823. *Molecular Polarisability. The Measurement of Molecular Kerr Constants in Solution.*

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The specific and molar Kerr constants (${}_{s}K$ and ${}_{m}K$ respectively) of a substance are defined and apparatus for their determinations described. To observations on binary mixtures, involving carbon tetrachloride or benzene as one component, an alligation formula is applied to find the apparent partial specific Kerr constant of the other substance. A new equation is developed whereby the specific Kerr constant of a solute may be deduced at infinite dilution in a solvent. The ${}_{\infty}({}_{m}K_2)$ values so obtained are first compared with those others which are calculable from earlier experiments on gaseous dielectrics by Stuart and Volkmann, and secondly used to compute specifications for the polarisability ellipsoids of the dissolved molecules. The results from solutions and gases are similar. Finally, it is noted that the molar Kerr constant of a pure polar liquid may be empirically converted into a value close to the ${}_{\infty}({}_{m}K_2)$ obtained in benzene.

The quantitative treatment of electric double refraction (the " Kerr effect ") developed by Langevin (*Le Radium*, 1918, **7**, 249), Born (*Ann. Physik*, 1918, **55**, 177), and Gans (*ibid.*, 1920, **62**, 331; **65**, 97) makes this phenomenon one of obvious significance in the investigation of molecular structures. The mathematical formulæ given are, however, strictly applicable only to gaseous dielectrics—a fact which may limit their usefulness, since many interesting substances cannot be vaporised without decomposition, and, in any case, observations with gases are practically difficult. Although, in these respects, the situation has some analogies with that in which dipole moments are measured, the further similarity of working with solutions, and ultimately securing some value for the solute at infinite dilution, has not been much explored.

The present communication reports an examination of the possibility of such a procedure with the aid of new data for a number of binary mixtures, in each of which either carbon tetrachloride or benzene has the role of solvent.

For our purposes we have adopted the " molecular Kerr constant " (here written as ${}_{\mathrm{m}}K$) used by Otterbein (*Physikal. Z.*, 1934, **35**, 249), *viz.*:

$$ {}_{\mathrm{m}}K = 6\lambda nBM/(n^2 + 2)^2(\varepsilon + 2)^2d \quad . \quad . \quad . \quad . \quad . \quad . \quad (1) $$

where M is the molecular weight, n the refractive index, ε the dielectric constant, and d the density of the medium under examination. Under the conditions employed to produce electric double refraction, this medium, normally having a refractive index n for light of wave-length λ, is subjected to an electric field of strength E absolute volts/cm., whereupon it behaves as though it has refractive indexes n_{p} and n_{s} respectively parallel and perpendicular to the lines of force. The factor B is observed by experiment as

$$ B = (n_{\mathrm{p}} - n_{\mathrm{s}})/\lambda E^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2) $$

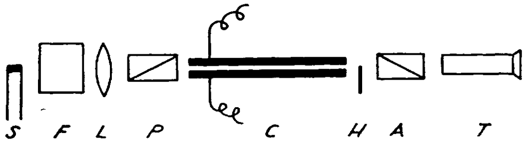
Relation (2) was established by Kerr (*Phil. Mag.*, 1880, **9**, 157; 1882, **13**, 153, 248). The magnitude ${}_{\mathrm{m}}K$ may be regarded as the difference between the molecular refractions (computed by the Lorentz–Lorenz formula), for the two directions mentioned, caused by application of a field of unit strength.

It should be noted that Briegleb (*Z. physikal. Chem.*, 1931, **14**, *B*, 97) and a few other authors have taken ${}_{\mathrm{m}}K$ as one-sixth of that shown by (1); their data have therefore been multiplied accordingly for quotation in this paper. Specific Kerr constants (${}_{\mathrm{s}}K$), to be mentioned later, are of course given by (1) after division throughout by M.

EXPERIMENTAL

The Determination of B.—Many of the measurements now to be reported were originally made before the war at University College, London; they have been checked and amplified more recently in Sydney. Much of the equipment used earlier was destroyed, and various modifications have been introduced during reassembly in Australia. The details given here refer only to the arrangements now in use.

FIG. 1.



Light from a 4-v projection bulb S passes through a tintometer cell F, 3 cm. long, containing a filtering solution (8·9 g. of $CuSO_4,5H_2O$ and 9·4 g. of $K_2Cr_2O_7$ in 300 g. of H_2O) (Fig. 1). This provides a better intensity in T and is a nearer approach to a point-source than the sodium discharge lamp without F at S with which we have made about half the observations for the present paper; since readings are the same with either source we have referred them to $\lambda = 5893$ Å in subsequent calculations. The beam of light becomes parallel on passing through L, and is plane-polarised at 45° to the vertical by the polariser, P; C is the condenser to which the high potential is applied; H is the compensator, A the analyser crossed with reference to P, and T a telescope focused on H. All the components are mounted on iron supports each of which has a side-ways screw adjustment between runners on its base-plate. The base-plates themselves are grooved on their undersides to allow movement backwards and forwards on an H-section girder which, with accurately machined straight top edges, serves as an optical bench.

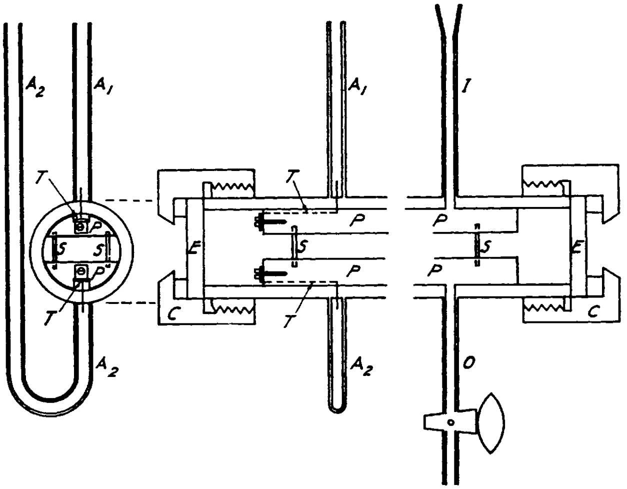
The two units *LP* and *AT* were constructed by Messrs. Adam Hilger Ltd., London, from their standard polarimeter M308.

