296. *Molecular Polarisability. Dependence of Apparent Molar Kerr Constants at Infinite Dilution on the Medium in which they are measured.*

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Measurements are reported of the apparent molar Kerr constants of carbon tetrachloride, carbon disulphide, benzene, and naphthalene as solutes in light petroleum, carbon tetrachloride, benzene, and carbon disulphide. Solvent influences are detected and can be correlated with such functions of the refractive index of the solvent as $(n_1^2 - 1)/(n_1^2 + 2)$. It is suggested that the semi-axes of the polarisability ellipsoid of a solute are modified in the presence of a surrounding medium. Four equations, containing empirical terms, are examined whereby " true " semi-axes may be calculated from values secured in carbon tetrachloride, and whereby in turn the apparent semi-axes in other solvents can be computed. Certain consequences such as the predicted increases in molecular anisotropy or electronic polarisation in passing from the liquid or dissolved states to the gas are also considered against the evidence from experiment.

In general, the molar Kerr constant of a compound is a property which may be divided into three [1,2] parts:

$$_mK = 2\pi N(\theta_1 + \theta_2 + \theta_3)/9 \qquad \qquad (1)$$

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

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

In eqn. (1), θ_1 is the "anisotropy" term, θ_2 the "dipole" term, and θ_3 is a temperature-independent term. Expansions of θ_1, θ_2, and θ_3 are given in refs. 1—3.* For a non-polar material θ_2 is, of course, zero. Treatments of θ_3, alternative to that of Le Fèvre, Le Fèvre, and Rao,[2] have been devised by Born and Jordan [4] and by Buckingham and Pople.[5] As a consequence of the development of an extrapolation method for the measurement [1,3] of molar Kerr constants of solutes at infinite dilution, the degree to which such $_{\infty}(_mK_2)$ values are solvent- or state-dependent is obviously important.

Observations by Le Fèvre and Le Fèvre [3,6] have shown that the ratios $_{\infty}(_mK_2)/(_mK_{\text{gas}})$ and $\mu^2_{\text{solution}}/\mu^2_{\text{gas}}$ (or $_0P_{\text{solution}}/_0P_{\text{gas}}$) are closely similar for substances with moments of 1 D or higher. Since these are cases where θ_2 (in equation 1) greatly exceeds θ_1 and θ_3, Le Fèvre and Le Fèvre [1] have concluded that:

$$(\theta_2)_{\text{solution}}/(\theta_2)_{\text{gas}} \sim \mu^2_{\text{solution}}/\mu^2_{\text{gas}}$$

Theoretical considerations (Buckingham [7]) support this. As empirical and other relations now exist [8-10] whereby ratios $\mu_{\text{solution}}/\mu_{\text{gas}}$ may be predicted *a priori*, the problem is almost solved *where strongly polar solutes in non-polar solvents are concerned.*

Unfortunately very little information exists from which the effects of medium or state on θ_1 or θ_3 can be assessed. Obviously such evidence should be sought among non-polar molecules, otherwise changes in θ_2 could mask those in $\theta_1 + \theta_3$. Three likely sources of data are: (*a*) the comparison of molar Kerr constants calculated from measurements on non-polar gases [11] with those found for the same substances as liquids or solutes; (*b*) the comparison of molecular anisotropies determined for non-polar species in the vapour and liquid states—this follows since the numerator of θ_1 is essentially produced by multiplying the molecular anisotropy by the square of the electronic polarisation, and the latter is known to be a property only very slightly affected by variations of temperature or state (for definitions, formulæ, etc., see Le Fèvre and Purnachandra Rao [12]); and (*c*) the comparisons of $_{\infty}(_mK_2)$'s found for non-polar solutes in a range of solvents.

Indications from (*a*) and (*b*) suggest that there is considerable change of $_mK$ with state: the molar Kerr constants of liquid benzene or carbon disulphide at 25° are $5{\cdot}9 \times 10^{-12}$ or 24×10^{-12} respectively,[1] against these the values for $_mK_{\text{gas}}$, deduced from the observations by Stuart and Volkmann [11] on the vaporised substances at 113·6° and 56·7°, are *ca.* 17×10^{-12} and 48×10^{-12}; light scattering and depolarisation data published [13] for benzene and carbon disulphide lead to anisotropies as follow:

	$10^3\delta^2_{\text{gas}}$	$10^3\delta^2_{\text{liquid}}$
C_6H_6	79·2	37·8
CS_2	221	145

Indications from (*c*) are indefinite. Only Briegleb [14] seems to have dealt with solvent effects where non-polar solutes are involved (see Table 1). Only for CS_2 and C_6H_6 has

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* On p. 309 of ref. 1, equation (1) is incorrectly shown without 9 as a denominator and without (26) as its serial number. Other errors which may mislead occur on p. 290, Table 9, where the data for $CHCl_3$ should read 0·673, 9·901, and 0·901; on p. 303, where the angle *A* should be 111° with those at *C* and *D* being 108°; and on p. 305, where the structures shown should be labelled *A*, *B*, and *C* respectively from the top of the page downwards.

