449. *A Molecular Theory of the Electro-optical Kerr Effect in Liquids.*

By A. D. BUCKINGHAM and R. E. RAAB.

The classical statistical-mechanical theory of the electro-optical Kerr constant is extended to include the effects of molecular interactions and of the dependence of molecular polarizabilities on field strength. The resulting formula is simple for molecules without permanent dipole moments for which it is found that at all densities the molecular Kerr constant is expressible in the form $A + B/T$, where A and B are constants characteristic of the substance. Experiments suggest that at room temperature A is responsible for about half of the observed Kerr constant of mesitylene. For pure polar liquids, the Kerr constant reduces to an expression involving, *inter al.*, the static and high-frequency dielectric constants. The final equation depends only on short-range effects, and for the Onsager model of a pure polar liquid leads to a simple result which agrees quite well with experimental data. The general result is applied to water, and Pople's molecular model used to compute the temperature dependence of its Kerr constant.

THE Langevin–Born theory of the electro-optical Kerr effect (double refraction induced in an isotropic medium by an electric field) was recently extended [1] to include contributions resulting from the dependence of molecular polarizability on field strength. For spherically symmetric molecules the observed Kerr constant is independent of temperature and directly proportional to the " hyperpolarizability " describing the initial deviation from a linear relation between dipole moment and field strength. However, this extended Langevin–Born theory is strictly applicable only to perfect gases, whereas most of the existing data refer to solutions or pure liquids.

Earlier attempts [2] to extend the simple-gas theory to assemblies of interacting molecules have depended on assumptions inherent in various models. Recently a classical statistical-mechanical theory was developed and this has been applied successfully to non-dipolar substances [3] and to dilute solutions of polar molecules in non-polar solvents.[4] The present paper aims to interpret observed Kerr constants, particularly those of pure polar liquids, in terms of molecular properties. The general theory leads to an expression relating the constant to the anisotropy in the polarizability and to the mean values of the scalar products of vectors involving the mean dipole moments of a fixed molecule and its near neighbours. The effects of molecular interactions are in part allowed for by relating the Kerr constant to the actual dielectric constant of the medium.

GENERAL THEORY

The molecular Kerr constant ${}_{\mathrm{m}}K$ as defined by Otterbein [5] is

$$ {}_{\mathrm{m}}K = \frac{6nV_{\mathrm{m}}}{(n^2+2)^2(\varepsilon+2)^2} \lim_{E\to 0} \frac{n_{\parallel}-n_{\perp}}{E^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1) $$

where $n_{\parallel}$ and $n_{\perp}$ are the refractive indices of the specimen in the directions of the strong static electric field $\mathbf{E}$ and at right angles to it, and n is the refractive index of the isotropic medium for the same wavelength; V_{m} is the molar volume and ε the static dielectric constant. Our discussion will be restricted to systems in which the strong electric field E is uniform.

---

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

[2] Raman and Krishnan, *Proc. Roy. Soc.*, 1927, *A*, **117**, 1; Oka, *Proc. Phys.-Math. Soc. Japan* (3), **19**, 156; Piekara, *Proc. Roy. Soc.*, 1939, *A*, **172**, 360; Klages, *Z. Naturforsch.*, 1952, **7a**, 669.

[3] Buckingham, *Proc. Phys. Soc.*, 1955, **68**, *A*, 910.

[4] Buckingham, *Trans. Faraday Soc.*, 1956, **52**, 611.

[5] Otterbein, *Physikal. Z.*, 1934, **35**, 249.

In order to isolate the " external " electric field E_0 as the effective macroscopic local field acting on a molecule, we shall consider a large spherical specimen of volume V_m containing N (Avogadro's number) similar molecules. If E_0 is the strength of the uniform field at large distances from the sphere, then classical electrostatics leads to the result $E = 3E_0/(\varepsilon + 2)$ (see Stratton [6]), and eqn. (1) becomes

$$_{\mathrm{m}}K = \frac{2nV_{\mathrm{m}}}{3(n^2+2)^2} \lim_{E_0 \to 0} \frac{n_{\parallel} - n_{\perp}}{E_0^{\,2}} \quad \ldots \ldots \quad (2)$$

We shall suppose that the dipole moment $m_\alpha^{(i)}$ of the i-th molecule can be developed as a power series in the electric field acting on it. Thus, small Greek letters being used as tensor suffixes :

$$m_\alpha^{(i)} = \mu_\alpha^{(i)} + \alpha_{\alpha\beta}^{(i)} (E_{0\beta} + F_\beta^{(i)}) + \tfrac{1}{2}\, \beta_{\alpha\beta\gamma}^{(i)} (E_{0\beta} + F_\beta^{(i)})(E_{0\gamma} + F_\gamma^{(i)}) + \\ (1/6)\gamma_{\alpha\beta\gamma\delta}^{(i)}(E_{0\beta} + F_\beta^{(i)})(E_{0\gamma} + F_\gamma^{(i)})(E_{0\delta} + F_\delta^{(i)}) + \quad . \quad . \quad (3)$$

where $\mu_\alpha^{(i)}$ is the permanent dipole moment of molecule i; $\alpha_{\alpha\beta}^{(i)}$, $\beta_{\alpha\beta\gamma}^{(i)}$, $\gamma_{\alpha\beta\gamma\delta}^{(i)}$, etc., are the polarizability tensors discussed by Buckingham and Pople; [1] these are symmetric in all suffixes. $\alpha_{\alpha\beta}^{(i)}$ is the normal low-field strength polarizability tensor, and $\beta_{\alpha\beta\gamma}^{(i)}$, $\gamma_{\alpha\beta\gamma\delta}^{(i)}$, etc., describe the field dependence of the polarizability. $F_\alpha^{(i)}$ is the field at the centre of molecule i due to the charge distributions of all of the others, and we shall assume that $F_\alpha^{(i)}$ is constant throughout the molecule. The dipolar contribution to $F_\alpha^{(i)}$ is

$$F_\alpha^{(i)} = -\sum_{j \neq i}^{N} \varepsilon_{\alpha\beta}^{(ij)}\, m_\beta^{(j)} \\ = -\sum_{j \neq i}^{N} \frac{1}{r_{ij}^{\,5}} (r_{ij}^{\,2}\, \delta_{\alpha\beta} - 3r_{ij\alpha} r_{ij\beta}) m_\beta^{(j)} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$r_{ij\alpha}$ being the vector between the centres of molecules i and j, and $\delta_{\alpha\beta}$ the substitution tensor ($= 1$ when $\alpha = \beta$; $= 0$ when $\alpha \neq \beta$).

