

ON THE DETERMINATION OF THE OCTOPOLE MOMENT OF TETRAHEDRAL MOLECULES FROM INVESTIGATION OF THE SECOND VIRIAL COEFFICIENTS

BY STANISŁAW KIELICH

Polish Academy of Sciences, Institute of Physics, Poznań*

(Received March 19, 1963)

The possibilities are discussed of deriving information on the value of the octopole moment of tetrahedral molecules from the investigation of the second virial coefficients of the equation of state for a gas or gas mixture, the dielectric polarization, the molecular refraction, the molecular scattering of light and the molecular Kerr and Cotton-Mouton constants. The respective coefficients are computed for the general case of molecules of different kinds and the results contain various contributions from molecular interactions of the octopole and mixed types (*e.g.* octopole-dipole, octopole-quadrupole *etc.*). Some of the expressions derived contain, in addition to the octopole moment Ω , the hyperpolarizabilities β, γ and ξ , which it will be possible to determine once the appropriate experimental data become available. Numerical evaluation for methane leads to reasonable values of the octopole moment for the CH_4 molecule.

1. Introduction

Molecules of the CR_4 type, where R is an atom (*e.g.* H, Cl, F, J) or a not very large group of atoms (CH_3, NO_2), possess the tetrahedral symmetry. They can be said to have the form of a regular tetrahedron whose corners are occupied by the four atoms R whereas the carbon atom is situated at its centre, being tied to the atoms R by single bonds. Tetrahedral molecules present neither a dipole nor a quadrupole electric moment; the first moment they are able to present is octopolar and is given, quite generally, by the tensor $\Omega_{\alpha\beta\gamma}$, wherein $\alpha, \beta, \gamma = x, y, z$. Of the 27 components of $\Omega_{\alpha\beta\gamma}$ in the general case, only the 6 equal components Ω_{xyz} remain in the case of the tetrahedral symmetry, the axes x, y, z being oriented parallel to the sides of the cube having atoms R in four of its corners.

Although the octopole moments of molecules can be computed directly, this is by no means a practicable procedure in all cases; this is why indirect information on their values,

* Address: Zakład Dielektryków PAN, Poznań, ul. Grunwaldzka 6, Polska

to be gleaned from the knowledge of various experimentally measurable quantities, is of great importance. In the first place, such information is to be derived from effects wherein molecular interactions of the octopole kind are pronouncedly apparent. Thus, if Q be a quantity characterizing appropriately chosen measurable variables of a real gas of molar volume V , the following virial expansion can be written according to Buckingham and Pople [1]:

$$Q = A_Q + \frac{B_Q}{V} + \frac{C_Q}{V^2} + \dots, \quad (1)$$

where A_Q is the first virial coefficient of the quantity Q describing the properties of a gas consisting of non-interacting molecules (perfect gas). The second virial coefficient B_Q accounts for pairwise interaction; the third and subsequent coefficients are due to multiple interactions, and will not be dealt with here. Thus, the experimentally measured deviations of the respective properties of a real gas from those of the perfect gas are due to molecular interactions and, in the range of not excessively high pressures, are essentially described by B_Q .

The expansion of Eq. (1) can be used for investigating the second virial coefficients B_Q of measurable properties of gases consisting of tetrahedral molecules; hence, in turn, information can be obtained concerning the octopole moments of the latter. The first to do this were Johnston, Oudemans and Cole [2], who computed theoretically and measured experimentally the second dielectric virial coefficient B_D for methane and determined the octopole moment of the CH_4 molecule. Similar information can also be derived from the investigation of the molecular dielectric polarization of gas mixtures consisting of unlike tetrahedral molecules [3]. In checking the information obtained in dielectric investigation, one can recur to molecular refraction measurements, applying Buckingham's theory [4] of the second refractivity virial coefficient B_R to gases consisting of tetrahedral molecules or to mixtures of such gases [3, 5]. Moreover, molecular interactions are apparent in the effect of molecular light scattering in real gases [6, 7, 8], in Kerr's effect [9] and in that of Cotton-Mouton [10]. Research on the second virial coefficient of the last two effects in the case of tetrahedral molecules can provide additional information about their octopole moments and, moreover, about their hyperpolarizabilities.