[3] Le Fèvre and Le Fèvre, *J.*, 1953, 4041; 1954, 1577.
[4] Born and Jordan, "Elementare Quantenmechanik," Springer Verlag, Berlin, 1930, p. 259.
[5] Buckingham and Pople, *Proc. Phys. Soc.*, 1955, **68**, *A*, 905.
[6] Le Fèvre and Le Fèvre, *J.*, 1955, 2750.
[7] Buckingham, *Trans. Faraday Soc.*, 1956, **52**, 611.
[8] Buckingham and Le Fèvre, *J.*, 1952, 1932.
[9] Le Fèvre, "Dipole Moments," Methuen, London, 1953, 3rd edn., p. 40.
[10] Le Fèvre and Le Fèvre, *Austral. J. Chem.*, 1954, **7**, 33.
[11] Stuart and Volkmann, *Ann. Phys.*, 1933, **18**, 121.
[12] Le Fèvre and Purnachandra Rao, *J.*, 1957, 3644.
[13] Bhagavantam, "Scattering of Light and the Raman Effect," Andhra Univ., Waltair, 1940.
[14] Briegleb, *Z. phys. Chem.*, 1932, **16**, *B*, 249.

more than one solvent been used; however, Briegleb's remaining $_\infty({}_mK_2)$'s in heptane may also be compared with determinations made here[3, 15] in carbon tetrachloride (1 : 4-$C_6H_4Me_2$ 10·6 × 10^{-12}, 1 : 4-$C_6H_4Cl_2$ 38·6 × 10^{-12}, diphenyl 40 × 10^{-12}, and phenanthrene 83 × 10^{-12}). In all cases variations are seen, but the changes from solvent to solvent are not consistent throughout, and the extents to which they are due to solvent effects or observational factors are not clear.

TABLE 1. *Molar Kerr constants* (× 10^{12}) *reported* * *by Briegleb.*

	Solutes						
Solvent	CS_2	C_6H_6	$C_{10}H_8$	1 : 4-$C_6H_4Me_2$	1 : 4-$C_6H_4Cl_2$	Ph_2	Phenanthrene
Heptane	30·0	7·8	111·0	15·6	28·2	44·4	114·0
CCl_4	27·0	5·4	—	—	—	—	—
C_6H_6	33·0	—	—	—	—	—	—

* Briegleb's molar Kerr constants are here multiplied by 6 to bring them into relation with those in the present paper.

Present Work.—At the outset, therefore, it appeared that the most immediately useful contribution would be to establish source (*c*) on a firm experimental basis. To this end, four solutes and four solvents have been systematically examined according to the scheme set out in Table 2, which also includes the $_\infty({}_mK_2)$'s observed and the considerations which guided the original choice of materials.

TABLE 2. *Solvent effects on* $_\infty({}_mK_2)$ × 10^{12} *for non-polar solutes.*

		Solvents			
		Non-polar and near-isotropic		Non-polar and anisotropic	
Solute	Shape and polarisability of solute	Pet *	CCl_4	C_6H_6	CS_2
CCl_4	Sphere, isotropic	1—2	1—2	1—2	1—2
CS_2	Rod, anisotropic	30·0	27·8	27·1	23·8
C_6H_6	Disc, —,,	8·3	7·2	5·9	6·3
$C_{10}H_8$	Flat sheet, anisotropic,	49·4	48·1	45·5	45·0

* Pet = light petroleum, b. p. *ca.* 90°.

Experimental.—Dielectric constants were determined in the circuit used by Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif,[16] and electric double refractions by the methods noted in refs. 1 and 3. Symbols and extrapolation procedures have already been fully listed and described respectively by Le Fèvre, Le Fèvre, and Oh,[17] and Le Fèvre and Le Fèvre.[1, 3]

Table 3 gives the solvent properties and constants required to proceed from the observations, presented in Table 4, to the results shown in Table 5. Materials were as pure as possible, stored over sodium or desiccant as appropriate, and—except naphthalene—redistilled before use. The solvent indicated by " Pet " was a bulk supply of light petroleum (b. p. *ca.* 90°), taken without further treatment other than drying (sodium wire).

TABLE 3. *Solvent properties, constants, etc.*

Solvent	Temp.	10^7B	ε	d	n_D	H	J	$10^{14}{}_sK_1$
Pet	25°	0·075	1·9449	0·71322	1·3970	1·976	0·5070	2·137
,, ...	30	—	1·9397	0·71042	—	—	—	—
CCl_4	25	0·070	2·2270	1·58454	1·4575	2·060	0·4731	0·749
C_6H_6	25	0·410	2·2725	0·87378	1·4973	2·114	0·4681	7·56
CS_2	25	3·145	2·6246	1·2559	1·6243	2·275	0·4325	31·26

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[15] Le Fèvre and Le Fèvre, unpublished observations.
[16] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.
[17] Le Fèvre, Le Fèvre, and Oh, *Austral. J. Chem.*, 1957, **10**, 218.

TABLE 4. *Kerr constants, refractions, dielectric constants, and densities, of mixtures containing weight fractions w_2 of solute.*

(Temp. = 25°, where not otherwise indicated)

Carbon tetrachloride in light petroleum

10^5w_2	8261	8556	14,437	21,239	25,308	27,144	34,713
Δn	0·0022	0·0023	0·0042	0·0064	0·0078	0·0086	0·0116

whence $\Delta n = 0{\cdot}0251w_2 + 0{\cdot}0240w_2^2$

$10^7\ \Delta B = 0$ at all concentrations examined

10^5w_2	8261	8556	14,437	21,239	25,308	27,144	34,713
ε^{25}	1·9552	1·9558	1·9641	1·9742	1·9792	1·9834	1·9965
d_4^{25}	0·74696	0·74826	0·77448	0·80705	0·82792	0·83789	0·88073

whence $\Delta\varepsilon = 0{\cdot}118w_2 + 0{\cdot}0854w_2^2$

$\Delta d = 0{\cdot}382w_2 + 0{\cdot}288w_2^2$

Carbon tetrachloride in benzene

10^5w_2	6709	13,009	14,749	20,322	25,398	30,466	32,475
$10^7\Delta B$	−0·013	−0·026	−0·027	−0·040	−0·048	−0·062	+0·064
Δn	—	−0·0027	—	—	−0·0056	−0·0063	−0·0076