The cell enclosing the condenser is made from Pyrex-glass tubing; its ends are ground optically plane so that they form a liquid-tight seal with the end plates E (Fig. 2). The caps C and washers hold E in position; I is the liquid inlet, and O the exit. The potential is introduced by means of mercury in the side arms A_1 and A_2 through platinum–glass seals to the tungsten strips T, the ends of which are respectively soldered to the platinum and attached to the ends of the electrodes P by means of small brass screws. These electrodes are made by splitting into two a brass rod along its axis, and running a small trough lengthwise at the top and the bottom to assist washing and draining of the cell. This shape was chosen in order to reduce the volume of liquid required for filling and to simplify the supporting of the lower plate. The opposing faces are milled flat and coated with platinum black to diminish surface reflection from them. Five pairs of hand-ground spacers S, made from thin Pyrex-glass rod, stand in small holes drilled along the edges of the electrodes, thus giving rigidity and a uniform gap between the lengths. The end plates E are polarimeter end-plates. It was found necessary to select only those *truly* free from strain; this was done by mounting them in a rotatable vertical plane in conjunction with a Brace compensator (*Phys. Review*, 1904, **18**, 70; **19**, 218) and testing them. Any strain causing birefringence of an order of more than $\lambda/20,000$ should have been detectable.

Various cells of similar construction are used according to the nature of the dielectric under observation; highly polar materials require shorter cells and larger gaps than those for substances or solutions having small values of B.

The phase differences induced in the dielectric of the Kerr cell by applying potential gradients up to the maximum available (*viz.*, *ca.* 50,000 v/cm.) are, for many non-polar substances, very small, and necessitate H being of high sensitivity. Two suitable designs are in the literature. The first, due to Brace (*loc. cit.*), in its various modifications is certainly adequate but requires *both* the precise standardisation of one mica plate and the accurate mounting of two; the second, that of Szivessy and Dierkesmann (*Z. Instrumentenkunde*, 1932, **52**, 337), by contrast, involves the standardisation and mounting of only a single plate. The latter pattern has therefore been chosen for the examination of solutions. (We have found, however, that for measurements on gases, the " hilfes Platte " of the Brace compensator is an indispensable factor in the determination of the effect, as without it, readings cannot be taken, owing to insufficient illumination of the field.)

FIG. 2.



The alternative procedure of comparing the actual intensities of the light, by means of a photo-electric cell, with the Nicol prisms first crossed and secondly parallel (Stevenson and Beams, *Phys. Review*, 1931, **38**, 133), and thence calculating $n_p - n_s$, has been tried and abandoned as unsuitable to the present work. The cell necessarily has to be moved and rocked to eliminate air bubbles while changing the dielectric, and errors due to any undetected slight alteration of alignment, which may cause surface reflection and hence unforeseen birefringence, are liable to lead to fictitious results.

We acknowledge with gratitude the advice and help we received from Professor G. Szivessy, during our visit to his laboratories at Bonn in 1937; in particular, we thank him for the gift of a standard compensator complete with its dispersion curve, which we used to calibrate the first series of plates of our own construction. These are made by inserting two sharp needles into opposite ends of a piece of clear mica, making two cleavages, and tearing apart gently and simultaneously. A fragment with a straight edge is then sealed with Canada balsam half-way across, and between, two polarimeter end-plates (which, as for those closing the cell, must be free from strain), care being taken to exclude air. When dry, the compensator is fixed by means of wax into a brass mount, which slides and can be clipped into two grooves on a circular scale. This is mounted in a vertical plane. The mica of the compensator then lies half-way across the field of vision, and is rotatable in front of the analysing prisms. The scale is fitted with slow-motion adjustment with Vernier. The phase differences of the various compensators used for this work range between 1° and 12°.

TABLE 1.

Benzene in carbon tetrachloride: $t = 20°$

10^5w_2	0	1749	6416	7897	22,621	26,683	45,763	45,894	60,817	77,581
10^7B_{12}	0·070	0·090	0·127	0·143	0·226	0·234	0·297	0·296	0·352	0·374

Chlorobenzene in carbon tetrachloride: $t = 20°$

10^5w_2	0	1990	4918	5183	5707_5	10,963	11,435	18,898	55,647
10^7B_{12}	0·070	0·318	0·650	0·618	0·783	1·40	1·36	2·39	6·19

Nitrobenzene in carbon tetrachloride: $t = 20°$

10^5w_2	0	123	437	438	511	801	1676	2638	5138
10^7B_{12}	0·070	0·212	0·435	0·436	0·499	0·740	$1·47_5$	$2·28_7$	$4·42_4$

Chloroform in carbon tetrachloride: $t = 20°$

10^5w_2	0	2413	2845	6609	9010	15,525	17,861	26,750	29,736	38,591
10^7B_{12}	0·070	+0·013	−0·027	−0·064	−0·146	−0·273	−0·345	−0·545	−0·556	−0·805

Diethyl ether in carbon tetrachloride: $t = 20°$

10^5w_2	0	483	4815	5404	19,480	20,482	36,356	36,894	41,311	54,095	61,102
10^7B_{12}	0·070	0·064	0·047	−0·012	−0·083	−0·086	−0·217	−0·234	−0·287	−0·380	−0·426

Acetone in carbon tetrachloride: $t = 20°$

10^5w_2	0	579	2476	3297	3599	3788
10^7B_{12}	0·070	0·178	0·471	0·604	0·652	0·679

TABLE 2. *Apparent values of* ${}_{m}K_2$ *found by application of the mixture rule to* ${}_{s}K_{12}$.