The *differential polarizability* $\pi_{\alpha\epsilon}^{(i)}$ of molecule i is defined as

$$\pi_{\alpha\epsilon}^{(i)} = \frac{\partial m_\alpha^{(i)}}{\partial E_{0\epsilon}} = \pi_{\epsilon\alpha}^{(i)} \quad \ldots \ldots \quad (5)$$

$$= \left\{\alpha_{\alpha\beta}^{(i)} + \beta_{\alpha\beta\gamma}^{(i)}(E_{0\gamma} + F_\gamma^{(i)}) + \tfrac{1}{2}\gamma_{\alpha\beta\gamma\delta}^{(i)}(E_{0\gamma} + \\ F_\gamma^{(i)})(E_{0\delta} + F_\delta^{(i)}) + \ldots\right\}\left\{\delta_{\beta\epsilon} + \partial F_\beta^{(i)}/\partial E_{0\epsilon}\right\} . \quad . \quad (6)$$

The effective molecular polarizability determining the refractivities in the directions of the unit vectors $\mathbf{e}^{\parallel}$ and $\mathbf{e}^{\perp}$ along and at right angles respectively to the strong field $\mathbf{E}_0$ is $\pi_{\alpha\beta}^{(i)}$, for they are proportional to the mean dipole moments induced in these directions by the incremental high-frequency electric fields of the light waves. Thus

$$\frac{n_{\parallel}^{\,2} - 1}{n_{\parallel}^{\,2} + 2} - \frac{n_{\perp}^{\,2} - 1}{n_{\perp}^{\,2} + 2} = \frac{4\pi N}{3\, V_{\mathrm{m}}}\, \overline{\Pi^{(1)}(\tau, \mathbf{E}_0)} \quad \ldots \ldots \quad (7)$$

where

$$\Pi^{(1)}(\tau, \mathbf{E}_0) = \pi_{\alpha\beta}^{(1)} (e_\alpha^{\parallel} e_\beta^{\parallel} - e_\alpha^{\perp} e_\beta^{\perp}) \quad \ldots \ldots \quad (8)$$

In our purely classical treatment, the continuous variable τ represents the configuration of

---

[6] Stratton, " Electromagnetic Theory," McGraw-Hill Book Co., New York, 1941, § 3.24.

the molecules of the specimen. The bar in eqn. (7) signifies an average over all configurations, so that

$$\overline{\Pi^{(1)}(\tau, \mathsf{E}_0)} = \frac{\int \Pi^{(1)}(\tau, \mathsf{E}_0) \exp\{-U(\tau, \mathsf{E}_0)/\boldsymbol{k}T\} \mathrm{d}\tau}{\int \exp\{-U(\tau, \mathsf{E}_0)/\boldsymbol{k}T\} \mathrm{d}\tau} \quad . \quad . \quad . \quad . \quad (9)$$

where $U(\tau, \mathsf{E}_0)$ is the potential energy of the system in the configuration τ and when the external field is E_0. The general relation

$$U(\tau, \mathsf{E}_0) = U(\tau, 0) - \int_0^{E_0} M_\alpha(\tau, \mathsf{E})\, e_\alpha{}^{\parallel}\, \mathrm{d}E \quad . \quad . \quad . \quad . \quad . \quad (10)$$

leads to the result

$$\partial U(\tau, \mathsf{E}_0)/\partial E_0 = -M_\alpha(\tau, \mathsf{E}_0) e_\alpha{}^{\parallel} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where $M_\alpha(\tau, \mathsf{E}) = \sum_i^N m_\alpha{}^{(i)}$ is the dipole moment of the whole spherical specimen when the external field is E.

We shall employ the notation $\langle X \rangle$ for the average value of a quantity $X(\tau, \mathsf{E}_0)$ in the assembly with $E_0 = 0$, that is,

$$\langle X \rangle = \frac{\int X(\tau, 0) \exp\{-U(\tau, 0)/\boldsymbol{k}T\} \mathrm{d}\tau}{\int \exp\{-U(\tau, 0)/\boldsymbol{k}T\} \mathrm{d}\tau} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

From eqns. (2) and (7)

$$_{\mathrm{m}}K = \frac{2\pi \boldsymbol{N}}{27} \left(\frac{\partial^2 \overline{\Pi^{(1)}(\tau, \mathsf{E}_0)}}{\partial E_0{}^2} \right)_{E_0 = 0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

which with eqn. (9) leads to

$$_{\mathrm{m}}K = \frac{2\pi \boldsymbol{N}}{27} \left\langle \frac{\partial^2 \Pi^{(1)}}{\partial E_0{}^2} - \frac{1}{\boldsymbol{k}T} \left(2 \frac{\partial \Pi^{(1)}}{\partial E_0} \frac{\partial U}{\partial E_0} + \Pi^{(1)} \frac{\partial^2 U}{\partial E_0{}^2} \right) + \frac{1}{\boldsymbol{k}^2 T^2} \Pi^{(1)} \left(\frac{\partial U}{\partial E_0} \right)^2 \right\rangle \quad (14)$$

whence, through eqn. (8),

$$_{\mathrm{m}}K = \frac{2\pi \boldsymbol{N}}{27} \left\langle \left\{ \frac{\partial^2 \pi_{\alpha\beta}{}^{(1)}}{\partial E_{0\gamma} \partial E_{0\delta}} + \frac{1}{\boldsymbol{k}T} \left(2 \frac{\partial \pi_{\alpha\beta}{}^{(1)}}{\partial E_{0\gamma}} M_\delta + \Pi_{\alpha\beta}{}^{(1)} \frac{\partial M_\gamma}{\partial E_{0\delta}} \right) + \frac{1}{\boldsymbol{k}^2 T^2} \pi_{\alpha\beta}{}^{(1)} M_\gamma M_\delta \right\} \left\{ e_\gamma{}^{\parallel} e_\delta{}^{\parallel} (e_\alpha{}^{\parallel} e_\beta{}^{\parallel} - e_\alpha{}^{\perp} e_\beta{}^{\perp}) \right\} \right\rangle \quad . \quad (15)$$

In averaging (15), we shall use the result [1] that when all directions of $\mathbf{e}^{\parallel}$ are equally likely (as when E_0 is zero)

$$\left\langle e_\gamma{}^{\parallel} e_\delta{}^{\parallel} (e_\alpha{}^{\parallel} e_\beta{}^{\parallel} - e_\alpha{}^{\perp} e_\beta{}^{\perp}) \right\rangle = (1/30)\{-2\delta_{\alpha\beta}\delta_{\gamma\delta} + 3\delta_{\alpha\gamma}\delta_{\beta\delta} + 3\delta_{\alpha\delta}\delta_{\beta\gamma}\} \quad . \quad . \quad (16)$$

so that (15) becomes

$$_{\mathrm{m}}K = \frac{2\pi \boldsymbol{N}}{405} \left\langle 2 \frac{\partial^3 m_\alpha{}^{(1)}}{\partial E_{0\alpha} \partial E_{0\beta} \partial E_{0\beta}} + \frac{4}{\boldsymbol{k}T} \frac{\partial^2 m_\alpha{}^{(1)}}{\partial E_{0\alpha} \partial E_{0\beta}} M_\beta + \frac{1}{\boldsymbol{k}T} \left\{ 3\pi_{\alpha\beta}{}^{(1)} \frac{\partial M_\alpha}{\partial E_{0\beta}} - \pi_{\alpha\alpha}{}^{(1)} \frac{\partial M_\beta}{\partial E_{0\beta}} \right\} + \frac{1}{\boldsymbol{k}^2 T^2} \left\{ 3\pi_{\alpha\beta}{}^{(1)} M_\alpha M_\beta - \pi_{\alpha\alpha}{}^{(1)} M_\beta M_\beta \right\} \right\rangle \quad (17)$$

Eqn. (17) is the complete classical statistical-mechanical formula for $_{\mathrm{m}}K$ and is the generalization of the perfect-gas result of Buckingham and Pople.[1]

Theory for the microscopic scale.