whence $10^7\Delta B = -\ 0{\cdot}185w_2 - 0{\cdot}043w_2^2$

$\sum\Delta n/\sum w_2 = -\ 0{\cdot}022$

10^5w_2	6709	13,009	14,749	20,322	25,398	30,466	32,475
ε^{25}	2·2713	—	—	2·2691	2·2687	2·2670	2·2671
d_4^{25}	0·90042	0·92801	0·93496	0·95900	0·98631	1·01125	1·02307

whence $\sum\Delta\varepsilon/\sum w_2 = -\ 0{\cdot}017$

$\Delta d = 0{\cdot}377w_2 + 0{\cdot}251w_2^2$

Carbon tetrachloride in carbon disulphide

10^5w_2	12,964	13,275	16,945	22,236	25,134	26,693
$10^7\Delta B$	−0·423	−0·429	−0·596	−0·770	−0·850	−0·889
Δn	−0·0191	—	−0·0254	−0·0334	—	—

whence $10^7\Delta B = -\ 3{\cdot}36_3w_2 - 0{\cdot}076w_2^2$

$\sum\Delta n/\sum w_2 = -\ 0{\cdot}149$

10^5w_2	10,493	12,964	15,605	15,754	16,945	22,236
ε^{25}	2·5828	2·5761	2·5662	2·5643	2·5615	2·5418
d^{25}	1·2818	1·2883	1·2950	1·2955	1·2990	1·3133

whence $\sum\Delta\varepsilon/\sum w_2 = -\ 0{\cdot}378$

$\Delta d = 0{\cdot}235w_2 + 0{\cdot}104w_2^2$

Carbon disulphide in light petroleum

10^5w_2	1716	3394	6458	7783	9424	13,063	13,812
$10^7\Delta B$	0·026	0·054	0·105	0·127	0·170	0·250	0·271

whence $10^7\Delta B = 1{\cdot}358w_2 + 4{\cdot}33w_2^2$

10^5w_2	3574	6009	8606
Δn	0·0045	0·0076	0·0105

whence $\sum\Delta n/\sum w_2 = 0{\cdot}1242$

10^5w_2	2582	4770	5696	8103	8811	9071
ε^{30}	1·9484	1·9566	1·9589	1·9677	1·9699	1·9710
d_4^{30}	0·71853	0·72532	0·72786	0·73563	0·73775	0·73877

whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}344$

$\sum\Delta d/\sum w_2 = 0{\cdot}311$

Carbon disulphide in carbon tetrachloride

10^5w_2	552	1801	2083	3359	3953	4452	4626	5458	8726
$10^7\Delta B$	0·019	0·065	0·073	0·110	0·141	0·145	0·158	0·185	0·303
Δn	0·0005	—	0·0035	0·0058	—	—	0·0084	0·0103	—

whence $10^7\Delta B = 3{\cdot}349w_2 + 1{\cdot}26w_2^2$

$\sum\Delta n/\sum w_2 = 0{\cdot}1773$

10^5w_2	829	1076	1633	1778	1905
ε^{25}	2·2320	2·2321	2·2345	2·2359	2·2362
d_4^{25}	1·58043	1·57894	1·57676	1·57610	1·57586

whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}494$

$\sum\Delta d/\sum w_2 = -\ 0{\cdot}4793$

TABLE 4. (*Continued.*)

Carbon disulphide in benzene

10^5w_2	2009	3308	4982	7370	9976	17,773
$10^7\Delta B$	0·028	0·058	0·086	0·135	0·196	0·359
10^5w_2	2837	4982	7370	11,942		
Δn	0·0022	0·0037	0·0057	0·0090		

whence $10^7\Delta B = 1{\cdot}716w_2 + 1{\cdot}761w_2^2$
$\sum\Delta n/\sum w_2 = 0{\cdot}076$

10^5w_2	2232	2994	3256	3608	4918
ε^{25}	2·2802	2·2808	2·2819	2·2828	2·2866
d_4^{25}	0·87953	0·88133	0·88221	0·88277	0·88623

whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}293$
$\sum\Delta d/\sum w_2 = 0{\cdot}253_8$

Benzene in light petroleum

10^5w_2	3882	8646	10,952	15,522	15,685	23,473	34,382
$10^7\Delta B$	0·012	0·024	0·037	—	0·056	0·087	0·127
Δn	—	—	0·0081	0·0117	—	0·0181	0·0273

whence $10^7\Delta B = 0{\cdot}324w_2 + 0{\cdot}145w_2^2$
$\sum\Delta n/\sum w_2 = 0{\cdot}0773$

10^5w_2	10,952	15,522	15,685	20,529	23,473	34,382
ε^{30}	1·9661	1·9769	1·9766	1·9890	1·9977	2·0268
d_4^{30}	0·72372	0·72962	—	0·73549	0·74002	0·75464

whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}2446$
$\sum\Delta d/\sum w_2 = 0{\cdot}1253$

Benzene in carbon disulphide

10^5w_2	5260	8167	9637	12,959	15,105	17,152	19,826
$10^7\Delta B$	−0·252	−0·401	−0·487	−0·630	−0·735	−0·828	−0·979

whence $10^7\Delta B = -4{\cdot}894w_2 + 0{\cdot}008w_2^2$

10^5w_2	3850	8167	9637	15,105	23,031
Δn	−0·0079	−0·0165	−0·0192	−0·0291	−0·0423

whence $\sum\Delta n/\sum w_2 = -0{\cdot}1923$

10^5w_2	3850	8167	9637	15,105	23,031	30,478
ε^{25}	2·6078	2·5850	2·5806	2·5558	2·5191	2·4884
d_4^{25}	1·2336	1·2096	1·2016	1·1731	1·1348	1·1008

whence $\sum\Delta\varepsilon/\sum w_2 = -0{\cdot}455$
$\Delta d = -0{\cdot}587w_2 + 0{\cdot}257w_2^2$

