535. *Molecular Polarisability. The Contributions of the Terms θ_1, θ_2, and θ_3 to the Kerr Constant of a Substance.*

By (MRS.) C. G. LE FÈVRE and R. J. W. LE FÈVRE.

The molar Kerr constants of bromobenzene at infinite dilution in carbon tetrachloride have been determined at 25°, 35°, and 45°, to test a possible routine method for the separation of the anisotropy and dipole terms contributing to the ${}_{\mathrm{m}}K$ of a polar solute. The temperature variation of the electric birefringence, measured as B, of five non-polar liquids has been examined for evidence of a temperature-independent term θ_3 in the ${}_{\mathrm{m}}K$'s of such substances.

THE " Kerr constant " B, measured as the difference between refractive indices parallel and perpendicular to an applied electric field E, can be deduced [1] *a priori* by the theory of Langevin, Born, and Gans for gaseous dielectrics and written as equation (2):

$$B = (n_{\mathrm{p}} - n_{\mathrm{s}})/\lambda E^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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

Symbols have conventional meanings; θ_1 and θ_2 are the " anisotropy " and " dipole " terms, expansions of which are given in refs. 1 and 2; these include the semi-axes of the molecular electro-optical polarisability ellipsoid and the resolutes of the molecular resultant dipole moment along the directions in the molecule corresponding to the said semi-axes. Stereochemical problems, which can be solved through polarisability considerations, necessitate a knowledge of the magnitudes of these semi-axes, so we need three equations from which they can be extracted. If θ_1 and θ_2 can be separated from eqn. (2), the introduction of eqn. (3) often completes the requisite information.

$$\text{Electronic polarisation} = {}_{\mathrm{E}}P = 4\pi N(b_1 + b_2 + b_3)/9 \quad . \quad . \quad . \quad (3)$$

Stuart and Volkmann,[3] using extant values of K (*i.e.*, $B\lambda/n$) and their own observations on organic substances well above the normal boiling points, evaluated polarisability ellipsoid semi-axes for about thirty compounds, θ_1 being computed from depolarisation factors for light scattered by the vapours (see refs. 1—3 for equations).

We have [1,4a,4b] developed a technique and extrapolation procedure for determining the specific or molar Kerr constant ${}_{\infty}({}_{\mathrm{m}}K_2)$ of a solute at infinite dilution in a solvent; these quantities follow if the refractive indices n_{p} and n_{s} in eqn. (1) are replaced by the corresponding specific or molecular refractions. The molar Kerr constant contains the sum $\theta_1 + \theta_2$ (see eqn. 4):

$${}_{\mathrm{m}}K = 2\pi N(\theta_1 + \theta_2)/9 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and by illustrating that ${}_{\mathrm{m}}K$'s from gases or solutions were similar, we extended [4] the applicability of the Kerr effect to soluble solids and involatile materials.

At the time the paucity and validity of available depolarisation factors severely limited the complete analysis of molecular polarisability, and alternative sources of information were sought (see ref. 1, p. 287 for summary, also refs. 4*b* and 4*c*); these were regarded as speculative and unsatisfactory.

Accordingly we tried to separate θ_1 from θ_2 by using their different temperature dependences. Bromobenzene was chosen, and its molar Kerr constants measured at

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[1] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Sci.*, 1955, **5**, 261.

[2] Le Fèvre and Purnachandra Rao, *J.*, 1957, 3644.

[3] Stuart and Volkmann, *Ann. Physik*, 1933, **18**, 121.

[4] Le Fèvre and Le Fèvre, (*a*) *J.*, 1953, 4041, (*b*) *J.*, 1954, 1577 (*c*) *J.*, 1955, 1641, 2750.

infinite dilution in carbon tetrachloride at 25°, 35°, and 45°; results and $_\infty({}_\mathrm{m}K_2)$'s obtained are in Tables 1 and 2. Nevertheless, the tedium and technical difficulties thus involved at higher temperatures led us to wait while Le Fèvre and Purnachandra Rao tried to determine molecular anisotropy by light scattering, which they have now done.[2]

TABLE 1. *Kerr effects, refractive indices, densities, and dielectric constants for solutions of bromobenzene in carbon tetrachloride.**