It is a well-known fact that investigation of the second virial coefficient $B(T)$ appearing in the equation of state of real gases provides a sure and unfailing method of collecting information on the nature and magnitude of the forces acting between the molecules, and on various molecular parameters. Accordingly, the present paper brings the calculation of certain contributions to $B^{(ij)}$ from interactions of the octopole-octopole, octopole-induced dipole, octopole-quadrupole and octopole-dipole types. The respective expressions thus derived allow to evaluate numerically the octopole moment of a tetrahedral molecule with relative ease, as will be demonstrated in the case of the CH_4 molecule. Moreover, we give a discussion of the second virial coefficients of dielectric polarization, molecular refraction, molecular light scattering and the molecular constants of Kerr and Cotton-Mouton; it is found that additional information concerning the octopole moment and hyperpolarizabilities of tetrahedral molecules can be obtained along these lines. All computations are carried out for molecules of various species so as to be applicable to mixtures of real gases.

2. Contributions of the octopole and mixed types to the second virial coefficient $B(T)$

In the case of central forces, when the potential energy of two molecules p and q depends solely on the distance r_{pq} between them, the second virial coefficient of the equation of state for real gases is given as follows [11]:

$$B_{\text{centr}}^{(ij)} = -2\pi N \int_0^{\infty} \left\{ e^{-\frac{u_{ij}(r_{pq})}{kT}} - 1 \right\} r_{pq}^2 dr_{pq}; \quad (2)$$

herein, $u_{ij}(r_{pq})$ is the potential energy of central interaction between the molecule p of species i and the molecule q of species j ; N is Avogadro's number, k — Boltzmann's constant and T — the absolute temperature.

In order to compute effectively the quantity $B_{\text{centr}}^{(ij)}$, we have to know the law according to which the forces of attraction and repulsion between the molecules vary with the distance r_{pq} . The most commonly employed central forces' potential is that of Lennard-Jones — particularly in its very convenient special form

$$u_{ij}(r_{pq}) = 4\varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{pq}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{pq}} \right)^6 \right\}, \quad (3)$$

where ε_{ij} and σ_{ij} have the dimensions of an energy and distance, respectively, and are constants characteristic of the species of the interacting molecules. With (3), Eq. (2) yields

$$B_{\text{centr}}^{(ij)} = -\frac{2}{3} \pi N \sigma_{ij}^3 F(y_{ij}) = b_{ij} F(y_{ij}), \quad (4)$$

where $F(y_{ij})$ is a function tabulated in the monograph by Hirschfelder *et al.* [11]; $y_{ij} = 2(\varepsilon_{ij}/kT)^{\frac{1}{2}}$.

In the case of a gas consisting of more complex molecules, the potential $u_{ij}(r_{pq})$ contains additionally the energy of non-central interaction $v_{ij}(r_{pq}, \omega_p, \omega_q)$ dependent on the distance and on the orientation of the molecules, ω_p and ω_q . If we assume with Pople [12] that $v_{ij}(r_{pq}, \omega_p, \omega_q)$ constitutes a perturbation of $u_{ij}(r_{pq})$, the quantity $B_{\text{centr}}^{(ij)}$ defined by (2) will contain additional contributions

$$B_{\text{non-centr}}^{(ij)} = -\frac{N}{2} \sum_{n=1}^{\infty} \frac{1}{n!} \left(-\frac{1}{kT} \right)^n \langle v_{ij}^n \rangle_{ij} \quad (5)$$

resulting from the presence of non-central forces (angular or tensorial), with

$$\langle v_{ij}^n \rangle = \frac{\iiint \{v_{ij}(r_{pq}, \omega_p, \omega_q)\}^n e^{-\frac{u_{ij}(r_{pq})}{kT}} dr_{pq} d\omega_p d\omega_q}{\iint d\omega_p d\omega_q}. \quad (6)$$

For the case of dipolar or quadrupolar gases, contributions (5) are discussed in a number of papers [11, 12, 13, 14] and, for mixtures of polar gases, in [15]; here, we shall compute them for octopolar gases, in particular for ones consisting of tetrahedral molecules or their mixtures with other gases.