Naphthalene in light petroleum

10^5w_2	3146	5543	7622	9777	10,947	13,088
$10^7\Delta B$	0·039	0·082	0·097	0·141	0·150	0·184
Δn	—	0·0087	—	0·0161	—	0·0217

whence $10^7\Delta B = 1{\cdot}321w_2 + 0{\cdot}646w_2^2$
$\sum\Delta n/\sum w_2 = 0{\cdot}1637$

10^5w_2	1605	2285	3393	4032
ε^{25}	—	1·9550	1·9607	1·9633
d_4^{25}	0·71762	0·71857	0·72105	0·72231

whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}455$
$\sum\Delta d/\sum w_2 = 0{\cdot}2411$

Naphthalene in benzene

10^5w_2	1154	3044	4056	4759	4843	4944	5315
$10^7\Delta B$	0·015	0·049	0·065	0·073	0·073	0·074	0·079

whence $10^7\Delta B = 1{\cdot}67_4w_2 - 3{\cdot}21w_2^2$

10^5w_2	4843	8674	17,010	24,800
Δn	0·0053	0·0093	0·0188	0·0277

whence $\sum\Delta n/\sum w_2 = 0{\cdot}110$

10^5w_2	3762	4843	6341	8674	17,010	24,800
ε^{25}	2·2855	2·2877	2·2924	2·3009	2·3287	2·3561

whence $\Delta\varepsilon = 0{\cdot}318w_2 + 0{\cdot}077w_2^2$

10^5w_2	1501	3030	4082	4843	8674	17,010	24,800
d_4^{25}	0·87588	0·87801	0·87944	0·88051	0·88577	0·89730	0·90870

whence $\sum\Delta d/\sum w_2 = 0{\cdot}139$

TABLE 4. (*Continued.*)

Naphthalene in carbon disulphide

10^5w_2	5186	8423	11,028	11,686	14,111	16,856
$10^7\Delta B$	$-0{\cdot}025$	$-0{\cdot}045$	$-0{\cdot}077$	$-0{\cdot}090$	$-0{\cdot}161$	$-0{\cdot}217$

whence $10^7\Delta B = -0{\cdot}194w_2 - 8{\cdot}84w_2^2$

10^5w_2	4139	9401	10,597	15,982
Δn	$-0{\cdot}0002$	$-0{\cdot}0005$	$-0{\cdot}0006$	$-0{\cdot}0008$

whence $\sum\Delta n/\sum w_2 = -0{\cdot}0052$

10^5w_2	4139	7150	9401	10,597	12,645	15,982
ε^{25}	2·6285	—	2·6328	2·6345	—	2·6392
d_4^{25}	1·2441	1·2358	1·2297	1·2262	1·2211	1·2120

whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}0912$
$\sum\Delta d/\sum w_2 = -0{\cdot}278$

TABLE 5. *Calculation of molar Kerr constants at infinite dilution.*

Solute	Solvent	$(\alpha\varepsilon_1)_{w_2=0}$	$(\beta)_{w_2=0}$	γ	$(\delta)_{w_2=0}$	$_\infty(_mK_2) \times 10^{12}$
CCl_4	Pet	0·118	0·535	0·018	0	1·3
CCl_4	C_6H_6	$-0{\cdot}017$	0·431	$-0{\cdot}015$	$-0{\cdot}452$	1·6
CCl_4	CS_2	$-0{\cdot}378$	0·187	$-0{\cdot}092$	$-1{\cdot}069$	1·2
CS_2	Pet	0·344	0·438	0·089	18·11	30·0
CS_2	CCl_4	0·494	$-0{\cdot}302_5$	0·122	47·84	27·8
CS_2	C_6H_6	0·293	$0{\cdot}290_5$	0·051	4·185	27·1
C_6H_6	Pet	0·245	0·176	0·055	$4{\cdot}32_0$	8·3
C_6H_6	CCl_4 *	0·227	$-0{\cdot}755$	0·067	10·5	7·2
C_6H_6	CS_2	$-0{\cdot}455$	$-0{\cdot}467$	$-0{\cdot}118$	$-1{\cdot}55_6$	6·3
$C_{10}H_8$	Pet	0·455	0·338	0·117	17·61	49·4
$C_{10}H_8$	CCl_4 †	0·617	$-0{\cdot}515$	0·181	49·0	48·1
$C_{10}H_8$	C_6H_6	0·318	0·160	0·073	$4{\cdot}08_3$	45·5
$C_{10}H_8$	CS_2	0·091	$-0{\cdot}221$	$-0{\cdot}003$	$-0{\cdot}062$	45·0

* Data from *J.*, 1954, 1577. † Data from *J.*, 1955, 1641.

Discussion.—Because of the difficulties experienced in measuring near-zero molar Kerr constants, the results with carbon tetrachloride as solute cannot be fixed with certainty between the limits 1—2 × 10^{-12}; with the other solutes, however, definite solvent effects can be discerned. The data of Table 2 give fairly satisfactory plots against the volume polarisations of the solvents or such functions of n_1 as $n_1^2/(n_1^2 + 2)$. The Figure shows $_\infty(_mK_2)$ *versus* $(n_1^2 - 1)/(n_1^2 + 2)$ as an example.

Various considerations, set out in the papers of Raman and Krishnan,[18] and Le Fèvre and Narayana Rao,[19] suggest that the above relations are not accidental, since the apparent semi-axes of polarisability of a molecule may be affected by the properties of the medium in which they are studied and by the shape of the ellipsoidal cavity the structure is assumed to occupy.