10^5w_2	$10^7\Delta B$	$(n)_{12}$	$(d_4^t)_{12}$	ε_{12}^t	10^5w_2	$10^7\Delta B$	$(n)_{12}$	$(d_4^t)_{12}$	ε_{12}^t
Temperature = 25°					Temperature = 25°				
0	—	1·4575	1·5845	2·2270	2411	0·254	1·4600	1·5822	2·3015
806	0·085	—	1·5837	2·2534	2599	0·285	1·4603	1·5820	2·3068
1122	0·118	1·4587	1·5835	2·2615	2664	0·291	1·4604	1·5818	2·3083
1398	0·143	—	1·5832	2·2698	3114	0·338	1·4607	1·5812	2·3220
1700	0·182	1·4594	1·5827	2·2795					

whence $10^7\Delta B = 10{\cdot}19w_2 + 23{\cdot}6w_2^2$; $\Sigma(n_{12} - n_1)/\Sigma w_2 = 0{\cdot}106_5$; $\Sigma(d_{12} - d_1)/\Sigma w_2 = -\ 0{\cdot}0993$; $\Sigma(\varepsilon_{12} - \varepsilon_1)/\Sigma w_2 = 3{\cdot}08$.

Temperature = 35°					Temperature = 35°				
0	—	1·4519	1·5651	2·2092	1681	0·152	1·4536	1·5638	2·2581
1333	0·126	—	1·5641	2·2472	2297	0·219	1·4542	1·5634	2·2770
1398	0·135	—	1·5641	2·2503	2411	0·224	1·4543	1·5633	2·2792
1584	0·146	—	1·5639	2·2552	3904	0·354	1·4557	1·5626	2·3243
1631	0·147	1·4535	1·5638	2·2567					

whence $10^7\Delta B = 9{\cdot}51w_2 - 10{\cdot}6w_2^2$; $\Sigma(n_{12} - n_1)/\Sigma w_2 = 0{\cdot}0990$; $(\Sigma d_{12} - d_1)/\Sigma w_2 = -\ 0{\cdot}0788$; $\Sigma(\varepsilon_{12} - \varepsilon_1)/(\Sigma w_2 = 2{\cdot}92$.

Temperature = 45°					Temperature = 45°				
0	—	1·4460	1·5458	2·1873	4973	0·440	1·4507	1·5430	2·3254
1378	0·119	1·4473	1·5450	2·2253	6363	0·546	1·4522	1·5422	2·3636
2131	0·186	1·4480	1·5446	2·2462	6461	0·546	1·4523	1·5421	2·3673
2526	0·255	1·4484	1·5444	2·2571	7215	0·624	1·4530	1·5417	2·3882
4271	0·332	1·4501	1·5434	2·3053	13758	1·211	1·4594	1·5378	2·5716

whence $10^7\Delta B = 8{\cdot}46w_2 + 2{\cdot}38w_2^2$; $\Sigma(n_{12} - n_1)/\Sigma w_2 = 0{\cdot}096_6$; $\Sigma(d_{12} - d_1)/\Sigma w_2 = -\ 0{\cdot}0570_5$; $\Sigma(\varepsilon_{12} - \varepsilon_1)/\Sigma w_2 = 2{\cdot}78$.

* Headings: w_2 = weight fraction of solute in solution, ΔB = increment in Kerr constant from solvent to solution, n = refractive index for Na light, d = density, ε = dielectric constant; subscripts 1, 2, and 12, denote solvent, solute, and solution respectively; for B_1^t when $w_2 = 0$ see Table 3.

TABLE 2. *Calculation * of molar Kerr constants at infinite dilution in carbon tetrachloride.*

						Solvent constants used		
Temp.	$\alpha\varepsilon_1$	β	γ	δ	$10^{12}\ _\infty({}_\mathrm{m}K_2)$	H	J	$10^{17}({}_\mathrm{s}K_1)$
25°	3·10	−0·075	0·073	145·6	170·7	2·060	0·4731	749
35	2·92	−0·050	0·068	137·8	163·4	2·053	0·4751	757
45	2·78	−0·037	0·067	126·3	149·3	2·044	0·4776	755

* For explanation of symbols and method of calculation, see p. 283 of ref. 1.