Mixture of tetrahedral molecules. Consider a real gas consisting of unlike molecules presenting a permanent octopole moment given by the tensor $\Omega_{\alpha\beta\gamma}$ and polarizability given by the tensor $\alpha_{\alpha\beta}$. The potential energy of tensorial interaction of two of these molecules can be expressed as follows [10]:

$$v_{ij}(r_{pq}, \omega_p, \omega_q) = \frac{1}{225} \Omega_{\alpha\beta\gamma}^{(pi)} T_{\alpha\beta\gamma\delta\epsilon\eta}^{(pq)} \Omega_{\delta\epsilon\eta}^{(qj)} - \frac{1}{450} (\alpha_{\alpha\beta}^{(pi)} \Omega_{\gamma\delta\epsilon}^{(qj)} \Omega_{\eta\theta\chi}^{(qj)} + \alpha_{\alpha\beta}^{(qj)} \Omega_{\gamma\delta\epsilon}^{(pi)} \Omega_{\eta\theta\chi}^{(pi)}) T_{\alpha\gamma\delta\epsilon}^{(pq)} T_{\beta\eta\theta\chi}^{(pq)} - \dots, \quad (7)$$

herein, the first term accounts for the energy of octopole-octopole interaction and the second — for octopole-induced dipole interaction. The tensors $\alpha_{\alpha\beta}^{(pi)}$ and $\Omega_{\alpha\beta\gamma}^{(pi)}$ are those of the p -th molecule of species i .

On substituting (7) in Eq. (5), we obtain the two principal contributions to the second virial coefficient resulting, respectively, from octopole-induced dipole and octopole-octopole interaction:

$$B_{\text{octop-ind.dip}}^{(ij)} = - \frac{2N}{5kT} \{ \alpha_i \Omega_{\alpha\beta\gamma}^{(j)} \Omega_{\alpha\beta\gamma}^{(j)} + \alpha_j \Omega_{\alpha\beta\gamma}^{(i)} \Omega_{\alpha\beta\gamma}^{(i)} \} \langle r_{pq}^{-10} \rangle_{ij}, \quad (8)$$

$$B_{\text{octop-octop}}^{(ij)} = - \frac{132N}{175k^2T^2} \Omega_{\alpha\beta\gamma}^{(i)} \Omega_{\alpha\beta\gamma}^{(i)} \Omega_{\delta\epsilon\eta}^{(j)} \Omega_{\delta\epsilon\eta}^{(j)} \langle r_{pq}^{-14} \rangle_{ij}, \quad (9)$$

where $\alpha_i = \frac{1}{3} \alpha_{\alpha\alpha}^{(i)}$ is the mean polarizability of the isolated molecule of species i .

For tetrahedral molecules, the tensor of the octopole moment $\Omega_{\alpha\beta\gamma}$ is expressed as follows:

$$\Omega_{\alpha\beta\gamma} = \Omega_{xyz} \{ i_\alpha (j_\beta k_\gamma + j_\gamma k_\beta) + j_\alpha (k_\beta i_\gamma + k_\gamma i_\beta) + k_\alpha (i_\beta j_\gamma + i_\gamma j_\beta) \}, \quad (10)$$

wherein $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are unit vectors along the axes x, y, z of the system of reference attached to the molecule. Since here $\Omega_{\alpha\beta\gamma} \Omega_{\alpha\beta\gamma} = 6\Omega_{xyz}^2 \equiv 6\Omega^2$, the expressions of (8) and (9) become

$$B_{\text{octop-ind.dip}}^{(ij)} = - \frac{12N}{5kT} \{ \alpha_i \Omega_j^2 + \Omega_i^2 \alpha_j \} \langle r_{pq}^{-10} \rangle_{ij}, \quad (11)$$

$$B_{\text{octop-octop}}^{(ij)} = - \frac{4752N}{175k^2T^2} \Omega_i^2 \Omega_j^2 \langle r_{pq}^{-14} \rangle_{ij}. \quad (12)$$

Eq. (12) is analogous to the result derived by Parsonage and Scott [16] for the free energy of a liquid mixture.