10^5w_2	10^7B_{12}	$(n_D^t)_{12}$	$(d_4^t)_{12}$	ε_{12}^t	$10^{12}{}_{m}K_2$
Carbon tetrachloride in benzene: $t = 20°$					
0	0·430	1·501	0·8791	$2·282_5$	—
8,474	0·417	1·499	0·9101	2·281	2·9
16,584	0·396	1·498	0·9454	2·279	$1·8_5$
22,419	0·384	1·495	0·9688	2·278	2·5
39,183	0·352	1·490	1·0405	2·273	2·9
54,106	0·296	1·485	1·1224	2·266	2·0
54,237	0·297	1·484	1·1253	2·265	2·1
73,317	0·234	1·474	1·2457	2·253	$2·1_5$
Chlorobenzene in benzene: $t = 23·5°$					
0	0·425	1·499	0·8754	2·276	—
1,520	0·510	$1·499_5$	0·8781	2·314	105
2,553	0·590	1·500	0·8801	2·341	123
2,582	0·606	1·500	0·8804	2·348	135
8,503	1·07	1·501	0·8902	2·488	137
12,582	1·40	1·502	0·8998	2·626	131
15,658	1·61	1·502	0·9046	2·696	122
27,609	2·76	1·505	0·9290	3·043	116
36,256	$3·12_5$	1·507	0·9473	3·268	92
53,666	5·13	1·511	0·9814	3·832	86
Nitrobenzene in benzene: $t = 22°$					
0	0·427	1·500	0·8770	2·278	—
262	0·557	1·500	0·8776	2·316	1043
334	0·586	1·500	0·8778	2·326	1004
368	0·626	1·500	0·8779	2·332	1146
761	0·771	1·500	0·8800	2·388	915
1,393	$1·12_9$	1·501	0·8804	2·480	972
2,071	$1·45_9$	0·501	0·8820	2·576	919
3,551	2·19	1·501	0·8859	2·808	817
4,091	$2·46_9$	1·502	0·8870	2·870	810
Chloroform in benzene: $t = 25°$					
0	0·424	1·498	0·8738	$2·272_5$	—
2,397	0·389	1·497	0·8831	2·295	−31
5,547	0·339	1·495	0·8942	2·339	−32
11,734	0·229	1·493	0·9180	2·420	−31
12,884	0·199	1·492	0·9256	2·438	−32
18,068	0·099	1·489	0·9446	2·514	−34
39,289	−0·341	1·480	1·0420	2·843	−27
48,560	−0·606	1·476	1·0942	3·025	−26
55,126	−0·876	1·473	1·1304	3·164	−26
Diethyl ether in benzene: $t = 20°$					
0	0·431	1·501	0·8791	$2·282_5$	—
2,009	0·416	1·598	0·8754	$2·320_5$	−1·6
4,064	0·398	1·495	0·8715	2·361	−7·0
6,495	0·381	1·493	0·8669	2·405	−6·7
11,214	0·343	1·485	0·8582	2·494	−6·7
23,557	0·238	1·466	0·8353	2·721	−6·8
35,442	0·136	1·449	0·8135	2·952	−6·2
47,559	0·038	1·431	0·7910	3·230	−5·6
60,373	−0·069	1·412	0·7722	3·479	−4·9
63,866	−0·104	1·407	0·7706	3·562	−4·9
Acetone in benzene: $t = 20°$					
0	0·429	1·501	0·8791	$2·282_5$	—
1,055	0·522	1·499	0·8781	2·433	65
2,721	0·671	1·496	0·8764	2·665	60
3,971	0·741	1·493	0·8751	2·842	47
5,424	0·805	1·490	0·8738	3·058	36
5,842	0·825	1·490	0·8734	3·112	33

Voltage generation is by an "R.F. E.H.T." unit (type 103/P/M/A, from Hazelhurst Designs Ltd., London) capable of producing 0·1—12 kv according to setting, and operating on the 240-v 50-cycle mains. The high-tension D.C. output is bled through resistors immersed in wax through a current-meter graduated directly in kv. (We thank Mr. E. P. A. Sullivan, M.Sc., for checking the calibration of this meter against a standard electrostatic voltmeter lent to us by the Division of Electrotechnology, C.S.I.R.O.) The potential and earth connections are led to *C* (Fig. 1) by car ignition cables terminating as thin brass rods; each of these rods is completely shrouded by a Polythene cylindrical tube, which fits loosely over the mercury-containing side-arms A_1 and A_2, and permits handling without shock.

The solutes and solvents, purified as specified by Weissberger and Proskauer (" Organic Solvents," Clarendon Press, 1935), were stored over sodium wire or fused calcium chloride as appropriate.

Tables 1 and 2 set out the values of *B* obtained for a number of mixtures of the components named. The concentrations of the solutes are shown as weight fractions, w_2; we express these to the accuracy usual in determinations of dipole moments since μ_{solution} has usually also to be deduced from the ε, *d*, etc., of the same solutions as are used for observing *B*. Subsequently in this paper we use the subscripts 1, 2, or 12, to indicate respectively solvent, solute, or solution.

DISCUSSION

The Apparent Kerr Constants of Solutes.—Briegleb (*loc. cit.*) seems to have been the first worker to analyse ${}_{\mathrm{m}}K_{12}$ by an alligation formula. To each solution of a series, in which a definite solute was dissolved in the same non-polar solvent throughout, he applied

$$ {}_{\mathrm{m}}K_{12} = {}_{\mathrm{m}}K_1 f_1 + {}_{\mathrm{m}}K_2 f_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3) $$

(where the concentrations were expressed as molar fractions). On the assumption that ${}_{\mathrm{m}}K_1$ was independent of f_1, the individual apparent partial values of ${}_{\mathrm{m}}K_2$ were calculable from experiment. They usually showed marked variation with f_2 and needed therefore to be extrapolated to infinite dilution to give the magnitude to be here represented by ${}_{\infty}({}_{\mathrm{m}}K_2)$. Briegleb's procedure has since been followed by Stuart and Volkmann (*Z. Physik*, 1933, **83**, 444), Otterbein (*Physikal. Z.*, 1934, **35**, 249), Sachsse (*ibid.*, 1935, **36**, 357), and Friedrich (*ibid.*, 1937, **38**, 318).