Anisotropy and Dipole Terms for Bromobenzene.—From $_\infty({}_\mathrm{m}K_2)$ (Table 2) the sums $(\theta_1 + \theta_2)_t$ follow as 40·59, 38·86, and 35·50 (all $\times 10^{-35}$). By writing the temperature-invariant parts of θ_1 and θ_2 as

$$C_1 = (b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2,$$

and

$$C_2 = \mu^2(2b_1 - b_2 - b_3)$$

we have generally:

$$(\theta_1 + \theta_2)_T = [({}_\mathrm{D}PC_1/{}_\mathrm{E}P)/45kT] + C_2/45k^2T^2$$

where T = temperature in °K and ${}_\mathrm{D}P/{}_\mathrm{E}P$ = distortion polarisation ÷ electronic polarisation = 1·091 for bromobenzene.[4b] Solutions of the consequent simultaneous equations are unsatisfactory: between 298° and 318° K, C_1 has a small negative value, while between

298° and 308° K, C_1 is $4{\cdot}7 \times 10^{-46}$ and C_2 is $10{\cdot}0 \times 10^{-60}$. Presumably wider temperature ranges and more observations would give better results, but this would be unsuitable for a *routine* procedure.

The temperature method is inadequate for our purpose because the difference between $\theta_1 + \theta_2$ for two temperatures is relatively small and liable to contain the errors of two much larger numbers. That the individual $_\infty({}_{\mathrm{m}}K_2)$ measurements are not seriously incorrect can be demonstrated, because we now know [5] that C_1 should be $0{\cdot}94 \times 10^{-46}$ and C_2 $26{\cdot}74 \times 10^{-60}$; therefore 10^{12} $_{\mathrm{m}}K_{\mathrm{calc.}}$ for 298°, 308°, and 318° K should be 171, 161, and 151, against 171, 163, and 149 recorded: the discrepancies, *ca.* 1·3%, are of the order sometimes experienced among repeated measurements of $_\infty({}_{\mathrm{m}}K_2)$. (This study of the bromobenzene–carbon tetrachloride system is the first attempt to check by experiment the influence of temperature on the molar Kerr constant of a solute at infinite dilution.)

Temperature-independent Component of the Molar Kerr Constant.—We considered the possible existence of a temperature-invariant term (denoted [1,6] by θ_3) in the right-hand side of eqns. (2) and (4). According to classical theory the differences $(b_1 - b_2)$, $(b_2 - b_3)$, and $(b_3 - b_1)$ for tetrahedral molecules (*e.g.*, CCl_4, CH_4,CBr_4) should be zero, and neither finite Kerr effects nor depolarisation factors should be displayed. In fact, small values for both these properties are observed.

It was shown,[6] *a priori*, that the apparent molar Kerr constant of a structure CX_4 might arise from distortion of the molecule by the applied electrostatic field; this could be part of the mechanism of the hyperpolarisability induced at high field strengths discussed by Coulson, Maccoll, and Sutton.[7] Alternatively, Buckingham and Pople [8] considered such non-zero values for $_{\mathrm{m}}K$ to be due to second-order effects from a curved relationship between molecular polarisability and field strength.

Whatever its origin, the negligibility or otherwise of the contribution of θ_3 to $_{\mathrm{m}}K$ of an anistropic molecule would obviously be important in stereochemical applications of the Kerr effect. This was noted in ref. 1 (p. 309. Correction: the equation in para. 8·1 should have 9 as a denominator) where we discussed the relative magnitudes of θ_3 in tetrahedral and centrosymmetric molecules; experimentally, for a non-polar liquid, $_{\mathrm{m}}K = 2\pi N(\theta_1 + \theta_3)/9$ and only θ_1 is temperature-dependent; hence a plot of $_{\mathrm{m}}K_T$ against $1/T$, by extrapolation to $1/T = 0$, should yield $2\pi N\theta_3/9$. Examples are reported below.

Carbon tetrachloride. The temperature-variation of its Kerr constant B (fundamental to our whole programme) appears never to have been examined. Table 3 contains results now obtained, together with other information leading to the apparent molar Kerr constants.

TABLE 3. *Apparent molar Kerr constants of carbon tetrachloride between* 20° *and* 45°.

t (°C)	d_4^t	n_D^t	ε^t	10^7B	$10^{12}({}_{\mathrm{m}}K_{\mathrm{liq.}})$
20	1·5940	1·4604	2·2360	0·072	$1{\cdot}1_7$
25	1·5845	1·4575	2·2270	0·070	$1{\cdot}1_5$
35	1·5651	1·4519	2·2092	0·069	$1{\cdot}1_6$
40	1·5557	1·4493	2·2003	0·068	$1{\cdot}1_6$
45	1·5458	1·4460	2·1873	0·067	$1{\cdot}1_6$

Within experimental limits set by the small B's, the $_{\mathrm{m}}K$'s are unaffected by temperature, as expected if the apparent molar Kerr constant contains only the temperature-independent term θ_3 and other constants.