Assuming, in order to simplify our computations, that the energy of central interaction of the tetrahedral molecules is given by the Lennard-Jones potential in the form (3), we have by Eqs. (11) and (12)

$$B_{\text{octop-ind.dip}}^{(ij)} = - \frac{3b_{ij}}{10y_{ij}^2} \left\{ \left(\frac{\alpha_i}{\sigma_{ij}^3} \right) \left(\frac{\Omega_j^2}{\sigma_{ij}^7 \epsilon_{ij}} \right) + \left(\frac{\Omega_i^2}{\sigma_{ij}^7 \epsilon_{ij}} \right) \left(\frac{\alpha_j}{\sigma_{ij}^3} \right) \right\} H_{10}(y_{ij}), \quad (13)$$

$$B_{\text{octop-octop}}^{(ij)} = - \frac{297}{350} b_{ij} \left(\frac{\Omega_i^2}{\sigma_{ij}^7 \epsilon_{ij}} \right) \left(\frac{\Omega_j^2}{\sigma_{ij}^7 \epsilon_{ij}} \right) H_{14}(y_{ij}), \quad (14)$$

where the H_n are functions introduced by Pople [12] and tabulated in [14].

Mixture of an atomic gas and of one consisting of tetrahedral molecules. The results derived above can be applied immediately to the case of a two-component gas wherein the one component consists of atoms with polarizability α_1 and the other consists of tetrahedral molecules with polarizability α_2 and octopole moment Ω_2 . If x_1 and x_2 denote the molar fractions of the components, the second virial coefficient of the mixture is given by

$$B_m = x_1^2 B^{(11)} + 2x_1 x_2 B^{(12)} + x_2^2 B^{(22)}, \quad (15)$$

where the virial coefficients $B^{(11)}$ and $B^{(22)}$ of the pure components and $B^{(12)}$ accounting for interaction between an atom and a tetrahedral molecule, by (4), (13) and (14), are of the form

$$B^{(11)} = b_{11} F(y_{11}), \quad (16)$$

$$B^{(12)} = b_{12} \left\{ F(y_{12}) - \frac{3}{10y_{12}^2} \left(\frac{\alpha_1}{\sigma_{12}^3} \right) \left(\frac{\Omega_2^2}{\sigma_{12}^7 \epsilon_{12}} \right) H_{10}(y_{12}) \right\}, \quad (17)$$

$$B^{(22)} = b_{22} \left\{ F(y_{22}) - \frac{3}{5y_{22}^2} \left(\frac{\Omega_2^2}{\sigma_{22}^7 \epsilon_{22}} \right) \left[\left(\frac{\alpha_2}{\sigma_{22}^3} \right) H_{10}(y_{22}) + \frac{99}{70} y_{22}^2 \left(\frac{\Omega_2^2}{\sigma_{22}^7 \epsilon_{22}} \right) H_{14}(y_{22}) \right] \right\}. \quad (18)$$

Mixture of quadrupolar molecules and tetrahedral molecules. We shall now consider a mixture whose one component is a gas of quadrupolar molecules and the other — a gas consisting of octopolar molecules. In the present case, the coefficient $B^{(11)}$ is that of the quadrupolar component and is to be found in [12, 14, 15], whilst $B^{(22)}$, relating to the tetrahedral molecules, is the same as in Eq. (18). Thus, the only quantity remaining to be computed is $B^{(12)}$, the coefficient accounting for the interaction between a quadrupolar and an octopolar molecule as described (neglecting anisotropy of the forces of dispersion) by the potential

$$v_{12} = \frac{1}{45} \Theta_{\alpha\beta}^{(p1)} \Omega_{\gamma\delta\epsilon}^{(q2)} T_{\alpha\beta\gamma\delta\epsilon}^{(pq)} - \frac{1}{18} \alpha_{\alpha\beta}^{(q2)} \Theta_{\gamma\delta}^{(p1)} \Theta_{\epsilon\eta}^{(p1)} T_{\alpha\gamma\delta}^{(pq)} T_{\beta\epsilon\eta}^{(pq)} - \dots \quad (19)$$