(a) *Non-polar Substances.*—For molecules with centres of inversion, μ_α and $\beta_{\alpha\beta\gamma}$ are zero, and to a good approximation eqn. (17) reduces to

$$
{}_{\mathrm{m}}K = \frac{2\pi N}{405}\left[2\gamma_{\alpha\alpha\beta\beta}{}^{(1)} + \frac{1}{kT}\sum_{i}^{N}\left\langle 3\alpha_{\alpha\beta}{}^{(1)}\alpha_{\alpha\beta}{}^{(0)(i)} - \alpha_{\alpha\alpha}{}^{(1)}\alpha_{\beta\beta}{}^{(0)(i)}\right\rangle\right] \quad . \quad . \quad (18)
$$

where $\alpha^{(1)}$ and $\gamma^{(1)}$ are polarizabilities for the frequency of the incident light, and $\alpha^{(0)}$ is a static field value; $\alpha^{(0)}$ may differ from α because of dispersion effects and atomic polarization. However, the frequency dependence of ${}_{\mathrm{m}}K$ is normally very small. In eqn. (18) terms in the cube of α and in $\alpha\gamma$ have been omitted, but these are normally unimportant. It has been shown [3] that eqn. (18) can be written in terms of the mean polarizabilities $\alpha = \frac{1}{3}\alpha_{\alpha\alpha}$ and $\alpha^{(0)}$ in the form

$$
\begin{aligned}
{}_{\mathrm{m}}K = \frac{2\pi N}{405}\Bigg[2\gamma_{\alpha\alpha\beta\beta}{}^{(1)} + \frac{3}{kT}\Bigg\{\sum_{s=1}^{3}\alpha_s\alpha_s{}^{(0)} - 3\alpha\alpha^{(0)} + {} \\
\sum_{s,t=1}^{3}\alpha_s\alpha_t{}^{(0)}\iint(\cos^2\theta_{st} - \tfrac{1}{3})n_2(\mathrm{r},\omega)\mathrm{d}\mathrm{r}\mathrm{d}\omega\Bigg\}\Bigg] \quad . \quad . \quad (19)
\end{aligned}
$$

where α_s and $\alpha_s{}^{(0)}$ are principal polarizabilities of a molecule in the oscillating and static fields, θ_{st} is the angle between the *s*-principal axis of molecule 1 and the *t*-principal axis of another molecule whose position and orientation are represented by (r, ω) relative to molecule 1 fixed at the origin, and where $n_2(\mathrm{r}, \omega)\mathrm{d}\mathrm{r}\mathrm{d}\omega$ is the probability of there being a molecule in the volume element dr and orientational element dω. For dipolar forces, the integral in eqn. (19) converges rapidly, there being no long-range contribution to $\langle\cos^2\theta_{st} - \frac{1}{3}\rangle$.

It is shown on p. 2350 that the integral in eqn. (19) is only about 0·001 for water, so that it is quite unimportant in this case. $\langle\cos^2\theta - \frac{1}{3}\rangle$ is in principle measurable through light-scattering experiments,[7] or through observations of magnetic double refraction,[8] but we shall assume that its contribution to ${}_{\mathrm{m}}K$ is negligible. Thus

$$
\begin{aligned}
{}_{\mathrm{m}}K &= A + B/T \\
&= \frac{2\pi N}{405}\left[2\gamma_{\alpha\alpha\beta\beta}{}^{(1)} + \frac{3}{kT}\left(\sum_{s=1}^{3}\alpha_s\alpha_s{}^{(0)} - 3\alpha\alpha^{(0)}\right)\right] \quad . \quad . \quad (20)
\end{aligned}
$$

where A and B are molecular constants. Equation (20) is the perfect-gas result, so that ${}_{\mathrm{m}}K$ for non-polar molecules should be nearly independent of density; this result was deduced earlier, and observations of the Kerr constants of non-polar substances over wide pressure ranges support the conclusion.[3]

The Langevin equation,[9] ${}_{\mathrm{m}}K = B/T$, omits the induced anisotropy term (the one in γ); as many of the principal polarizabilities α_s quoted in the literature are derived from this incomplete equation, they must be viewed with reservation until the importance of the γ term has been experimentally determined for a variety of substances. The magnitude of this term in the case of carbon disulphide may be obtained from Lyon and Wolfram's observations [10] of the temperature dependence of ${}_{\mathrm{m}}K$ in the liquid. The plot of ${}_{\mathrm{m}}K$ against $1/T$ shows that the γ term, obtained by extrapolation to $1/T = 0$, contributes about one quarter of the room-temperature value of ${}_{\mathrm{m}}K$ (see Figure). Again, the temperature dependence of ${}_{\mathrm{m}}K$ for mesitylene, measured by Grodde,[11] shows that the γ term is responsible for approximately one half of the observed ${}_{\mathrm{m}}K$ at room temperature.

[7] Benoit and Stockmayer, *J. Phys. Radium*, 1956, **17**, 21.
[8] Buckingham and Pople, *Proc. Phys. Soc.*, 1956, **69**, *B*, 1133.
[9] Langevin, *Le Radium*, 1910, **7**, 249.
[10] Lyon and Wolfram, *Ann. Physik*, 1920, **63**, 739.
[11] Grodde, *Physikal. Z.*, 1938, **39**, 772.

In applying eqn. (20) we shall, following Le Fèvre and Le Fèvre,[12] take $\alpha_s^{(0)}/\alpha_s = {}_{\mathrm{D}}P/{}_{\mathrm{E}}P$ where ${}_{\mathrm{D}}P$ and ${}_{\mathrm{E}}P$ are the distortion and electronic polarizations respectively (this assumption may sometimes be doubtful [4]). α is evaluated from $4\pi N\alpha/3 = {}_{\mathrm{E}}P$.

For molecules that are symmetric about the 1-axis, eqn. (20) becomes

$$ {}_{\mathrm{m}}K = \frac{2\pi N}{405}\left[2\gamma_{\alpha\alpha\beta\beta} + \frac{9}{2kT}\frac{{}_{\mathrm{D}}P}{{}_{\mathrm{E}}P}(\alpha_1 - \alpha)^2\right] \quad . \quad . \quad . \quad . \quad . \quad (21) $$

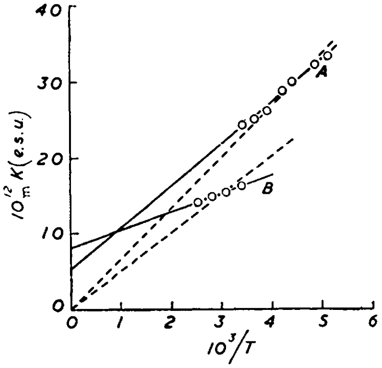
The results of calculations on data for carbon disulphide and mesitylene are shown in Table 1.