Following the work of ref. 19, equation (2) is proposed for non-polar solutes:

$$b_i^s/b_i^v = 3n_1^2/\{(n_1^2 + 2)(1 - f_ib_i^v)[n_1^2 + (1 - n_1^2)k_i]\} \quad . \quad . \quad . \quad . \quad (2)$$

in which the b_i's are the usual three semi-axes of a molecular polarisability ellipsoid, either as they appear in a solution (b_i^s) or as their " true " values in a gas (b_i^v), n_1 is the refractive index of the solvent, the k_i's are shape factors, and the f_i's are quantities given by:

$$f_i = 3k_i(1 - k_i)(n_1^2 - 1)/abc[n_1^2 + (1 - n_1^2)k_i]$$

where *abc* is the product of the radii defining the volume of the cavity. Since Le Fèvre and Narayana Rao [19] obtained reasonable results in a related problem by computing *abc* from the minimum volume of the solute in the liquid state, *i.e.*, $abc = 3M_2/4\pi Nd_{mp}$, d_{mp} being the density at the m. p., this method has been adopted here. The k_i's have been read from

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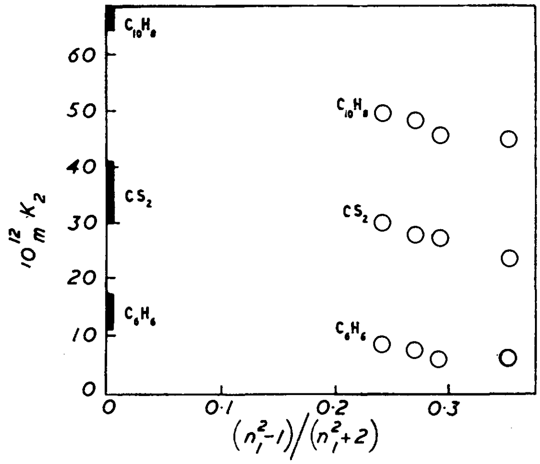
[18] Raman and Krishnan, *Proc. Roy. Soc.*, 1928, *A*, **117**, 589.
[19] Le Fèvre and Narayana Rao, *Austral. J. Chem.*, 1955, **8**, 329.

curves due to Osborn,[20] in conjunction with ratios B/A and C/A, in which A, B, and C are linear dimensions derived by calculation, or from scale-drawings, in the way described by Barclay and Le Fèvre,[21] Buckingham and Le Fèvre,[8] and Holland and Le Fèvre [23] (cf. also refs. 1 and 9). For a spherical molecule, of course, $k_1 = k_2 = k_3 = \frac{1}{3}$. Table 6 lists data for the solutes examined. Table 7 gives the polarisability semi-axes deduced from the $_\infty({}_mK_2)$'s in carbon tetrachloride contained in Table 5; the cases of benzene and naphthalene are brought forward from previous papers, that of carbon disulphide is new (the ${}_EP$ required for this calculation being 20·39 c.c., taken from Le Fèvre and Narayana Rao's work [23]).



Plot of $10^{12}{}_mK_2$ *against* $(n_1^2 - 1)/(n_2^2 + 2)$. *The thick lines on the ordinate show the ranges of* ${}_mK_{gas}$ *calculated by equations* (2), (3*a*), (3*b*), *and* (3*c*). *The values for* $C_{10}H_8$ *should extend up to* 93·4.

With the help of equation (2), the semi-axes of Table 7 can be transformed into others, b_i^v (see Table 8), which should be those found by direct measurement on vapours. Extant information is too sparse for a check of Table 8 from experiment. The Kerr effect of

TABLE 6. *Shape factors and dimensions of solutes.*

Solute *	A	B	C	k_1	k_2	k_3
CS_2	6·18	3·08	3·08	$0·17_4$	$0·41_3$	$0·41_3$
C_6H_6	6·70	6·70	2·90	$0·21_5$	$0·21_5$	0·57
$C_{10}H_8$	8·98	7·18	2·90	0·16	0·22	0·62

* Carbon tetrachloride, being spherically symmetrical, has $k_1 = k_2 = k_3 = 1/3$.

TABLE 7. *Semi-axes of the apparent polarisability ellipsoids in carbon tetrachloride as solvent.*

Solute	$10^{23}b_1^s$	$10^{23}b_2^s$	$10^{23}b_3^s$
CS_2	1·308	0·558	0·558
C_6H_6 *	1·114	1·114	0·733
$C_{10}H_8$ †	2·15	1·76	1·03

* From *J.*, 1954, 1577. † From *J.*, 1955, 1641.

TABLE 8. *Semi-axes for molecules in gaseous state, calculated by equation* (2).

	$10^{23}b_1^v$	$10^{23}b_2^v$	$10^{23}b_3^v$
CS_2	1·363	0·525	0·525
C_6H_6	1·214	1·214	0·632
$C_{10}H_8$	$2·41_3$	$1·89_7$	$0·86_3$

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[20] Osborn, *Phys. Rev.*, 1945, **67**, 351.
[21] Barclay and Le Fèvre, *J.*, 1950, 556.
[22] Holland and Le Fèvre, *J.*, 1950, 2166.
[23] Le Fèvre and Narayana Rao, *Austral. J. Chem.*, 1954, **7**, 135.

naphthalene has not yet been studied as a gas, but Stuart and Volkmann[24] report $10^{23}b_i^v$'s for carbon disulphide and benzene respectively as 1·512, 0·550, 0·550, and 1·231, 1·231, 0·635. Since Stuart and Volkmann adopted mean polarisabilities which differ from those used here, comparisons are best made by ratios. This is done in Table 9, from which it is obvious that the calculated semi-axes of Table 8 show a near approach to the Stuart and Volkmann's " gas " values.