In the present investigation we have introduced the arithmetical simplification of using specific Kerr constants and weight fractions in place of the molar quantities of the foregoing authors. Accordingly, for (3) we write : ${}_{\mathrm{s}}K_{12} = {}_{\mathrm{s}}K_1 w_1 + {}_{\mathrm{s}}K_2 w_2$, whence :

$$ {}_{\mathrm{s}}K_2 = {}_{\mathrm{s}}K_1 + ({}_{\mathrm{s}}K_{12} - {}_{\mathrm{s}}K_1)/w_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4) $$

Specific Kerr constants have been defined on p. 4042. For their evaluation from B_{12}, knowledge of the dielectric constants, densities, and refractive indexes of the solutions is also necessary; such measurements have therefore been made by the methods described by Le Fèvre (" Dipole Moments," Methuen, 2nd edtn., 1948, Chap. II). Table 2 summarises our observations for the six systems in which the solvent has been benzene; *via* equation (4), the figures in the last column emerge as ${}_{\mathrm{s}}K_2 M_2$.

Molar Kerr Constants at Infinite Dilution.—It is clear from Table 2 that direct graphical extrapolation of the apparent partial Kerr constants of solutes to $w_2 = 0$ could only provide somewhat uncertain estimates of the ${}_{\infty}({}_{\mathrm{m}}K_2)$ for each substance, and a similar remark applies to the data published by the authors cited above. The problem is not unexpected since—apart from composition (which, depending only upon weighing, we take as accurate in this connection)—each figure in the right-hand column of Table 2 requires for its determination the measurement of four properties (*B*, ε, *n*, and *d*) the errors in which may combine unpredictably to affect the ${}_{\mathrm{m}}K_2$ ultimately deduced. As a remedy, therefore, we decided to smooth the individual observations and proceed straight to the desired quantities, *i.e.*, to ${}_{\infty}({}_{\mathrm{m}}K_2)$ in each case.

The following argument is used : equations (5)—(8) inclusive are assumed to apply at high dilutions :

$$ \varepsilon_{12} = \varepsilon_1(1 + \alpha w_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5) $$

$$ d_{12} = d_1(1 + \beta w_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6) $$

$$ n_{12} = n_1(1 + \gamma w_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7) $$

$$ B_{12} = B_1(1 + \delta w_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8) $$

Over the concentrations convenient in actual practice, B_{12} usually and ε_{12} and d_{12} sometimes show curvature with w_2 as w_2 increases. In such instances the observed differences between solutions and solvent are fitted to power series in w_2, and the coefficient of the term containing w_2 utilised to obtain the limiting magnitude of δ (or α, β, or γ) when $w_2 = 0$. Thus: if $(B_{12} - B_1)_{w_2} = \Delta B_{12} = (\text{first constant})w_2 + (\text{second constant})w_2^2$, then the first constant is $(\delta B_1)_{w_2} = 0$; an analysis in this way of the B_{12}'s already given is summarised in Table 3. A similar treatment is applied to the dielectric constant or density where necessary. For the refractive index, however, the mean *via* $\gamma n_1 = \Sigma(n_{12} - n_1)/\Sigma w_2$ is almost always satisfactory.

TABLE 3. *Equations for* ΔB_{12} *fitted by method of least squares.*

Solute	Solvent	T	R.H.S. of equation for ΔB_{12}	Solute	Solvent	T	R.H.S. of equation for ΔB_{12}
C_6H_6	CCl_4	20°	$0{\cdot}726w_2 - 0{\cdot}441w_2^2$	$CHCl_3$ ...	CCl_4	20°	$-2{\cdot}26w_2 + 0{\cdot}074w_2^2$
CCl_4	C_6H_6	20	$-0{\cdot}161w_2 - 0{\cdot}147w_2^2$	$CHCl_3$ ...	C_6H_6	25	$-1{\cdot}41w_2 - 1{\cdot}59w_2^2$
C_6H_5Cl ...	CCl_4	20	$12{\cdot}27w_2 - 2{\cdot}28w_2^2$	Et_2O	CCl_4	20	$-0{\cdot}972w_2 + 0{\cdot}330w_2^2$
C_6H_5Cl ...	C_6H_6	23·5	$7{\cdot}02w_2 + 3{\cdot}0w_2^2$	Et_2O	C_6H_6	20	$-0{\cdot}807w_2 - 0{\cdot}043w_2^2$
$C_6H_5{\cdot}NO_2$	CCl_4	20	$83{\cdot}25w_2 + 29{\cdot}2w_2^2$	$COMe_2$ ...	CCl_4	20	$17{\cdot}14w_2 - 28{\cdot}5w_2^2$
$C_6H_5{\cdot}NO_2$	C_6H_6	22	$49{\cdot}25w_2 + 15{\cdot}1w_2^2$	$COMe_2$ ...	C_6H_6	20	$10{\cdot}3w_2 - 61w_2^2$

Now from (4):

$$_\infty({}_sK_2) = {}_sK_1 + [\mathrm{d}({}_sK_{12})/\mathrm{d}w_2]_{w_2=0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and (cf. equation 1)

$${}_sK_{12} = 6\lambda n_{12}B_{12}/(n_{12}^2 + 2)^2(\varepsilon_{12} + 2)^2 d_{12} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

By substituting (5)—(8) inclusive in (10), and differentiating with respect to w_2, etc., we can rewrite (9) as

$$_\infty({}_sK_2) = [(1 - \beta + \gamma + \delta - H\gamma - J\alpha\varepsilon_1)]_sK_1 \quad . \quad . \quad . \quad . \quad (11)$$

where $H = 4n_1^2/(n_1^2 + 2)$ and $J = 2/(\varepsilon_1 + 2)$.

