Chem. Physics*, 1938, **6**, 620) have approached the problem *via* the "free volumes" and the "free angle ratios" (f.a.r.) of molecules in a condensed phase. Both these concepts, to a first approximation, concern the regions in which displacement can occur. For molecules with three degrees of freedom the f.a.r. is written δ_3 and the rotation taken as restricted between the limits of the polar angles 0 and θ_1 , then $\mu_{\text{liq.}}^2/\mu_{\text{gas.}}^2 = 1 - [(1 + \cos \theta_1)/2]^2$. Since it is often approximately true that the potential curves for the rotation of the molecule about the three axes are symmetrical, $\delta_2 = \delta_3^{2/3}$ and $\delta_2 = (1 - \cos \theta_1)/2$. For the angular water molecule, $1/\delta_3$ is calculable from the product (6.1×10^{-120}) of the principal moments of inertia and various constants as $10.14 \times 10^{60} \times (ABC)^{\frac{1}{2}} = 25.05$; δ_2 therefore is 0.116, whence $\mu_{\text{liq.}}^2/\mu_{\text{gas.}}^2 = {}_0P_{\text{liq.}}/{}_0P_{\text{gas.}} = 0.22$, *i.e.*, of the order found by direct measurement (0.19). A parallel calculation cannot yet be made for sulphur dioxide ($ABC = 13.9 \times 83.2 \times 97.1 \times 10^{-120}$, Mulliken, *Rev. Mod. Physics*, 1942, **14**, 204) since the frequencies associated with hindered translation or rotation do not seem to have been observed (*cf.* Cartwright, *Nature*, 1935, **136**, 181; *Physical Rev.*, 1936, **49**, 470; Strong and Woo, *ibid.*, 1932, **42**, 267; for the Einstein functions in the water case just cited we have used $\nu = 170$ and 500 cm.^{-1} from Hibben, "The Raman Effect and its Chemical Applications," Reinhold, 1939, p. 320).

The required $(\delta_3)_{\text{SO}_2}$ has therefore been estimated from the product $\delta_3 V_f (= RT/p \cdot \exp \Delta H_{\text{vap.}}/RT$; Kincaid and Eyring, *loc. cit.*) and the equation: $(v_f)^{1/3} = 2RTV^{0.33}/N^{0.33}\Delta E_{\text{vap.}}$ (Glasstone, Laidler, and Eyring, "Theory of Rate Processes," McGraw-Hill, 1941, p. 479), in which the symbols have conventional meanings or are defined in the sources cited; $T = 298^\circ$; p , the vapour pressure of liquid sulphur dioxide at 298° , is 3.863 atm. (International Critical Tables, Vol. III, p. 236), the molecular volume, 46.8 (present paper), and the latent heat of evaporation 345 joules/g. (estimated from data given by International Critical Tables, Vol. V, p. 138). Thus $\delta_3 = 0.03$ and $\delta_2 = 0.097$, whence $\mu_{\text{liq.}}^2/\mu_{\text{gas.}}^2$ should be *ca.* 0.2. This is 2.5 times too small. From the observed ratio, δ_2 is seen to be 0.29. Kincaid and Eyring note that δ_2 from dielectric constant measurements tends to exceed $(\delta_3)^{2/3}$ from other sources (*e.g.*, with methanol, $\delta_2 = 0.25$ from ϵ methods and 0.13 by the alternative routes). Nevertheless the theory evidently fits the simple molecule sulphur dioxide too inadequately for it to merit the status of a general *a priori* explanation of solvent effects. In its present form it has the further disadvantage that it cannot forecast correctly those circumstances which lead to ${}_0P_{\text{liq.}}/{}_0P_{\text{gas}}$ ratios greater than one.

Concluding Remarks.—We have disregarded certain early empirical relationships, such as those proposed by Müller, Jenkins, Arkel and Snoek, Sugden, Henriquez, etc. (*cf.* Glasstone, *Ann. Reports*, 1936, **33**, 117 for summary and references) since they all required the ratio $\mu_{\text{liq. or soln.}}/\mu_{\text{gas}}$ to be less than unity—a forecast already adequately established as not always correct (*e.g.*, Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374; compare paraldehyde, following paper). The present work on sulphur dioxide has now demonstrated the inapplicability of a number of other treatments which have hitherto shown signs of sufficiency. The Ross-Sack theory alone remains with promise of explaining apparent moment ratios in dilute solutions. Even it will not cover pure polar liquids. Perhaps it is impracticable to hope for a "universal formula" in the latter problem. Indeed, as knowledge of liquid "structures" accumulates, the need for such a "formula" will decline, since the calculations necessary should then require only the ordinary considerations of electrostatics.

Materials not Specified Previously.—*Carbon tetrachloride.* Technical carbon tetrachloride was refluxed over mercury for 16 hours, then shaken for some hours successively with concentrated sulphuric acid, dilute sodium hydroxide solution, and water. After storage over calcium chloride for a week, it was fractionally distilled from paraffin wax, again dried (P_2O_5) for further week, redistilled, left over phosphoric oxide for 3 weeks, and distilled immediately before use, the middle half of the distillate (b. p. 76.7°) only being collected.

Toluene. Commercial toluene was shaken several times with small quantities of concentrated sulphuric acid and washed with dilute aqueous sodium hydroxide and distilled water; it was then dried ($CaCl_2$), refluxed for some hours over mercury, dried (P_2O_5) for a week, and redistilled; b. p. 110.6° .

Ether. To remove the chief impurities present in "B.P." ether, it was shaken with $\frac{1}{10}$ th of its volume of 10% silver nitrate solution (*cf.* Werner, *Analyst*, 1933, **58**, 335), washed with water, concentrated sulphuric acid, and water, dried (Na wire), fractionally distilled, dried, and again distilled; b. p. 34.6° .

Chloroform. An "AnalaR" supply was successively shaken with sodium hydrogen sulphite solution, water (twice), concentrated sulphuric acid (3 times) and water, dried ($CaCl_2$) for 3 weeks, distilled, dried (P_2O_5), and redistilled, b. p. 61.2° .

Ethyl bromide. Ethyl bromide (from B.D.H.) was shaken successively with concentrated sulphuric acid, sodium carbonate solution, and water (each 4 times, and for some hours). It was then dried

(CaCl₂), fractionally distilled, dried (P₂O₅), distilled again, and stored over phosphoric oxide, being distilled before use; b. p. 38·4°.

Ethylene dichloride. The commercial liquid was washed with dilute potassium hydroxide solution and water, dried (CaCl₂), distilled, and twice dried (over P₂O₅), and redistilled; b. p. 83·5°.

Acetone. This was shaken with a small quantity of 15% silver nitrate, to which had been added an equal volume of *n*-sodium hydroxide (Werner, *loc. cit.*). It was then dried (K₂CO₃), distilled, set aside over potassium carbonate, and redistilled before use. This specimen was still sufficiently moist to damp the oscillations appreciably; a further rapid distillation over phosphoric oxide failed to bring about an adequate improvement; b. p. 56·3°.

Benzene. "AnalaR" thiophen-free benzene was dried over sodium wire, purified twice by fractional crystallisation, and stored over sodium wire.

The authors acknowledge their gratitude to the Chemical Society for the continued loan of apparatus originally purchased by a Research Grant, and to the Commonwealth Science Fund for financial assistance with this investigation, and for a Senior Studentship (to I. G. R.).

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

[Received, September 12th, 1949.]