Carbon disulphide, mesitylene, benzene, p-*xylene, and tetrachloroethylene.* Buckingham and Raab [9] used values of B/temperature given by Lyon and Wolfram [10] for carbon

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[5] Le Fèvre and Purnachandra Rao, *J.*, 1958, 1465.

[6] Le Fèvre, Le Fèvre, and Narayana Rao, *J.*, 1956, 708.

[7] Coulson, Maccoll, and Sutton, *Trans. Faraday Soc.*, 1952, **48**, 106.

[8] Buckingham and Pople, *Proc. Phys. Soc.*, 1955, **68**, *A*, 905.

[9] Buckingham and Raab, *J.*, 1957, 2341.

[10] Lyon and Wolfram, *Ann. Physik*, 1920, **63**, 739.

disulphide, and Grodde's four figures[11] for mesitylene, to estimate theoretically the temperature-independent parts of ${}_{\mathrm{m}}K$. Having obtained results for some non-polar liquids (including mesitylene, values for which differed from Grodde's), and having noted that data in the literature for carbon disulphide did not agree, we considered (with Dr. A. D. Buckingham) that all observations merited repetition; this has now been done, except for carbon disulphide (see Table 4).

Owing to lack of facilities for low-temperature work, carbon disulphide was not studied. A fairly large number of *B versus t* data are available from Leiser[12] (14° to 28°), Lyon and Wolfram[10] (—78° to 18°), Bergholm[13] (—20° to 41·5°), and Kurten[14] (2° to 38°); these, in

TABLE 4. *Temperature-dependence of* ${}_{\mathrm{m}}K_{\mathrm{liq.}}$.