Equation (11) has been used to compile Table 4. For the solvents and over the small temperature range shown, the requisite constants are:

	$10^{12}{}_sK_1$	H	J
For CCl_4(20°)	0·00740	$2{\cdot}06_4$	$0{\cdot}472_1$
,, C_6H_6 (20°)	0·0782	$2{\cdot}11_9$	$0{\cdot}467_0$
,, ,, (25°)	0·0782	$2{\cdot}11_5$	$0{\cdot}468_1$

(These are computed from data already tabulated, supplemented, in the case of carbon tetrachloride, by the following for 20°: ε 2·2360, d_4^{20} 1·5940, and n_D 1·4604.)

TABLE 4. *Extrapolation of molar Kerr constants to infinite dilution.*

Temp.	Solute	Solvent	$\alpha\epsilon_1$ *	β *	γ	δ	±% S.E. on δ	$_\infty({}_mK_2)10^{12}$
20°	C_6H_6	CCl_4	0·078	−0·754	0·026	10·4	5	7·0
20	CCl_4	C_6H_6	−0·020	0·455	0·031	−0·374	36	2·6
20	C_6H_5Cl	CCl_4	4·84	−0·431	0·043	175·3	1	145
23·5	C_6H_5Cl	C_6H_6	2·52	0·211	$0{\cdot}011_5$	16·5	4	142
20	$C_6H_5{\cdot}NO_2$	CCl_4	25·6	−0·322	0·063	1189	1	1073
22	$C_6H_5{\cdot}NO_2$	C_6H_6	14·6	0·290	0·039	115·3	1	1050
20	$CHCl_3$	CCl_4	2·15	−0·068	−0·010	−32·3	3	−28·5
25	$CHCl_3$	C_6H_6	1·23	0·406	−0·031	−3·32	10	−30·5
20	Et_2O	CCl_4	3·87	−1·00	−0·074	−13·9	5—6	− 7·5
20	Et_2O	C_6H_6	1·96	−0·204	−0·098	− 1·87	0·5	− 8·5
20	$COMe_2$	CCl_4	26·9	−1·00	−0·185	244·8	1	101
20	$COMe_2$	C_6H_6	14·2	−0·112	−0·130	24·0	1—2	83·4

* The figures shown in these columns are computed from Table 2, for solutions in benzene, or from measurements given in papers listed by Wesson ("Tables of Electric Dipole Moments," Technology Press, M.I.T., 1948) for solutions in carbon tetrachloride; those under γ are from determinations made during the present work.

It is not easy to state the errors in the $_\infty({}_mK_2)$ values listed above. Concentrations, voltages, and cell dimensions are each ascertainable to at least three significant figures. The "effective light path" through the condenser in the cell C (Fig. 1) is computed from the lengths and average thicknesses of the electrodes P by Chaumont's formula (*Ann. Physique*, 1916, **5**, 31). The determination of B with the Szivessy–Dierkesmann compensator necessitates the recording of eight positions of match for the half-shade plate H; these should ideally fall into four equal pairs, commonly referred to as the azimuthal angle β. The circular scale divisions giving β can be read to 0·01° with the Vernier, but the actual matchings of intensities depend on the sensitivity of the eye of the observer. We find that the best results (*i.e.*, variations among the four β's only in the fourth significant figure) are achieved when β itself is between about 5° and 22°; outside these limits matching becomes difficult owing to too great or too little illumination of the field of vision. In practice we control the value of β by choosing a suitable half-shade plate or altering the potential fall across the dielectric. These " instrumental " considerations, together with experience, underlie the quotations of B in Tables 1 and 2.

In the application of equation (11) the factors $\alpha\varepsilon_1$, β, and γ have in general much less influence on the ultimate $_{\infty}({}_{\mathrm{s}}K_2)$ than has δ. This may be illustrated by running through the calculations for Table 4 using δ alone; *e.g.*, the solutions in carbon tetrachloride being taken in the descending order there given, the following figures for $_{\infty}({}_{\mathrm{m}}K_2)$ respectively are obtained: 6·0, 146, 1083, −28·4, −7·6, 105; these do not differ greatly from the values produced by the full expression. Moreover, since partial differentiation of (11) with respect to δ shows

$$\frac{\partial[{}_{\infty}({}_{\mathrm{s}}K_2)]}{{}_{\infty}({}_{\mathrm{s}}K_2)} = \frac{\partial\delta}{\delta}\cdot\frac{\delta}{(1 - \beta + \gamma + \delta - H\gamma - J\alpha\varepsilon_1)}$$

it is clear that the larger δ becomes the more will the relative error in $_{\infty}({}_{\mathrm{m}}K_2)$ converge towards that in δ; even for moderate values of δ the fraction $\delta/(1 - \beta + \gamma + \delta - H\gamma - J\alpha\varepsilon_1)$ is usually not far from unity (*e.g.*, for the two cases of ether as a solute the ratios are 0·96 and 1·2), although for small values it may be higher (*e.g.*, for carbon tetrachloride in benzene the ratio is 1·7). Evidently, therefore, through the degree to which the observations of B_{12} imperfectly fit the regressions $\Delta B = aw_2 + bw_2^2$, it is possible to make an estimate of the uncertainty of the final $_{\infty}({}_{\mathrm{m}}K_2)$.

Accordingly, the standard errors of the "*a*" terms in the equations shown in Table 3 have been evaluated as:

$$s_{\mathrm{a}} = \pm\{n\Sigma\Delta^2/(n-2)[n\Sigma w_2^2 - (\Sigma w_2)^2]\}^{\frac{1}{2}}$$

where Δ is the difference between $(\Delta B)_{\mathrm{obs.}}$ and $(\Delta B)_{\mathrm{calc.}}$ n is the number of solutions examined, and w_2 has its previous significance. A review of several dozen determinations