TABLE 9. *Ratios of semi-axes found and calculated for gases and observed in carbon tetrachloride.*

	Carbon disulphide			Benzene		
	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
From ref. 24	2·75	1	1	1·94	1·94	1
From Table 7	2·34	1	1	1·52	1·52	1
From Table 8	2·60	1	1	1·92	1·92	1

Next, from the semi-axes of Table 8, and again by using equation (2), the " apparent " semi-axes which the solutes should exhibit in light petroleum, benzene, and carbon disulphide may be computed, and therefrom estimates made of the molar Kerr constants to be expected in these media. Table 10 shows the outcome of such calculations. Agreement between prediction and observation is good for carbon disulphide, somewhat less so for benzene, and worst for naphthalene. This is not surprising, since the assumptions which underlie equation (2)—especially those associated with linear dimensions, shape factors, and the products *abc*—are probably least valid for naphthalene, the *C* for which (see Table 6) has been taken equal to that of benzene although in reality it is likely to be greater. If the ratio *C*/*A* were larger, then the differences between the ${}_mK$'s forecast for naphthalene in the three solvents in Table 10 would be reduced. Similar remarks would apply also to benzene, two estimates[26] of the " thickness " of which have been 3·2 and 3·7 Å. These both exceed the value of 2·90 Å used here. However, since no reported " thicknesses " of naphthalene can be found in the literature, the matter will not be pursued now, as the present objective is to explore methods of calculation which utilise, for the various solutes, data which are as consistently accessible as possible.

TABLE 10. *Calculations of apparent semi-axes and molar Kerr constants in petroleum ether, benzene, and carbon disulphide.*

Solvent	$10^{23}b_1^s$	$10^{23}b_2^s$	$10^{23}b_3^s$	$10^{12}{}_mK$ calc.	$10^{12}{}_mK$ obs.
	Solute: CS_2; $abc = 2{\cdot}08 \times 10^{-23}$ c.c.				
Pet	1·331	0·562	0·652	29·6	30·0
C_6H_6	1·290	0·555	0·555	27·0	27·1
CS_2	1·230	0·539	0·539	23·9	23·8
	Solute: C_6H_6; $abc = 3{\cdot}47 \times 10^{-23}$ c.c.				
Pet	$1{\cdot}139_5$	$1{\cdot}139_5$	0·731	8·3	8·3
C_6H_6	1·097	1·097	0·733	6·6	5·9
CS_2	1·038	1·038	0·727	4·8	6·3
	Solute: $C_{10}H_8$; $abc = 5{\cdot}194 \times 10^{-23}$ c.c.*				
Pet	$2{\cdot}20_5$	$1{\cdot}79_8$	$1{\cdot}02_3$	54·1	49·4
C_6H_6	$2{\cdot}11_3$	$1{\cdot}73_3$	$1{\cdot}03_2$	45·1	45·5
CS_2	$1{\cdot}99_0$	$1{\cdot}64_3$	$1{\cdot}03_0$	35·4	45·0

* $d_{mp} = 0{\cdot}978$ g./c.c. from ref. 25.

Other equations (3*a*, 3*b*, and 3*c*) have been investigated as alternatives to (2). They

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[24] Stuart and Volkmann, *Ann. Phys.*, 1933, **18**, 121.

[25] Egloff, " Physical Constants of Hydrocarbons," Reinhold, New York, 1947, Vol. IV, p. 81.

[26] Listed by Stuart, " Die Struktur des Freien Molekuls," Springer Verlag, Berlin–Göttingen–Heidelberg, 1952, p. 99.

differ among themselves only in the values adopted for K: in 3*a*, $K = 1$, in 3*b*, $K = n_1^2$, in 3*c*, $K = n_1$:

$$b_i^s/b_i^v = 1 - K(n_1^2 - 1)(0{\cdot}333 - k_i)/(n_1^2 + 2) \quad . \quad . \quad (3a), (3b), \text{ or } (3c)$$

otherwise symbols have the same meanings as in eqn. (2). The quantity $(0{\cdot}333 - k_i)$ is introduced to reflect the departure of the solute molecule from sphericality. Table 12 illustrates the degrees of success in which ${}_mK_2$'s may be predicted by these three relations. Table 11 gives the b_i^v's, deduced from the measurements in carbon tetrachloride (Table 7), which are necessary for the production of Table 12.

By summing the squares of the differences between ${}_mK$ calc. and ${}_mK$ obs. in Tables 10 and 12 it appears that the order of best fit is (3*a*) superior in turn to (3*c*), to (2), and to (3*b*). In large part, however, this situation is determined by the results for naphthalene, comment on which has already been made. If the case of naphthalene is omitted the order appears as (3*c*) better than (3*a*), than (2), than (3*b*), while for carbon disulphide alone it is (2) better than (3*c*), than (3*a*), than (3*b*).

TABLE 11. *Semi-axes for molecules in gaseous state, calculated by equations* (3*a*), (3*b*), *and* (3*c*).

	Equation	$10^{23}b_1^v$	$10^{23}b_2^v$	$10^{23}b_3^v$		Equation	$10^{23}b_1^v$	$10^{23}b_2^v$	$10^{23}b_3^v$
CS_2	3*a*	1·367	0·546	0·546	$C_{10}H_8$ ...	3*a*	2·25$_6$	1·81$_6$	0·955
	3*b*	1·440	0·533	0·533		3*b*	2·28$_3$	1·88$_0$	0·882
	3*c*	1·396	0·541	0·541		3*c*	2·30$_7$	1·84$_1$	0·924
C_6H_6 ...	3*a*	1·151	1·151	0·688					
	3*b*	1·195	1·195	0·645					
	3*c*	1·169	1·169	0·670					

TABLE 12. *Calculations of apparent semi-axes and molar Kerr constants in light petroleum, benzene, and carbon disulphide using equations* (3*a*), (3*b*), *and* (3*c*).