t (°C)	$d_4^{\,t}$	n^t	ε_t	10^7B_t	$10^{12}({}_{\mathrm{m}}K_t)_{\mathrm{obs.}}$	$10^{12}({}_{\mathrm{m}}K_t)_{\mathrm{calc.}}$
			Benzene			
15	0·8842	1·5044	$2{\cdot}292_5$	0·423	$5{\cdot}9_4$	$5{\cdot}9_8$
20	0·8790	1·5010	$2{\cdot}282_5$	0·412	$5{\cdot}8_6$	$5{\cdot}8_8$
25	0·8738	1·4979	$2{\cdot}272_5$	0·401	$5{\cdot}7_{75}$	$5{\cdot}7_8$
30	0·8684	1·4949	2·263	0·390	$5{\cdot}6_9$	$5{\cdot}6_8$
35	0·8612	1·4907	2·254	0·379	$5{\cdot}6_2$	$5{\cdot}5_8$
40	0·8576	1·4876	2·243	0·368	$5{\cdot}5_2$	$5{\cdot}4_9$
45	0·8529	1·4851	2·233	0·356	$5{\cdot}4_0$	$5{\cdot}4_2$
50	0·8466	1·4811	2·223	0·345	$5{\cdot}3_{15}$	$5{\cdot}3_2$
55	0·8400	1·4776	2·213	0·334	$5{\cdot}2_2$	$5{\cdot}2_3$
60	0·8359	1·4744	$2{\cdot}203_5$	0·324	$5{\cdot}1_3$	$5\ 1_5$
65	0·8299	1·4720	$2{\cdot}193_5$	0·314	$5{\cdot}0_4$	$5{\cdot}0_7$
whence $10^{12}({}_{\mathrm{m}}K_t) = -\,0{\cdot}1_5 + 1766/T$; standard error in constant term, $\pm 0{\cdot}1_8$.						
			p-Xylene			
15	$0{\cdot}8653_5$	1·4984	2·278	0·740	$14{\cdot}5_8$	$14{\cdot}7_4$
20	0·8610	1·4958	2·270	0·727	$14{\cdot}4_8$	$14{\cdot}5_3$
25	$0{\cdot}8566_5$	1·4932	2·262	0·710	$14{\cdot}3_0$	$14{\cdot}3_2$
30	0·8523	1·4906	2·254	0·695	$14{\cdot}1_4$	$14{\cdot}1_2$
35	$0{\cdot}8480_5$	1·4880	2·246	0·680	$13{\cdot}9_9$	$13{\cdot}9_2$
40	0·8436	1·4854	2·238	0·662	$13{\cdot}7_7$	$13{\cdot}7_4$
45	$0{\cdot}8392_5$	1·4828	2·230	0·650	$13{\cdot}6_7$	$13{\cdot}5_9$
50	0·8349	1·4802	2·222	0·637	$13{\cdot}5_4$	$13{\cdot}3_8$
55	$0{\cdot}8305_5$	1·4776	2·214	0 616	$13{\cdot}2_4$	$13{\cdot}2_1$
60	0·8262	1·4750	2·206	0·605	$13{\cdot}1_4$	$13{\cdot}0_4$
65	$0{\cdot}8218_5$	1·4724	2·198	0·588	$12{\cdot}9_2$	$12{\cdot}8_8$
70	0·8175	1·4698	2·190	0·573	$12{\cdot}7_3$	$12{\cdot}7_2$
75	$0{\cdot}8131_5$	1·4672	2·182	0·559	$12{\cdot}4_9$	$12{\cdot}5_7$
80	0·8088	1·4646	2·174	0·545	$12{\cdot}3_7$	$12{\cdot}4_3$
85	$0{\cdot}8054_5$	1·4620	2·166	0·530	$12{\cdot}1_5$	$12{\cdot}2_8$
whence $10^{12}({}_{\mathrm{m}}K_t) = 2{\cdot}1_7 + 3620/T$; standard error in constant term, $\pm 0{\cdot}2_5$.						
			Mesitylene			
15	0·8678	1·5021	2·279	0·760	$16{\cdot}8_5$	$17{\cdot}3_0$
20	0·8637	1·4998	2·270	0·748	$16{\cdot}7_{65}$	$17{\cdot}0_0$
25	0·8596	1·4975	2·263	$0{\cdot}725_5$	$16{\cdot}4_2$	$16{\cdot}7_2$
30	0·8557	1·4952	2·256	$0{\cdot}703_5$	$16{\cdot}0_7$	$16{\cdot}4_2$
35	0·8512	1·4929	2·249	0·692	$15{\cdot}9_8$	$16{\cdot}1_5$
40	0·8476	1·4906	2·241	0·681	$15{\cdot}8_7$	$15{\cdot}8_8$
45	0·8429	1·4883	2·233	$0{\cdot}666_5$	$15{\cdot}7_1$	$15{\cdot}6_8$
50	0·8393	1·4859	2·225	0·650	$15{\cdot}4_7$	$15{\cdot}3_7$
55	0·8341	1·4836	2·216	0·634	$15{\cdot}2_8$	$15{\cdot}1_3$
60	0·8310	1·4813	2·207	0·620	$15{\cdot}0_8$	$14{\cdot}9_0$
65	0·8253	1·4790	2·198	0·604	$14{\cdot}8_8$	$14{\cdot}6_7$
70	0·8209	1·4767	2·189	0·584	$14{\cdot}5_6$	$14{\cdot}4_4$
75	0·8158	1·4744	2·181	0·571	$14{\cdot}4_0$	$14{\cdot}2_3$
80	0·8119	1·4721	2·172	0·556	$14{\cdot}1_7$	$14{\cdot}0_2$
85	0·8074	1·4698	2·164	0·543	$14{\cdot}0_0$	$13{\cdot}8_2$
whence $10^{12}({}_{\mathrm{m}}K_t) = -\,0{\cdot}5_1 + 5130/T$; standard error in constant term, $\pm 0{\cdot}4_2$.						

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[11] Grodde, *Physikal. Z.*, 1938, **39**, 772.

[12] Leiser, " Elektrische Doppelbrechung der Kohlenstoff Verbindungen," Abh. Deut. Bunsen Gesellschaft, No. 4, Halle a.S., 1910.

[13] Bergholm, *Ann. Physik*, 1921, **65**, 128.

[14] Kurten, *Physikal. Z.*, 1931, **32**, 251.