TABLE 5. *Comparison of present with previous results.*

Solute	Solvent	Temp.	$10^{12}\,.\,{}_{\infty}({}_{\mathrm{m}}K_2)$	Source	No. of solns. for which data recorded
C_6H_6	CCl_4	20°	5·4	Briegleb, 1932 *	6
,,	,,	20	6·48	Otterbein, 1934	None given
,,	,,	20	7·0 ± 0·4	Present paper	9
CCl_4	C_6H_6	20	2·6 ± 0·9	,,	7
C_6H_5Cl	CCl_4	20	142	Otterbein, 1934	None given
,,	,,	20	145 ± 1·4	Present paper	8
,,	C_6H_6	23·5	142 ± 5·7	,,	9
$C_6H_5{\cdot}NO_2$	CCl_4	20	666	Stuart and Volkmann 1933 †	4
	,,	20	1073 ± 11	Present paper	8
	C_6H_6	20	606	Stuart and Volkmann, 1933 †	2
,,	,,	23	Not stated ‡	Friedrich, 1937	9
,,	,,	22	1050 ± 11	Present paper	8
$CHCl_3$	CCl_4	20	−23·4	Briegleb, 1932	5
,,	,,	4	−28·2	Sachsse, 1935	None given
,,	,,	20	−28·5 ± 0·9	Present paper	9
,,	C_6H_6	25	−30·5 ± 3·1	,,	8
Et_2O	CCl_4	20	−3·6	Briegleb, 1932	9
,,	,,	20	−7·5 ± 0·5	Present paper	10
,,	C_6H_6	20	−8·5 ± 0·04	,,	9
$COMe_2$	CCl_4	20	93·0	Briegleb, 1932	5
,,	,,	20	102	Otterbein, 1934	5
,,	,,	20	101 ± 1·0	Present paper	5
,,	C_6H_6	20	51·0	Briegleb, 1932	5
,,	,,	20	72·6	Otterbein, 1934	5
,,	,,	20	83·4 ± 1·7	Present paper	5

* *Z. physikal. Chem.*, 1932, **16**, *B*, 249. † *Z. Physik*, 1933, **83**, 444.

‡ From Fig. 7 of Friedrich's paper $_{\infty}({}_{\mathrm{m}}K_2)$ appears to be *ca.* 1000.

made at intervals during this work shows that $10^{-7}B_1$ for either benzene or carbon tetrachloride can, for a given temperature, be reproduced within a standard error of 0·002. Thus we have: $\delta \pm s_\delta = (\delta B_1 \pm s_a)/(B_1 \pm 0{\cdot}002)$. Col. 8 of Table 4 lists $\pm 100 s_\delta/\delta$. We submit that these percentages, applied to their appropriate $_\infty({}_\mathrm{m}K_2)$ figures, afford a reasonable indication of the reproducibilities of the latter.

Table 5 compares our values for $_\infty({}_\mathrm{m}K_2)$ with those published previously. For the first three solutes and acetone in carbon tetrachloride agreement is fairly satisfactory. The apparent discrepancies between the results of Stuart and Volkmann and those now recorded for nitrobenzene are due to the method of extrapolation to infinite dilution used by the German authors; recalculation of their data by equation (11) leads to $_\infty({}_\mathrm{m}K_2)$'s approaching ours.

Relation between $_\infty({}_\mathrm{m}\mathrm{K}_2)$ *and* $({}_\mathrm{m}\mathrm{K})_\mathrm{gas}$.—It is desirable to ascertain how the molar Kerr constants as now measured in solution are related to the " true " values which should be obtained from the same solutes as gases. Stuart and Volkmann (*Ann. Physik*, 1933, **18**, 121) have summarised the only extant experimental work from which the latter may be estimated. They report for each compound a quantity K ($= B\lambda/n$) at 760 mm. pressure and a specified temperature. By the Langevin–Born–Gans treatment K is expressible by equation (12):

$$K = \frac{(n^2+2)^2}{3n^2}\cdot\frac{(\varepsilon+2)^2}{9}\cdot\frac{\pi N d}{M}(\theta_1+\theta_2) \quad . \quad . \quad . \quad . \quad . \quad (12)$$

i.e., as $K = K_1 + K_2$, where K_1 and K_2 contain respectively the temperature-dependent " anisotropy " and " dipole " terms θ_1 and θ_2. The last-named are expanded as (13) and (14):

$$\theta_1 = \frac{1}{45kT}[(a_1-a_2)(b_1-b_2)+(a_2-a_3)(b_2-b_3)+(a_3-a_1)(b_3-b_1)] \quad . \quad . \quad (13)$$

$$\theta_2 = \frac{1}{45k^2T^2}[(\mu_1{}^2-\mu_2{}^2)(b_1-b_2)+(\mu_2{}^2-\mu_3{}^2)(b_2-b_3)+(\mu_3{}^2-\mu_1{}^2)(b_3-b_1)] \quad (14)$$

in which a_1, a_2, a_3, and b_1, b_2, b_3 are the half-axes of the electrostatic and the electro-optical polarisability ellipsoids of a molecule, and μ_1, μ_2, and μ_3 are the appropriate resolutes of the resultant dipole moment along the three perpendicular directions denoted by subscripts 1, 2, and 3. On the assumption (Gans, *loc. cit.*) that $a_1/b_1 = a_2/b_2 = a_3/b_3 = (\varepsilon - 1)/(n^2 - 1)$ Stuart and Volkmann used (15) for the depolarisation factor Δ of scattered light (cf. Cabannes, " La Diffusion Moléculaire de la Lumière," Les Presses Universitaires de France, 1929, Chap. XIII), and (16) for the molecular refraction R_∞ for light of infinite wave-length

$$\frac{10\Delta}{6-7\Delta} = \frac{(b_1-b_2)^2+(b_2-b_3)^2+(b_3-b_1)^2}{(b_1+b_2+b_3)^2} \quad . \quad . \quad . \quad . \quad (15)$$

$$R_\infty = \frac{4\pi N}{3}\cdot\frac{b_1+b_2+b_3}{3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

(cf. Debye and Sack, " Handbuch der Radiologie," Leipzig, 1925, Chap. 2), to split K into K_1 and K_2.