Solvent	Equation	$10^{23}b_1^s$	$10^{23}b_2^s$	$10^{23}b_3^s$	$10^{12}{}_mK$ calc.	$10^{12}{}_mK$ obs.
			Solute: CS_2			
Pet	3*a*	1·315	0·556	0·556	28·8	30·0
,, ...	3*b*	1·332	0·553	0·553	29·3	,,
,, ...	3*c*	1·322	0·556	0·556	29·3	,,
C_6H_6	3*a*	1·303	0·559	0·559	27·7	27·1
,, ...	3*b*	1·290	0·561	0·561	25·6	,,
,, ...	3*c*	1·298	0·560	0·560	27·2	,,
CS_2	3*a*	1·290	0·561	0·561	26·5	23·8
,, ...	3*b*	1·227	0·573	0·573	20·6	,,
,, ...	3*c*	1·268	0·566	0·566	24·6	,,
			Solute: C_6H_6			
Pet	3*a*	1·119	1·119	0·727	7·7	8·3
,, ...	3*b*	1·129	1·129	0·697	9·1	,,
,, ...	3*c*	1·122	1·122	0·724	7·9	,,
C_6H_6	3*a*	1·111	1·111	0·735	7·1	5·9
,, ...	3*b*	1·103	1·102	0·746	6·2	,,
,, ...	3*c*	1·108	1·108	0·740	6·8	,,
CS_2	3*a*	1·103	1·103	0·746	6·4	6·3
,, ...	3*b*	1·064	1·064	0·787$_5$	3·7	,,
,, ...	3*c*	1·090	1·090	0·761	5·4	,,
			Solute: $C_{10}H_8$			
Pet	3*a*	2·16$_4$	1·76$_9$	1·02$_2$	50·4	49·4
,, ...	3*b*	2·19$_2$	1·78$_2$	1·00$_2$	54·9	,,
,, ...	3*c*	2·17$_6$	1·77$_3$	1·01$_5$	52·1	,,
C_6H_6	3*a*	2·14$_3$	1·75$_8$	1·03$_6$	47·3	45·5
,, ...	3*b*	2·11$_4$	1·74$_5$	1·05$_0$	43·4	,,
,, ...	3*c*	2·13$_4$	1·75$_3$	1·04$_1$	46·2	,,
CS_2	3*a*	2·12$_1$	1·74$_5$	1·05$_2$	44·1	45·0
,, ...	3*b*	2·00$_4$	1·68$_8$	1·12$_0$	29·9	,,
,, ...	3*c*	2·08$_3$	1·72$_5$	1·07$_7$	39·0	,,

Three other subjects of interest arise from the semi-axes in the above Tables. From the data of Tables 8 and 11, the molar Kerr constants for carbon disulphide and benzene as gaseous dielectrics at 25° may be directly calculated. Values emerge as follows:

From Table 8, involving equation (2), ${}_mK_{\text{gas}} \times 10^{12} = 35$ for CS_2 and 17 for C_6H_6;
From Table 11, involving equations (3*a*), (3*b*), and (3*c*), ${}_mK_{\text{gas}} \times 10^{12} = 34$—41 for CS_2 and 11—15 for benzene.

The only measurements available are those by Stuart and Volkmann [11] to which reference has already been made. Transformation of their observations into ${}_mK$'s for 25° gives *ca.* 48×10^{-12} and *ca.* 17×10^{-12} for CS_2 and C_6H_6 respectively. Agreement thus seems good for benzene and correct in order for carbon disulphide. However, it should be remarked that the quoted experimental work is solitary and urgently requires re-examination, in view of the practical difficulties always inherent in the determination of small Kerr effects—difficulties which are greatly increased by working at elevated temperatures.

The second subject concerns the molecular anisotropies [12, 13] of gases, reference to which has also been made at the outset. From Tables 8 and 11, values of δ^2_{gas} can be computed:

For CS_2, from Table 8 (eqn. 2), $10^3\delta^2_{\text{gas}} = 179$
„ C_6H_6 „ „ „ „ $= 72$
„ $C_{10}H_8$ „ „ „ „ $= 140$
„ CS_2, from Table 11 (eqns. 3*a*, 3*b*, 3*c*) $10^3\delta^2_{\text{gas}} = 238$—259
„ C_6H_6 „ „ „ „ $= 48$—67
„ $C_{10}H_8$ „ „ „ „ $= 104$—123

Bhagavantam (ref. 13, pp. 54, 55) lists, as most probable, 221, 79, and 145 for $10^3 \times \delta^2_{\text{gas}}$ for CS_2, C_6H_6, and $C_{10}H_8$ respectively. However it is clear, *e.g.*, from data cited by Ramakrishna Rao,[27] that considerable variations exist among the results of different observers; this is particularly the case for CS_2 for which $10^3\delta^2_{\text{gas}}$, determined by six workers, lies between the limits 204 (Ramakrishna Rao) and 346 (Ganesan [28]). In such circumstances therefore the applicabilities of equations (2), (3*a*), (3*b*), and (3*c*) cannot be adjudged unsatisfactory.