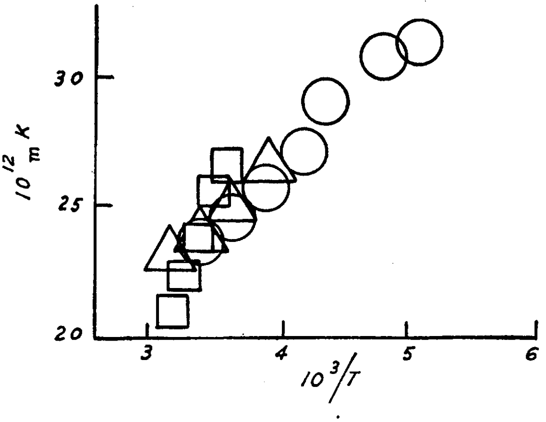
TABLE 4. (*Continued.*)

t (°c)	$d_4{}^t$	n^t	ε_t	10^7B_t	$10^{12}({}_{\mathrm{m}}K_t)_{\text{obs.}}$	$10^{12}({}_{\mathrm{m}}K_t)_{\text{calc.}}$
Tetrachloroethylene						
15	1·63109	1·5078	2·32	0·820	$15{\cdot}2_2$	$15{\cdot}4_7$
20	1·62285	1·5053	2·31	0·788	$14{\cdot}7_9$	$14{\cdot}9_4$
25	1·61461	1·5028	2·30	0·765	$14{\cdot}5_3$	$14{\cdot}6_8$
30	1·60637	1·5003	2·29	0·748	$14{\cdot}3_7$	$14{\cdot}4_3$
35	1·59813	1·4978	2·28	0·729	$14{\cdot}1_7$	$14{\cdot}2_0$
40	1·58989	1·4953	2·27	0·712	$14{\cdot}0_0$	$13{\cdot}9_7$
45	1·58165	1·4928	2·26	0·693	$13{\cdot}7_9$	$13{\cdot}7_9$
50	1·57341	1·4903	2·25	0·674	$13{\cdot}5_7$	$13{\cdot}5_2$
55	1·56517	1·4878	2·24	0·658	$13{\cdot}4_1$	$13{\cdot}3_1$
60	1·55693	1·4853	2·23	0·645	$13{\cdot}3_0$	$13{\cdot}1_1$
65	1·54869	1·4828	2·22	0·625	$13{\cdot}0_4$	$12{\cdot}9_1$
70	1·54045	1·4803	2·21	0·604	$12{\cdot}7_5$	$12{\cdot}7_2$
75	1·53221	1·4778	2·20	0·583	$12{\cdot}4_6$	$12{\cdot}5_3$
80	1·52397	1·4753	2·19	0·564	$12{\cdot}2_0$	$12{\cdot}3_5$
85	1·51573	1·4728	2·18	0·545	$11{\cdot}9_3$	$12{\cdot}1_7$

whence $10^{12}({}_{\mathrm{m}}K_t) = -0{\cdot}30 + 4465/T$; standard error in constant term, $\pm 0{\cdot}6_1$.

Dielectric constants were obtained from " Tables of Dielectric Constants of Pure Liquids," Maryott and Smith, Nat. Bur. Stand. Circular No. 514 (1951), except for mesitylene for which data were interpolated from Grodde's figures. Densities and refractive indexes ($\mathrm{Na_D}$) were from Timmermans, " Physico-chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950, or Egloff, " Physical Constants of Hydrocarbons," Vol. III, Amer. Chem. Soc. Monographs, Reinhold, New York, 1946, pp. 88, 89.

conjunction with density, refractive index, etc., values, are shown as molar Kerr constants in the Figure. The points do not lie on a single straight line, but roughly in a corridor;



Plot of ${}_{\mathrm{m}}K$ *for* CS_2 *against the reciprocal of absolute temperature.*

○ Lyon and Wolfram.
△ Bergholm.
☐ Kurten.

their scatter is such that the possibility that ${}_{\mathrm{m}}K$ for CS_2 is negligible at very high temperatures is by no means eliminated. The other substances, except *p*-xylene, appear to have near-zero θ_3 terms. For *p*-xylene the temperature-independent part of ${}_{\mathrm{m}}K$ is *ca.* 2×10^{-12}; this is surprising in comparison with the results for benzene and mesitylene and cannot readily be explained without questioning our observations of B and those for n, $d_4{}^t$, etc., which are from the literature. Even so, 2×10^{-12} is only one seventh of the ${}_{\mathrm{m}}K$ of *p*-xylene at ordinary temperatures.

Conclusions.—(1) For a polar solute θ_1 and θ_2 cannot be found separately by measuring the temperature coefficient of ${}_{\infty}({}_{\mathrm{m}}K_2)$, thus avoiding recourse to light-scattering, sufficiently precisely with present apparatus over a convenient temperature range.