TABLE 1. *Principal polarizabilities.*

	Carbon disulphide			Mesitylene		
Principal polarizabilities	Calc. with ${}_{\mathrm{m}}K = A + B/T$	Calc. with ${}_{\mathrm{m}}K = B/T$	Previous values	Calc. with ${}_{\mathrm{m}}K = A + B/T$	Calc. with ${}_{\mathrm{m}}K = B/T$	Previous values
$10^{24}\alpha_1$ (cm.^{3})	12·1	12·5	13·9 [a]	12·8	11·6	12·5 [b]
$10^{24}\alpha_2 = \alpha_3$ (cm.^{3})	6·04	5·83	5·10 [a]	16·9	17·5	17·0 [b]
$10^{36}\gamma = 10^{36}\gamma_{\alpha\beta\beta\beta}/5$ (e.s.u.)	54·4	0	—	85·2	0	—

[a] Landolt–Börnstein Tabellen, 1951, **3**, 514, 515. [b] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261.

We have used, for carbon disulphide, ${}_{\mathrm{D}}P = 22{\cdot}7$ cm.^{3} and ${}_{\mathrm{E}}P = 20{\cdot}3$ cm.^{3}, and, for mesitylene, ${}_{\mathrm{D}}P = 41{\cdot}4$ cm.^{3} and ${}_{\mathrm{E}}P = 39{\cdot}2$ cm.^{3} (ref. *a*, Table 1).



A, Carbon disulphide.
B, Mesitylene.
Broken and full lines relate respectively to the exclusion and inclusion of the temperature-independent contribution to m*K*.

The agreement between the α_s values of Le Fèvre and Le Fèvre (ref. *b*, Table 1) and those found by us for mesitylene, using Grodde's data,[11] may be fortuitous, since the former were obtained through the application of the Langevin equation to dilute-solution measurements. However, γ should be as important in solutions as in a gas or pure liquid.

It may be noted that the graphs of ${}_{\mathrm{m}}K$ against $1/T$ for carbon disulphide and mesitylene are approximately linear, providing further justification for our neglect of $\langle\cos^2\theta - \frac{1}{3}\rangle$ in the derivation of eqn. (20).

(b) *Polar Substances.*—For polar substances, the final term in eqn. (17) will be important; in it we shall approximate $\pi_{\alpha\beta}$ by $\alpha_{\alpha\beta}$. By expressing $\alpha_{\alpha\beta}$ in terms of the principal components α_1, α_2, α_3 we find

$$ \left\langle 3\alpha_{\alpha\beta}^{(1)}M_\alpha M_\beta - \alpha_{\alpha\alpha}^{(1)}M^2 \right\rangle = 3\left\langle \sum_{s=1}^{3} \alpha_s M_s^2 - \alpha M^2 \right\rangle \quad . \quad . \quad . \quad (22) $$

If the molecule is symmetric about the 1-axis, then $\langle M_2^2\rangle = \langle M_3^2\rangle$; we shall suppose that this relation is also true for assemblies of molecules whose permanent moments lie

---

[12] Le Fèvre and Le Fèvre, *J.*, 1953, 4041.

along the principal axes of their polarizability ellipsoids, despite the possibility that α_2 may not be equal to α_3. Thus

$$\left\langle \sum_{s=1}^{3} \alpha_s M_s^2 - \alpha M^2 \right\rangle = (3/2)(\alpha_1 - \alpha)\left\langle M_1^2 - \tfrac{1}{3}M^2 \right\rangle = (3/2)(\alpha_1 - \alpha) f \qquad (23)$$

We shall evaluate $f\ (= \langle M_1^2 - \frac{1}{3}M^2 \rangle)$ by putting $\mathsf{M} = \sum_i \mathsf{m}^{(i)}$ and $M_1 = (1/\mu)\sum_i \boldsymbol{\mu}^{(1)} \cdot \mathsf{m}^{(i)}$. Thus

$$f = \frac{1}{\mu^2}\sum_i{}' \left\langle \boldsymbol{\mu}^{(1)} \cdot \mathsf{m}^{(i)} \boldsymbol{\mu}^{(1)} \cdot \mathsf{M} - \tfrac{1}{3}\mu^2 \mathsf{m}^{(i)} \cdot \mathsf{M} \right\rangle + \frac{1}{\mu^2}\sum_j{}'' \left\langle \boldsymbol{\mu}^{(1)} \cdot \mathsf{m}^{(j)} \boldsymbol{\mu}^{(1)} \cdot \mathsf{M} - \tfrac{1}{3}\mu^2 \mathsf{m}^{(j)} \cdot \mathsf{M} \right\rangle \quad (24)$$

where Σ' is a summation over molecule i and all those in short-range interaction with it (that is, those within a small macroscopic sphere centred on molecule 1), and Σ'' implies a sum over the remainder of the molecules. On writing $\mathsf{m}^{(i)} = \boldsymbol{\mu}^{(i)} + \mathsf{m}'^{(i)}$ and $\mathsf{M}' = \sum_i \mathsf{m}'^{(i)}$, and neglecting terms proportional to $(m')^2$ [that is, those of $0(\alpha^2)$], we obtain from eqn. (24)

$$f = \tfrac{2}{3}\left\langle \boldsymbol{\mu}^{(1)} \cdot (\mathsf{M} + \mathsf{M}') \right\rangle + \frac{1}{\mu^2} \sum_{i \neq 1}{}' \left\langle \left\{ \boldsymbol{\mu}^{(1)} \cdot \boldsymbol{\mu}^{(i)} \boldsymbol{\mu}^{(1)} - \tfrac{1}{3}\mu^2 \boldsymbol{\mu}^{(i)} \right\} \cdot \left\{ \mathsf{M} + \mathsf{M}' \right\} \right\rangle$$
$$+ \frac{1}{\mu^2}\sum_j{}'' \left\langle \left\{ \boldsymbol{\mu}^{(1)} \cdot \boldsymbol{\mu}^{(j)} \boldsymbol{\mu}^{(1)} - \tfrac{1}{3}\mu^2 \boldsymbol{\mu}^{(j)} \right\} \cdot \left\{ \mathsf{M} + \mathsf{M}' \right\} \right\rangle \quad . \quad (25)$$

To evaluate $\langle \boldsymbol{\mu}^{(1)} \cdot (\mathsf{M} + \mathsf{M}') \rangle$ we must know the mean value of $(\mathsf{M} + \mathsf{M}')$ when $\boldsymbol{\mu}^{(1)}$ is fixed, and, for terms of the type $\langle (\boldsymbol{\mu}^{(1)} \cdot \boldsymbol{\mu}^{(i)})(\boldsymbol{\mu}^{(1)} \cdot (\mathsf{M} + \mathsf{M}')) \rangle$, the mean value of $(\mathsf{M} + \mathsf{M}')$ when $\boldsymbol{\mu}^{(1)}$ and $\boldsymbol{\mu}^{(i)}$ are fixed. The problems involved are similar to those found in the general theory of the static dielectric constant ε, where $\langle \boldsymbol{\mu}^{(1)} \cdot (\mathsf{M} + \mathsf{M}') \rangle$ occurs.[13] The essential step is the replacement of the medium outside a sphere enclosing the fixed molecules and those in short-range interaction with them, by a continuum having the bulk properties of the specimen. Then, if $\mathsf{m}_{\text{av.}}\ (= (\sum_i{}' \mathsf{m}^{(i)})_{\text{av.}})$ is the mean dipole moment of this small macroscopic sphere, the average value of M is given by

$$\frac{9\varepsilon}{(2\varepsilon + 1)(\varepsilon + 2)}\,\mathsf{m}_{\text{av.}}$$