The third subject relates to the dependence of electronic polarisations on state. From the semi-axes listed in Tables 8 and 11 " vapour values " of electronic polarisations should be calculable by the relation: ${}_EP_{\text{gas}} = 4\pi N(b_1^{\text{v}} + b_2^{\text{v}} + b_3^{\text{v}})/3$. Table 13 summarises the position and also makes comparison with the corresponding polarisations drawn from the " solution semi-axes " of Table 7. It is seen that in all cases, except CS_2 by equation (2), the electronic polarisation of each species as a gas is forecast to be slightly greater than as a solute. No data exist whereby this can be checked against experiment. However it seems reasonable to assume that ${}_EP_{\text{gas}}/{}_EP_{\text{liquid}}$ ratios will be close to the corresponding

TABLE 13. *Electronic polarisations of* CS_2 *and* C_6H_6 *as vapours and as solutes in carbon tetrachloride.*

	CS_2	C_6H_6	CS_2	CS_2	CS_2	C_6H_6	C_6H_6	C_6H_6
Table and equation involved	8(2)	8(2)	11(3*a*)	11(3*b*)	11(3*c*)	11(3*a*)	11(3*b*)	11(3*c*)
${}_EP_{\text{gas}}$ calc.	20·29	25·73	20·68	21·07	20·84	25·15	25·52	25·30
${}_EP_{\text{gas}}/{}_EP_{CCl_4}$	0·995	1·033	1·014	1·033	1·022	1·010	1·025	1·016
Table and equation involved	10(2)	10(2)	12(3*a*)	12(3*b*)	12(3*c*)	12(3*a*)	12(3*b*)	12(3*c*)
${}_EP_{\text{liquid}}$ calc.	19·41	24·62	20·28	19·96	20·18	24·87	24·81	24·86
${}_EP_{\text{gas}}/{}_EP_{\text{liquid}}$	1·045	1·045	1·020	1·056	1·033	1·011	1·029	1·018

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[27] Ramakrishna Rao, *Ind. J. Phys.*, 1927, **2**, 61.
[28] Ganesan, *Phil. Mag.*, 1925, **49**, 1221.

molecular refraction ratios, which can be found accurately. At N.T.P. and for $\lambda = 5893$ Å, $(n - 1) \times 10^6$ is [29] for CS_2 1478 and for C_6H_6 1823, whence, with $V = 22414{\cdot}6$ c.c., $(R_D)_{gas}$ is 22·08 and 27·23 c.c. respectively; the related $(R_D)_{liquid}$ values [30] are 21·18 and 26·18 c.c., from which $(R_D)_{gas}/(R_D)_{liquid}$ ratios follow as 1·042 and 1·041. The last three lines of Table 13 deal with the ${}_EP_{gas}/{}_EP_{liquid}$ ratios predicted by the four equations under consideration, all of which appear qualitatively correct, while eqn. (2) is nearly quantitatively so.

Finally, the quasi-spherical solute, carbon tetrachloride may be mentioned. For such a structure the k_i's are each 1/3, and it is immediately obvious by equations (3*a*), (3*b*), and (3*c*) that $b_i^s/b_i^v = 1$. By eqn. (2), using $abc = 3{\cdot}64 \times 10^{-23}$ from $d_{mp} = 1{\cdot}67_5$ g./c.c.), $n^2_{CCl_4} = 2{\cdot}1243$, and $b_1^s = b_2^s = b_3^s = 1{\cdot}026 \times 10^{-23}$ (from ${}_EP_{liquid} = 25{\cdot}89$ c.c.), the b_i^v's appear as $1{\cdot}022 \times 10^{-23}$—the ratio b_i^s/b_i^v being thus $1{\cdot}00_4$. Actually, to judge from $(R_D)_{liquid}/(R_D)_{gas}$ values [29,30] the ratio should be $26{\cdot}51/26{\cdot}58 = 0{\cdot}997_4$. To produce such a result abc needs to be $3{\cdot}86_3 \times 10^{-23}$ c.c. which corresponds to $d_{mp} = 1{\cdot}578$; this is far lower than that (1·675 g./c.c.) obtained by extrapolating to —22·9° the densities listed by Timmermans.[31] It is perhaps a coincidence that by using a C–Cl inter-centre distance of 1·76 Å and a " Wirkungs-radius " of 1·6 Å for chlorine,[32] abc becomes $3{\cdot}79 \times 10^{-23}$ c.c., a value which makes b_i^s/b_i^v unity. Of course, if ${}_mK_{CCl_4}$ is in fact due to distortion,[3] the assumption that $k_i = 1/3$ is slightly incorrect, and small solvent effects should be expected (see, however, conclusion 7 below).

Conclusions.—(1) The molar Kerr constants of non-polar solutes show a small dependence on the solvent, being larger in media with lower refractive indexes, and *vice versa.*

(2) Such solvent effects can be attributed to apparent variations in the polarisability semi-axes of a molecule caused by its environment.

(3) Equations may be developed whereby the " true " semi-axes can be calculated from corresponding " apparent " values, determined from work on solutions.

(4) In the two cases for which measurements as gases have been made (CS_2 and C_6H_6), the calculated $({}_mK_{gas})$'s are of the order of magnitude found by experiment.

(5) A similar claim may be made regarding the molecular anisotropies as gases of CS_2, C_6H_6, and $C_{10}H_8$.

(6) The equations predict that the electronic polarisations of substances should be slightly greater as vapours than as liquids or solutes; this also is in conformity with known facts regarding molecular refractions.

(7) In the one instance (CCl_4) where the molar Kerr constant is believed to be wholly due to a " θ_3 term," alterations of ${}_mK_2$ by the medium, if they occur at all, are undetectable at the level of experimental accuracy at present available.

The authors acknowledge with gratitude the award of a Research Scholarship to M. R. Smith by the Australian Atomic Energy Commission.

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[*Received, October 28th,* 1957.]

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[29] International Critical Tables, 1930, Vol. VII, 1st edn., p. 10.

[30] Landolt–Börnstein, " Tabellen," 1912 edn.

[31] Timmermans, " Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

[32] Stuart, *Z. phys. Chem.*, 1935, *B*, **27**, 350.