(2) Measurements at 25° involving light scattering give ${}_{\infty}({}_{\mathrm{m}}K_2)$ of bromobenzene at 35° and 45° within 1·3% of the values found.

(3) The apparent molar Kerr constant of carbon tetrachloride, being invariant with temperature, is wholly due to θ_3

(4) Anisotropic molecules may have ${}_{\mathrm{m}}K$'s containing θ_1, θ_2, and θ_3, where in general

$\theta_2 > \theta_1 > \theta_3$. When the molecule is non-polar, $\theta_2 = 0$. For benzene, mesitylene, and tetrachloroethylene, θ_3 appears to be near zero; for *p*-xylene it may cause *ca.* 15% of the observed molar Kerr constant; for carbon disulphide the situation is indefinite.

EXPERIMENTAL

The apparatus used with the bromobenzene–carbon tetrachloride mixtures was as previously [4a] described apart from small modifications to the cell. An extra tube, admitting a thermometer readable to 0·1° to the liquid, was added parallel and close to the inlet (*I* in Fig. 2 of ref. 4*a*). The ends of the cell body were ground plane and polished, so that optically flat fused-silica end-plates made liquid-tight closure by gentle contact. The end-plates were selected to have less inherent strain than that measured as $10^{-6}\lambda$. They were held in position by Polythene film covers, suitably pierced for the light to pass, the "skirts" being secured around the cell by rubber bands; brass rings cemented near the cell ends prevented slipping. This minimised pressure on the end-plates, and eliminated strains due to warming of metal end-caps or to swelling of washers through absorption of liquids. The quartz plates did not develop detectable strain on heating to 45°.

The cell was supported, well inside an asbestos-cement air-oven, on a cradle [4a] having a slow-motion adjustment so that the cell could be moved vertically to centralise the light-path between the electrodes; such compensation of the thermal expansion of the metal pillars proved essential. The lower parts of the inside walls of the oven carried heating tapes fed through a Variac transformer; uniformity of temperature was maintained by a small vibration-free fan. Control was checked to ensure that all temperatures in the oven and cell were the same within 0·1°.

Above *ca.* 60° the Polythene and rubber bands became unreliable, and the risk of thermal strains' appearing in the end-plates increased. The first difficulty was met by replacing the ground ends of the cell with accurately fitted B.24 Pyrex sockets, in which two fused-silica B.24 cones, to whose smaller ends optically-plane silica discs had been sealed and well annealed, were held lightly by springs running between lugs. It was necessary to increase by grinding the clearance between cone and socket for about 0·5 in. behind the optical flat to avoid strain on the end-plate due to the springs or creep of the liquid, particularly at higher temperatures.

Strains in the end-plates, being liable to appear unpredictably, are a major problem in measurements of the Kerr effect. Even if (as is unlikely) the strains in the end-plates were uniformly along diameters, so that their net effect would be that of a uniaxial crystal, one would not know where the principal axes of that crystal lay. If therefore this effect were appreciable, the slightest relative movement of cell and light-path would change it, and determinations of B (particularly if small) could be invalidated. The only precaution possible, since the polariser is in a fixed azimuth of 45°, is to rotate the cell through 45° about its long axis and to search the optical field with a Brace compensator; this procedure should ensure the absence of mechanical strains.

Several further factors need care. It is assumed that the light pencil is incident normally on both end-plates. However, even for the fused-silica plates, if the light does not fall normally on the plate nearer the polariser, refraction by the dielectric results in the beam striking the other end-plate at an angle α out of the normal, and by means of the Brace compensator the phase difference δ arising from this non-normal transmission of the light can be measured. If now the electric field E is applied, orientation of the molecules changes the refractive index of the liquid, and α will become α' and have associated with it a phase difference δ'; δ' is included in the phase difference Δ observed for the dielectric plus cell, but because $\delta' \neq \delta$, the phase difference due solely to the Kerr effect cannot be obtained by subtracting δ from Δ. There is no method of determining δ', which alters with E. The apparatus should therefore be aligned, and end-plates be selected, so that the position of the light spot seen through the observer's telescope is unchanged by the electric field. If all components are correctly arranged, the same value of B_{liquid} is obtained by the use of different voltages.

UNIVERSITY OF SYDNEY, NEW SOUTH WALES,
AUSTRALIA.

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