It will be noted from (12), (13), and (14) that $(\theta_1 + \theta_2)$ depends on the number of molecules per unit volume, while θ_1 and θ_2 respectively depend on $1/T$ and $1/T^2$. K_1 and K_2 therefore vary, in order, inversely as T^2 and T^3. We have accordingly transformed the K_1 and K_2 values given by Stuart and Volkmann to the temperatures used by us, and inserted their sum into (17), a relation which follows directly from the definition of K and equations (1) and (12):

$${}_\mathrm{m}K = 6n^2KM/(n^2+2)^2(\varepsilon+2)^2d = 2\pi N(\theta_1+\theta_2)/9 \quad . \quad . \quad . \quad (17)$$

The results are included in Table 6. It is noticeable at once that, except with ether, the ratios between the "apparent" and "true" molar Kerr constants of the polar solutes roughly resemble those for the squares of the " apparent " and " true " dipole moments (when the former of these are drawn from observations on benzene solutions). From

Stuart and Volkmann's values of K_1 for benzene vapour at 113·6° ($5{\cdot}5_6 \times 10^{-15}$) we estimate ${}_{\mathrm{m}}K_{\mathrm{gas}}$ at 20° as 17×10^{-12}, while ${}_{\infty}({}_{\mathrm{m}}K_2)$ in carbon tetrachloride at 20° is 7×10^{-12}. Since for this molecule $\mu = 0$ and therefore $\theta_2 = 0$, it is unjustifiable to expect the anistotropy terms for the polar substances to be invariant with state. *A priori* it seems likely that θ_2, being a function of μ^2, may vary with the medium as does $\mu^2{}_{\mathrm{apparent}}$, and consequently the more θ_2 exceeds θ_1 the more will the ${}_{\mathrm{m}}K_{\mathrm{soln.}}$ containing their sum appear to run in harmony with $\mu^2{}_{\mathrm{apparent}}$. In agreement with this we find (using information incorporated in Table 7) the anisotropy and dipole terms of the substances listed in Table 6 to be related numerically as 1 to 5·8, to 34·2, to 9·7, to $2{\cdot}3_5$, and to 31, respectively. The lowest of these figures is that for ether, the θ_1 for which is *ca.* 2×10^{-35} for the gaseous material: this needs only to be 4×10^{-35} for ether as a solute at 20° to make $(\theta_2)_{\mathrm{soln.}}/(\theta_2)_{\mathrm{gas}}$ about 1·2 (*i.e.*, the $\mu^2{}_{\mathrm{soln.}}/\mu^2{}_{\mathrm{gas}}$ ratio). Such a change is less than that which present facts indicate, for example, with benzene.

TABLE 6. *Ratios* $({}_{\mathrm{m}}\mathrm{K})_{\mathrm{soln.}}/({}_{\mathrm{m}}\mathrm{K})_{\mathrm{gas}}$ *for polar solutes.*

Substance	T	${}_{\mathrm{m}}K_{\mathrm{gas}}$ (calc.)	Solvent	${}_{\mathrm{m}}K_{\mathrm{soln.}}/{}_{\mathrm{m}}K_{\mathrm{gas}}$	$\mu^2{}_{\mathrm{soln.}}/\mu^2{}_{\mathrm{gas}}$
C_6H_5Cl	20°	192	CCl_4	0·76	—
	23·5	188	C_6H_6	0·76	0·84 [1]
$C_6H_5{\cdot}NO_2$	20	1332	CCl_4	0·81	—
	22	1315	C_6H_6	0·80	0·87 [1]
$CHCl_3$	20	−26·7	CCl_4	1·1	—
	25	−25·8	C_6H_6	1·2	1·1 [1]
Et_2O	20	−11·7	CCl_4	0·64	—
			C_6H_6	0·73	1·2 [2]
$COMe_2$	20	106	CCl_4	0·95	—
			C_6H_6	0·79	0·82—0·92 [1]

[1] From Buckingham and Le Fèvre (*J.*, 1952, 1932). [2] From Barclay and Le Fèvre (*J.*, 1952, 1643).

Polarisability Ellipsoids of Solutes.—From the ${}_{\infty}({}_{\mathrm{m}}K_2)$ values given in Table 4, *via* equations (13)—(17) inclusive, we have calculated the principal half-axes of the polarisability ellipsoids for benzene and the five polar solutes. Except for benzene and chloroform (where from symmetry two are the same), each molecule presents three unknowns b_1, b_2, and b_3 provided that a_1, a_2, and a_3 are transformed into b_1, b_2, and b_3 in (13); we have done this by writing $a_i/b_i =$ (distortion polarisation)/(electronic polarisation) $= {}_{\mathrm{D}}P/{}_{\mathrm{E}}P = {}_{\mathrm{D}}P/R_{\infty}$. As depolarisation factors (Δ in equation 15) we have taken those given in Cabannes's monograph (*op. cit.*) as " la depolarisation limite "; $\delta_0{}^2$ is $5\Delta/(6 - 7\Delta)$. In view of the conclusions drawn above from Table 6, we have used the appropriate " solution " rather than " gas " moments.

Table 7 summarises the results and gives source references. It will be seen that these half-axes are not seriously affected by the solvent (except with acetone, whose ${}_{\mathrm{m}}K$ in benzene seems unaccountably to be 20% lower than in carbon tetrachloride). For brevity when comparing (in Table 8) the estimates of Table 7 with those of previous workers we therefore omit those deduced from benzene solutions. For uniformity $\mu_{\mathrm{resultant}}$ is taken as μ_1 throughout. Our data are shown first in each case.