and that of M' by

$$\frac{3(2\varepsilon + \varepsilon_\infty)}{(2\varepsilon + 1)(\varepsilon_\infty + 2)}\,\mathsf{m}_{\text{av.}} - \boldsymbol{\mu}_{\text{av.}}$$

where $\boldsymbol{\mu}_{\text{av.}} (= (\sum_i{}' \boldsymbol{\mu}^{(i)})_{\text{av.}})$ is the mean " permanent " moment of the small sphere, and ε_∞ the high-frequency dielectric constant. Thus the mean of $(\mathsf{M} + \mathsf{M}')$ is

$$(\mathsf{M} + \mathsf{M}')_{\text{av.}} = \frac{6(\varepsilon^2 + 5\varepsilon + 2\varepsilon\varepsilon_\infty + \varepsilon_\infty)}{(2\varepsilon + 1)(\varepsilon + 2)(\varepsilon_\infty + 2)}\,\mathsf{m}_{\text{av.}} - \boldsymbol{\mu}_{\text{av.}} \quad . \quad . \quad . \quad (26)$$

With this result, the complete formula for f becomes

$$f = \tfrac{2}{3}\left[\frac{6(\varepsilon^2 + 5\varepsilon + 2\varepsilon\varepsilon_\infty + \varepsilon_\infty)}{(2\varepsilon + 1)(\varepsilon + 2)(\varepsilon_\infty + 2)}\,\boldsymbol{\mu} \cdot \bar{\mathsf{m}} - \boldsymbol{\mu} \cdot \bar{\boldsymbol{\mu}} \right] + \frac{1}{\mu^2} \sum_{i \neq 1}{}' \left\langle \left\{ \boldsymbol{\mu}^{(1)} \cdot \boldsymbol{\mu}^{(i)} \boldsymbol{\mu}^{(1)} \right.\right.$$
$$\left.\left. - \tfrac{1}{3}\mu^2 \boldsymbol{\mu}^{(i)} \right\} \cdot \left\{ \frac{6(\varepsilon^2 + 5\varepsilon + 2\varepsilon\varepsilon_\infty + \varepsilon_\infty)}{(2\varepsilon + 1)(\varepsilon + 2)(\varepsilon_\infty + 2)}\,\bar{\bar{\mathsf{m}}}^{(1i)} - \bar{\bar{\boldsymbol{\mu}}}^{(1i)} \right\} \right\rangle + \frac{1}{\mu^2}\sum_j{}'' \left\langle \left\{ \boldsymbol{\mu}^{(1)} \cdot \boldsymbol{\mu}^{(j)} \boldsymbol{\mu}^{(1)} \right.\right.$$
$$\left.\left. - \tfrac{1}{3}\mu^2 \boldsymbol{\mu}^{(j)} \right\} \cdot \left\{ \frac{6(\varepsilon^2 + 5\varepsilon + 2\varepsilon\varepsilon_\infty + \varepsilon_\infty)}{(2\varepsilon + 1)(\varepsilon + 2)(\varepsilon_\infty + 2)}\,(\bar{\mathsf{m}}^{(1)} + \bar{\mathsf{m}}^{(j)}) - (\bar{\boldsymbol{\mu}}^{(1)} + \bar{\boldsymbol{\mu}}^{(j)}) \right\} \right\rangle \quad (27)$$

---

[13] Buckingham, *Proc. Roy. Soc.*, 1956, *A*, **238**, 235.

where $\overline{\overline{\mathbf{m}}}^{(1i)}$ and $\overline{\overline{\boldsymbol{\mu}}}^{(1i)}$ are the mean total and " permanent " moments of a small macroscopic sphere surrounding the fixed molecules 1 and i when these are in short range interaction with each other; $\overline{\mathbf{m}}^{(j)}$ and $\overline{\boldsymbol{\mu}}^{(j)}$ refer to the average moments of the small sphere when molecule j only is fixed. Since [13]

$$\frac{3(\varepsilon-\varepsilon_{\infty})}{(\varepsilon+2)(\varepsilon_{\infty}+2)}=\frac{4\pi}{9kTV}\left\langle M^2\right\rangle=\frac{4\pi N}{9kTV}\left\{\frac{6(\varepsilon^2+5\varepsilon+2\varepsilon\varepsilon_{\infty}+\varepsilon_{\infty})}{(2\varepsilon+1)(\varepsilon+2)(\varepsilon_{\infty}+2)}\boldsymbol{\mu}\cdot\overline{\mathbf{m}}-\boldsymbol{\mu}\cdot\overline{\boldsymbol{\mu}}\right\} \quad (28)$$

eqn. (27) becomes

$$f=\frac{2(\varepsilon-\varepsilon_{\infty})}{(\varepsilon+2)(\varepsilon_{\infty}+2)}\frac{9kTV}{4\pi N}\left\{1+\sum_{j}{}''\left\langle\cos\theta^{(1j)}\right\rangle\right\}$$

$$+\frac{1}{\mu^2}\sum_{i\neq 1}{}'\left\langle\left\{\boldsymbol{\mu}^{(1)}\cdot\boldsymbol{\mu}^{(i)}\boldsymbol{\mu}^{(1)}-\tfrac{1}{3}\mu^2\boldsymbol{\mu}^{(i)}\right\}\cdot\left\{\frac{6(\varepsilon^2+5\varepsilon+2\varepsilon\varepsilon_{\infty}+\varepsilon_{\infty})}{(2\varepsilon+1)(\varepsilon+2)(\varepsilon_{\infty}+2)}\overline{\overline{\mathbf{m}}}^{(1i)}-\overline{\overline{\boldsymbol{\mu}}}^{(1i)}\right\}\right\rangle \quad (29)$$

Now

$$\sum_{j}{}''\left\langle\cos\theta^{(1j)}\right\rangle=\frac{1}{\mu^2}\left\langle\boldsymbol{\mu}^{(1)}\cdot(\mathbf{M}-\mathbf{M}'-\overline{\boldsymbol{\mu}}^{(1)})\right\rangle$$

$$=-\frac{6(\varepsilon-1)(\varepsilon-\varepsilon_{\infty})}{(2\varepsilon+1)(\varepsilon+2)(\varepsilon_{\infty}+2)}\frac{\boldsymbol{\mu}\cdot\overline{\mathbf{m}}}{\mu^2} \quad . \quad . \quad . \quad (30)$$

so that the general microscopic expression for f is

$$f=\frac{(\varepsilon-\varepsilon_{\infty})}{(\varepsilon+2)(\varepsilon_{\infty}+2)}\frac{9kTV}{2\pi N}\left\{1-\frac{6(\varepsilon-1)(\varepsilon-\varepsilon_{\infty})}{(2\varepsilon+1)(\varepsilon+2)(\varepsilon_{\infty}+2)}\frac{\boldsymbol{\mu}\cdot\overline{\mathbf{m}}}{\mu^2}\right\}$$

$$+\frac{1}{\mu^2}\sum_{i\neq 1}{}'\left\langle\left\{\boldsymbol{\mu}^{(1)}\cdot\boldsymbol{\mu}^{(i)}\boldsymbol{\mu}^{(1)}-\tfrac{1}{3}\mu^2\boldsymbol{\mu}^{(i)}\right\}\cdot\left\{\frac{6(\varepsilon^2+5\varepsilon+2\varepsilon\varepsilon_{\infty}+\varepsilon_{\infty})}{(2\varepsilon+1)(\varepsilon+2)(\varepsilon_{\infty}+2)}\overline{\overline{\mathbf{m}}}^{(1i)}-\overline{\overline{\boldsymbol{\mu}}}^{(1i)}\right\}\right\rangle \quad (31)$$