TABLE 7. *The polarisability ellipsoids.*

Solute	R_{∞} (c.c.)	${}_{\mathrm{D}}P$ (c.c.)	$10^3\delta_0{}^2$	Solvent	$\mu_s\ D$	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
C_6H_5Cl	29·9 [1]	34·9 [2]	43·9 [3]	CCl_4	1·59 [4]	1·445	1·404	0·685
″	″	″	″	C_6H_6	1·59 [5]	1·446	1·403	0·685
$C_6H_5{\cdot}NO_2$	30·9 [1]	36·2 [2]	50·0 [3]	CCl_4	3·97 [4]	1·601	1·361	0·690
″	″	″	″	C_6H_6	3·96 [5]	1·600	1·361	0·691
$CHCl_3$	20·8 [1]	25·3 [6]	—	CCl_4	1·10 [7]	0·588	0·935	0·935
″	″	″	—	C_6H_6	1·13 [5,6]	0·587	0·936	0·936
Et_2O	22·0 [1]	$24{\cdot}4_5$ [8]	23·3 [3]	CCl_4	1·24 [7]	0·808	1·120	0·673
″	″	″	″	C_6H_6	1·26 [8]	0·806	1·107	0·687
$COMe_2$	15·7 [1]	17·3 [9]	15·3 [3]	CCl_4	2·74 [4]	0·695	0·695	0·465
″	″	″	″	C_6H_6	2·74 [4]	0·681	0·734	0·442
C_6H_6	25·05 [1]	26·9 [10]	—	CCl_4	0 [7]	1·112	1·112	0·737

[1] Calculated from molecular refractions listed by Landolt–Bōrnstein, " Tabellen," 1912 edn. [2] Sudgen and Groves, *J.*, 1934, 1094. [3] From Cabannes, *op. cit.* [4] From data in Table 4 and the relevant ${}_{\mathrm{D}}P$ listed here. [5] Le Fèvre, *Trans. Faraday Soc.*, 1950, **46**, 1. [6] Barclay and Le Fèvre, *J.*, 1950, 556. [7] Wesson, M.I.T. Tables, 1948. [8] Barclay and Le Fèvre, *J.*, 1952, 1643. [9] Taken as $1{\cdot}1R_{\infty}$. [10] McAlpine and Smyth, *J. Chem. Physics*, 1933, **1**, 190.

The results of Sachsse and Briegleb are, like ours, derived from electric double refraction measurements on solutions; those of Parthasarathy are from light-scattering studies. It is, however, with the polarisabilities deduced by Stuart and Volkmann for the same compounds as gases at elevated temperatures that we particularly wish to make comparison. To begin with, the German authors themselves (ref. under Table 8) speak of their b values as " genähert bestimmen " and in another paper (*Z. Physik*, 1933, **80**, 107) say " die Zahlen für die Polarisierbarkeiten um einige Prozente ändern können." Then, to obtain the sums $(b_1 + b_2 + b_3)$ we have used R_∞—consequently our estimates of these quantities are consistently below those of Stuart and Volkmann. Moreover, we have introduced distortion polarisations and dipole moments which were not available in 1933, and believe we have utilised better figures for δ_0^2 than are obtainable from the Δ's listed by these earlier workers. Accordingly, we claim to have demonstrated that, in the present state of knowledge, molecular polarisability ellipsoids can be determined from solution as dependably as from the vapour phase.

TABLE 8. *Comparison between present and previous estimates of b_1, b_2 and b_3.*

Substance	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	Author(s) *
C_6H_5Cl	1·445	1·404	0·685	L. and L.
	1·593	1·324	0·758	S. and V.
$C_6H_5{\cdot}NO_2$	1·601	1·361	0·690	L. and L.
	1·776	1·325	0·775	S. and V.
$CHCl_3$	0·588	0·935	0·935	L. and L.
	0·668	0·901	0·901	S. and V.
	0·73	0·90	0·90	Sachsse †
	0·810	1·202	1·202	Parthasarathy ‡
Et_2O	$0{\cdot}807_5$	1·120	0·673	L. and L.
	0·787	1·126	0·707	S. and V.
$COMe_2$	0·695	0·695	0·465	L. and L.
	0·708	0·715	0·482	S. and V.
C_6H_6	1·112	1·112	0·737	L. and L.
	1·231	1·231	0·635	S. and V.
	1·17	1·17	0·78	Briegleb, 1932 †
	1·283	1·283	0·647	Parthasarathy ‡

* L. and L., present work; S. and V., Stuart and Volkmann, *Ann. Physik*, 1933, **18**, 121.
† *Loc. cit.* ‡ *Indian J. Physics*, 1933, **8**, 275.

Molar Kerr Constants of Pure Liquids.—When data for pure liquids are used with equation (1) the ${}_{\mathrm{m}}K_{\mathrm{liquid}}$ found is much smaller than ${}_{\mathrm{m}}K_{\mathrm{gas}}$ (see Table 9, col. 7). The same sort of reduction occurs, of course, when the conventional Clausius–Mosotti–Debye relations are applied without modification to a gas and to its condensed phase (Tables 1 and 2 of Buckingham and Le Fèvre, *loc. cit.*, give some numerical illustrations of this), but from ${}_{\mathrm{m}}K_{\mathrm{gas}}$ to ${}_{\mathrm{m}}K_{\mathrm{liquid}}$ the shrinkage is relatively greater than that from μ_{gas} to μ_{liquid}. Empirically, however, we observe that multiplication of ${}_{\mathrm{m}}K_{\mathrm{liquid}}$ by the ratio $\varepsilon/n_{\mathrm{D}}^2$ provides figures not dissimilar from those deduced at infinite dilution in benzene (cf. Table 9, cols. 8 and 9).

TABLE 9. *Molar Kerr constants of pure liquids.*

	Temp.	10^7B	d_4^t	n_{D}^t	$\varepsilon_{\mathrm{D}}^t$	$10^{12}({}_{\mathrm{m}}K)$	$10^{12}\varepsilon({}_{\mathrm{m}}K)/n^2$	$10^{12}({}_{\mathrm{m}}K_2)$
C_6H_5Cl	23·5°	11·4	1·1026	1·524	5·634	57·7	140	142
$C_6H_5{\cdot}NO_2$ [1]	23	354	1·1992	1·560	34·5	70·9	1010	1050
$CHCl_3$	25	−2·56	1·4790	1·443	4·724	−14·0	−31·8	−30·5
Et_2O	25	−0·614	0·7078	1·352	4·265	− 5·3	−12·3	− 8·5
$COMe_2$	20	16·3	0·7905	1·3591	19·6	8·33	88·3	83·4

[1] The data for nitrobenzene are from Friedrich, *Physikal. Z.*, 1937, **38**, 318.

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