For polar substances, eqn. (17) can be expressed approximately in the form

$$_{\mathrm{m}}K=\frac{2\pi N}{405}\left[2\gamma_{\alpha\alpha\beta\beta}+\frac{4}{kT}\frac{9\varepsilon}{(2\varepsilon+1)(\varepsilon+2)}\beta_{\alpha\alpha\beta}\,\overline{\mathrm{m}}_{\beta}+\right.$$

$$\left.\frac{3}{kT}\left(\sum_{s=1}^{3}\alpha_s\alpha_s^{(0)}-3\alpha\alpha^{(0)}\right)+\frac{9}{2(kT)^2}(\alpha_1-\alpha)f\right] \quad . \quad . \quad (32)$$

where f is related to microscopic quantities by eqn. (31).

Application to Polar Substances.—We shall use Onsager's model [14] of a polar liquid to evaluate eqn. (32). As this model represents the immediate surroundings of a molecule by a continuum of dielectric constant ε it excludes all short range orientational forces. We may therefore neglect the second term of f in eqn. (31). Also, for this model

$$\mathbf{m}=\frac{(2\varepsilon+1)(\varepsilon_{\infty}+2)}{3(2\varepsilon+\varepsilon_{\infty})}\boldsymbol{\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

so that eqn. (31) becomes

$$f=\frac{27kTV}{2\pi N}\frac{\varepsilon(\varepsilon-\varepsilon_{\infty})}{(\varepsilon+2)^2(2\varepsilon+\varepsilon_{\infty})}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

The Kerr constant may now be written as

$$_{\mathrm{m}}K=\frac{2\pi N}{405}\left[2\gamma_{\alpha\alpha\beta\beta}+\frac{12}{kT}\frac{\varepsilon(\varepsilon_{\infty}+2)}{(\varepsilon+2)(2\varepsilon+\varepsilon_{\infty})}\beta_{\alpha\alpha\beta}\,\bar{\mu}_{\beta}+\right.$$

$$\left.\frac{3}{kT}\left(\sum_{s=1}^{3}\alpha_s\alpha_s^{(0)}-3\alpha\alpha^{(0)}\right)+\frac{9}{2(kT)^2}(\alpha_1-\alpha)f\right] \quad . \quad . \quad (35)$$

---

[14] Onsager, *J. Amer. Chem. Soc.*, 1936, **58**, 1486.

If we ignore the β and γ terms, and in the absence of reliable information about their magnitudes it is difficult to do otherwise, eqn. (35) reduces to

$${}_{\mathrm{m}}K = \frac{2\pi N}{135kT}\left[\sum_{s=1}^{3}\alpha_s\alpha_s^{(0)} - 3\alpha\alpha^{(0)} + \frac{3}{2kT}(\alpha_1 - \alpha)f\right] \quad . \quad . \quad . \quad (36)$$

For evaluating ${}_{\mathrm{m}}K$ at different temperatures through eqn. (36), we used eqn. (34), and in addition supposed that

$$\sum_{s=1}^{3}\alpha_s\alpha_s^{(0)} - 3\alpha\alpha^{(0)} = \tfrac{3}{2}(\alpha_1 - \alpha)(\alpha_1^{(0)} - \alpha^{(0)}) \quad . \quad . \quad . \quad . \quad . \quad (37)$$

which is precise for axially symmetric molecules. It is in principle possible to determine $(\alpha_1 - \alpha)$ and $\sum_{s=1}^{3}\alpha_s\alpha_s^{(0)} - 3\alpha\alpha^{(0)}$ in the general case through the constant for the gas ${}_{\mathrm{m}}K_{\mathrm{g}}$ and the dilute-solution value ${}_{\infty}({}_{\mathrm{m}}K_2)$, but this procedure is unnecessary, as the use of eqn. (37), together with the assumption that $\alpha_s^{(0)} = \alpha_s$, does not significantly affect the results; this is because both of these simplifications influence only the term of $0(\alpha^2)$ in eqn. (36).

We used the solution results to calculate $(\alpha_1 - \alpha)$ from

$${}_{\mathrm{m}}K = \frac{\pi N}{45kT}(\alpha_1 - \alpha)\left[(\alpha_1 - \alpha) + \frac{f}{kT}\right] \quad . \quad . \quad . \quad . \quad . \quad (38)$$

and [4]

$$f_{\mathrm{soln.}} = (2/3)\,{}_{\infty}\mu^2_{\mathrm{soln.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

(see Table 2). ${}_{\infty}\mu_{\mathrm{soln.}}$ is the apparent dipole moment of a polar solute molecule in a non-polar solvent at infinite dilution. We then compared the values of ${}_{\mathrm{m}}K_{\mathrm{g}}$, calculated from eqn. (38) with $f_{\mathrm{gas}} = 2\mu^2/3$, and ${}_{\mathrm{m}}K_{\mathrm{liq.}}$, calculated from eqns. (38) and (34), with the experimental results (see Tables 3 and 4).

TABLE 2. *Calculations of* $(\alpha_1 - \alpha)$ *from* ${}_{\infty}({}_{\mathrm{m}}K_2)$ *in* CCl_4 *at* 20°.

Substance	μ (D)	$\frac{{}_{\infty}\mu^2_{\mathrm{soln.}}}{\mu^2}$ [12]	$10^{12}\,{}_{\infty}({}_{\mathrm{m}}K_2)$ (e.s.u.) [12]	$10^{24}\,(\alpha_1 - \alpha)$ (cm.^{3})
$CHCl_3$	1·02	1·1	−28·5	$-1{\cdot}58_9$
$(CH_3)_2CO$	2·89	0·90	101	$0{\cdot}78_0$
$C_6H_5{\cdot}NO_2$	4·24	0·87	1073	$3{\cdot}94_9$
C_6H_5Cl	1·73	0·83	145	$3{\cdot}16_6$

TABLE 3. *Calculations of* ${}_{\mathrm{m}}K_{\mathrm{g}}$.

Substance	Temp.	$10^{12}\,{}_{\mathrm{m}}K_{\mathrm{g}}$ (e.s.u.) (Calc.)	$10^{12}\,{}_{\mathrm{m}}K_{\mathrm{g}}$ (e.s.u.) [15] (Obs.)
$CHCl_3$	89·5°	−16·4	−16·96
$(CH_3)_2CO$	83·1	76·0	69·47
$C_6H_5{\cdot}NO_2$	235·5	413	451·1
C_6H_5Cl	153·7	83·6	96·45

TABLE 4. *Calculations of* ${}_{\mathrm{m}}K_{\mathrm{liq.}}$ *for polar liquids.*

Substance	Temp.	$10^{12}\,{}_{\mathrm{m}}K_{\mathrm{liq.}}$ (e.s.u.) (Calc.)	$10^{12}\,{}_{\mathrm{m}}K_{\mathrm{liq.}}$ (e.s.u.) [12] (Obs.)
$CHCl_3$	25°	−16·9	−14·0
$(CH_3)_2CO$	20	8·31	8·33
$C_6H_5{\cdot}NO_2$	23	50·3	70·9
C_6H_5Cl	23·5	61·2	57·7

The observed values of ${}_{\mathrm{m}}K_{\mathrm{g}}$ are those of Stuart and Volkmann;[15] the agreement shown in Table 3 illustrates the consistency of the gas and the solution data, and justifies our use of the simplifications discussed in the previous paragraph.

The agreement in Table 4 between the calculated and observed values of ${}_{\mathrm{m}}K$ for polar liquids is satisfactory, for the unknown contributions of the β and γ terms were neglected and some of the approximations inherent in the Onsager model were used.

For highly polar anisotropic molecules, ${}_{\mathrm{m}}K_{\mathrm{g}}$ is dominated by the term proportional to T^{-2}. Hence for liquids consisting of molecules of this type, eqn. (38) yields

$$\frac{{}_{\mathrm{m}}K_{\mathrm{liq.}}}{{}_{\mathrm{m}}K_{\mathrm{g}}} = \frac{3kT}{2\mu^2}(\alpha_1 - \alpha) + \frac{81kTV}{4\pi N\mu^2}\,\frac{\varepsilon(\varepsilon - \varepsilon_\infty)}{(\varepsilon + 2)^2(2\varepsilon + \varepsilon_\infty)} \quad . \quad . \quad . \quad (40)$$

Eqn. (40) can be put into a form similar to an expression deduced by Klages,[2] by means of the assumption that μ is related to ε by the Onsager relation

$$\frac{4\pi N\mu^2}{9kTV} = \frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

The second term in eqn. (40) then becomes $\left[\dfrac{3\varepsilon(\varepsilon_\infty + 2)}{(\varepsilon + 2)(2\varepsilon + \varepsilon_\infty)}\right]^2$ which is Klages's result.

Application to Water.—In applying the theory for polar substances to water, we shall employ the Pople model[16] of the structure of water to evaluate the short-range interaction terms in eqn. (31). In this model a water molecule influences, through hydrogen bonding, its neighbours in the first three shells only, and these contain approximately 4, 11, and 22 molecules. Thus our macroscopic sphere containing all short-range effects consists of a central molecule and its first three shells of neighbours.

$\boldsymbol{\mu} \cdot \bar{\mathrm{m}}$ in eqn. (31) may be expressed through eqn. (28) in terms of $\boldsymbol{\mu} \cdot \bar{\boldsymbol{\mu}}$, which was evaluated by Pople.[16] We shall write

$$\frac{\boldsymbol{\mu} \cdot \bar{\boldsymbol{\mu}}}{\mu^2} = g = \sum_i{}' \left\langle \cos \theta^{(1i)} \right\rangle \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

To evaluate the second term in eqn. (31), we use the Onsager result (33). This is believed to be a good approximation for water.[13] Thus

$$\sum_{i \neq 1}{}' \left\langle \left\{ \boldsymbol{\mu}^{(1)} \cdot \boldsymbol{\mu}^{(i)}\boldsymbol{\mu}^{(1)} - \tfrac{1}{3}\mu^2\boldsymbol{\mu}^{(i)} \right\} \cdot \left\{ \frac{6(\varepsilon^2 + 5\varepsilon + 2\varepsilon\varepsilon_\infty + \varepsilon_\infty)}{(2\varepsilon + 1)(\varepsilon + 2)(\varepsilon_\infty + 2)} \bar{\bar{\mathrm{m}}}^{(1i)} - \bar{\bar{\boldsymbol{\mu}}}^{(1i)} \right\} \right\rangle$$

$$= \frac{3\varepsilon(\varepsilon_\infty + 2)}{(\varepsilon + 2)(2\varepsilon + \varepsilon_\infty)} \sum_{i \neq 1}{}' \left\langle \boldsymbol{\mu}^{(1)} \cdot \boldsymbol{\mu}^{(i)}\boldsymbol{\mu}^{(1)} \cdot \bar{\bar{\boldsymbol{\mu}}}^{(1i)} - \tfrac{1}{3}\mu^2\boldsymbol{\mu}^{(i)} \cdot \bar{\bar{\boldsymbol{\mu}}}^{(1i)} \right\rangle \quad . \quad . \quad (43)$$

and

$$\sum_{i \neq 1}{}' \left\langle \boldsymbol{\mu}^{(1)} \cdot \boldsymbol{\mu}^{(i)}\boldsymbol{\mu}^{(1)} \cdot \bar{\bar{\boldsymbol{\mu}}}^{(1i)} - \tfrac{1}{3}\mu^2\boldsymbol{\mu}^{(i)} \cdot \bar{\bar{\boldsymbol{\mu}}}^{(1i)} \right\rangle = \mu^4 \sum_{i \neq 1}{}' \left[\tfrac{2}{3}\left\langle \cos \theta^{(1i)} \right\rangle + \left\langle \cos^2 \theta^{(1i)} - \tfrac{1}{3} \right\rangle \right.$$

$$\left. + \sum_{j \neq 1, i}{}' \left\langle \cos \theta^{(1i)} \cos \theta^{(1j)} - \tfrac{1}{3} \cos \theta^{(ij)} \right\rangle \right] \quad . \quad . \quad . \quad (44)$$

Now

$$\sum_{i \neq 1}{}' \left[\tfrac{2}{3}\left\langle \cos \theta^{(1i)} \right\rangle + \left\langle \cos^2 \theta^{(1i)} - \tfrac{1}{3} \right\rangle \right] =$$

$$\tfrac{2}{3}\sum_{K=1}^{3} N^{(K)} \left\langle \cos \theta_K{}^{(12)} \right\rangle + \sum_{K=1}^{3} N^{(K)} \left\langle \cos^2 \theta_K{}^{(12)} - \tfrac{1}{3} \right\rangle \quad . \quad . \quad (45)$$

where $N^{(K)}$ is the number of molecules in the K-th shell, and $\theta_K{}^{(12)}$ is the angle between the permanent dipoles of molecule 1 and molecule 2 in the K-th shell around 1.

---

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

[16] Pople, *Proc. Roy. Soc.*, 1951, *A*, **205**, 163.

The averages in eqn. (45) have been evaluated for Pople's model and are

$$\left\langle \cos \theta_K^{(12)} \right\rangle = 3^{1-K} \cos^{2K} \frac{\beta}{2} \left[1 - \frac{kT}{G} \right]^{2K} \quad . \quad . \quad . \quad . \quad (46)$$

$$\left\langle \cos^2 \theta_1^{(12)} \right\rangle = \left[\tfrac{3}{2} \cos^4 \frac{\beta}{2} - \cos^2 \frac{\beta}{2} \right] \left[1 - \frac{3kT}{G} \left(1 - \frac{kT}{G} \right) \right]^2$$
$$+ \tfrac{1}{2} \left[1 - \frac{2kT}{G} \left(1 - \frac{kT}{G} \right) + 3 \left\{ \frac{kT}{G} \left(1 - \frac{kT}{G} \right) \right\}^2 \right] \quad . \quad . \quad . \quad (47)$$

$$\left\langle \cos^2 \theta_2^{(12)} \right\rangle = \tfrac{1}{2} - \left\langle \cos^2 \theta_1^{(12)} \right\rangle + \tfrac{3}{2} \left(\left\langle \cos^2 \theta_1^{(12)} \right\rangle \right)^2 \quad . \quad . \quad . \quad . \quad (48)$$

$$\left\langle \cos^2 \theta_3^{(12)} \right\rangle = \tfrac{9}{4} \left(\left\langle \cos^2 \theta_1^{(12)} \right\rangle \right)^3 - \tfrac{9}{4} \left(\left\langle \cos^2 \theta_1^{(12)} \right\rangle \right)^2 + \tfrac{3}{4} \left\langle \cos^2 \theta_1^{(12)} \right\rangle + \tfrac{1}{4} \quad (49)$$

where β is the observed value of the H–O–H angle, 105° (β is also the angle between the lone-pair orbitals), and G is a temperature-dependent constant, chosen by Pople to give agreement between the theoretical and experimental radial distribution functions.

For the approximate evaluation of $\langle \cos \theta^{(1i)} \cos \theta^{(1j)} - \tfrac{1}{3} \cos \theta^{(ij)} \rangle$ in eqn. (44) we shall consider only first neighbours of molecules 1 and i. When molecule j belongs to the same shell as i (relative to molecule 1), then the last term of eqn. (44) vanishes. Thus it can be shown that for this model

$$\sum_{i \neq 1}' \sum_{j \neq 1, i}' \left\langle \cos \theta^{(1i)} \cos \theta^{(1j)} - \tfrac{1}{3} \cos \theta^{(ij)} \right\rangle = \sum_{i \neq 1}' \sum_{j \neq 1, i}' \left\langle \cos \theta^{(ij)} \right\rangle \left\langle \cos^2 \theta^{(1i)} - \tfrac{1}{3} \right\rangle \quad (50)$$

where i and j are summed over molecules in the first and second shells respectively.

The contribution at 0° C to eqn. (44) of each of its terms is shown as follows :

	Shell 1	Shell 2	Shell 3
$N^{(K)} \left\langle \cos \theta_K^{(12)} \right\rangle$	1·201	0·330	0·067
$N^{(K)} \left\langle \cos^2 \theta_K^{(12)} - \tfrac{1}{3} \right\rangle$	$4{\cdot}4 \times 10^{-3}$	2×10^{-5}	3×10^{-7}
$\sum_{i \neq 1}' \sum_{j \neq 1, i}' \left\langle \cos \theta^{(1i)} \cos \theta^{(1j)} - \tfrac{1}{3} \cos \theta^{(ij)} \right\rangle$	5×10^{-3}	—	

(We have used $G/kT = 10$, as found by Pople for 0°.)

We note that $\sum_{i \neq 1}' \left\langle \cos^2 \theta^{(1i)} - \tfrac{1}{3} \right\rangle$ and $\sum_{i \neq 1}' \sum_{j \neq 1, i}' \left\langle \cos \theta^{(1i)} \cos \theta^{(1j)} - \tfrac{1}{3} \cos \theta^{(ij)} \right\rangle$ are together less than 1% of $\tfrac{2}{3} \sum_{i \neq 1}' \left\langle \cos \theta^{(1i)} \right\rangle$ for water at 0°, and may therefore reasonably be neglected. (Some further justification for our neglect of $\iint (\cos^2 \theta_{st} - \tfrac{1}{3}) n_2(\mathrm{r}, \omega) d\mathrm{r}\, d\omega$ in the derivation of eqn. (20) is provided by these calculations for water.)

Thus eqn. (43) becomes

$$\frac{3\varepsilon(\varepsilon_\infty + 2)}{(\varepsilon + 2)(2\varepsilon + \varepsilon_\infty)} \sum_{i \neq 1}' \left\langle \boldsymbol{\mu}^{(1)} \cdot \boldsymbol{\mu}^{(i)} \boldsymbol{\mu}^{(1)} \cdot \overline{\overline{\boldsymbol{\mu}}}{}^{(1i)} - \tfrac{1}{3} \mu^2 \boldsymbol{\mu}^{(i)} \cdot \overline{\overline{\boldsymbol{\mu}}}{}^{(1i)} \right\rangle$$
$$= \frac{2\varepsilon(\varepsilon_\infty + 2)}{(\varepsilon + 2)(2\varepsilon + \varepsilon_\infty)} \mu^4 (g - 1) \quad . \quad . \quad (51)$$

Hence for water, eqn. (31) is given approximately by

$$f = \frac{9kTV}{2\pi N} \frac{(\varepsilon - \varepsilon_\infty)}{(\varepsilon + 2)(\varepsilon_\infty + 2)} \left[1 - \frac{6(\varepsilon - 1)(\varepsilon - \varepsilon_\infty)}{(2\varepsilon + 1)(\varepsilon + 2)(\varepsilon_\infty + 2)} \frac{\boldsymbol{\mu} \cdot \overline{\mathrm{m}}}{\mu^2} \right]$$
$$+ \frac{2\varepsilon(\varepsilon_\infty + 2)}{(\varepsilon + 2)(2\varepsilon + \varepsilon_\infty)} \mu^2 (g - 1) \quad . \quad . \quad (52)$$

In the absence of data on hyperpolarizability, we shall approximate the expression for the Kerr constant to

$$_{\mathrm{m}}K = \frac{\pi N}{45(kT)^2}(\alpha_1 - \alpha)f \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

We have omitted terms in higher powers of the polarizability, but this should be reasonable for water with its small value for α. From eqn. (53) we can predict the value of $_{\mathrm{m}}K$ for water at a given temperature in terms of its value $_{\mathrm{m}}K_0$ at 0°; the results are shown in Table 5. We have taken μ to be 1·84 D. The ε values are those of Wyman and Ingalls,[17] and the g's are Pople's. Unfortunately there are at present no data to test our predictions.

TABLE 5. *Temperature dependence of* $_{\mathrm{m}}K_{\mathrm{liq.}}$ *for water.*

Temp.	V_{m} (cm.^{3})	ε	ε_∞	g	$10^{37}<M_1^2 - M^2/3>$ (e.s.u.)	$_{\mathrm{m}}K_{\mathrm{T}}/_{\mathrm{m}}K_0$
0°	18·02	88·2	$1{\cdot}79_7$	2·60	$-3{\cdot}66_9$	1·000
25	18·07	78·5	$1{\cdot}79_5$	2·55	$-3{\cdot}71_8$	0·851
62	18·34	66·4	$1{\cdot}78_0$	2·49	$-3{\cdot}82_2$	0·692
83	18·58	60·4	$1{\cdot}76_7$	2·46	$-3{\cdot}87_4$	0·621

One of us (A. D. B.) thanks the Commissioners for the Exhibition of 1851 for a Senior Studentship, and the other is indebted to the Rhodes Trustees for a Scholarship.

THE PHYSICAL CHEMISTRY LABORATORY,
UNIVERSITY OF OXFORD.

[*Received, October* 22*nd*, 1956.]

---

[17] Wyman and Ingalls, *J. Amer. Chem. Soc.*, 1938, **60**, 1182.