Herein, the first term represents the energy of interaction between the quadrupole $\Theta_{\alpha\beta}^{(p1)}$ of the p -th molecule of species 1 and the octopole $\Omega_{\alpha\beta\gamma}^{(q2)}$ of the q -th molecule of species 2, whereas the second term represents the energy of interaction between the quadrupole $\Theta_{\alpha\beta}^{(p1)}$ and the dipole moment induced by this quadrupole in the octopolar molecule.

By (19), Eq. (5) yields

$$B_{\text{non-centr}}^{(12)} = -\frac{N}{2kT} \Theta_{\alpha\beta}^{(1)} \Theta_{\alpha\beta}^{(1)} \left\{ \alpha_2 \langle r_{pq}^{-8} \rangle_{12} + \frac{4}{5kT} \Omega_{\gamma\delta\epsilon}^{(2)} \Omega_{\gamma\delta\epsilon}^{(2)} \langle r_{pq}^{-12} \rangle_{12} \right\}. \quad (20)$$

In particular, if the quadrupolar molecules present the axial symmetry *i.e.* if the tensor $\Theta_{\alpha\beta}$ is of the form [17]

$$\Theta_{\alpha\beta} = \frac{1}{2} \Theta (3k_\alpha k_\beta - \delta_{\alpha\beta}), \quad (21)$$

and if the octopolar molecules are tetrahedral with octopole moment given by Eq. (10), we have by (20)

$$B_{\text{non-centr}}^{(12)} = -\frac{3\Theta_1^2 N}{4kT} \left\{ \alpha_2 \langle r_{pq}^{-8} \rangle_{12} + \frac{24}{5kT} \Omega_2^2 \langle r_{pq}^{-12} \rangle_{12} \right\}, \quad (22)$$

wherein $\Theta_1 = \Theta_{zz}^{(1)}$ is the quadrupolar moment of a molecule symmetric with respect to the z -axis of the molecular coordinate system.

For the case of a 6-12 Lennard-Jones potential, Eq. (22) accounting for interaction between the quadrupolar and the tetrahedral molecule assumes the form

$$B_{\text{non-centr}}^{(12)} = - \frac{3b_{12}}{32\gamma_{12}^2} \left(\frac{\Theta_1^2}{\sigma_{12}^5 \epsilon_{12}} \right) \left\{ \left(\frac{\alpha_2}{\sigma_{12}^3} \right) H_8(\gamma_{12}) + \frac{6}{5} \gamma_{12}^2 \left(\frac{\Omega_2^2}{\sigma_{12}^7 \epsilon_{12}} \right) H_{12}(\gamma_{12}) \right\}. \quad (23)$$

Mixture of dipolar molecules and tetrahedral molecules. We now proceed to compute the contributions to $B^{(12)}$ arising from interaction between a dipolar molecule of species 1 and an octopolar molecule of species 2 *i.e.* in the case of tensorial interaction energy of the form

$$v_{12} = \frac{1}{15} \mu_\alpha^{(p1)} \Omega_{\beta\gamma\delta}^{(q2)} T_{\alpha\beta\gamma\delta}^{(pq)} - \frac{1}{2} \alpha_{\alpha\beta}^{(q2)} \mu_\gamma^{(p1)} \mu_\delta^{(p1)} T_{\alpha\gamma}^{(pq)} T_{\beta\delta}^{(pq)} - \dots \quad (24)$$

The above expression leads to

$$B_{\text{non-centr}}^{(12)} = - \frac{\mu_1^2 N}{2kT} \left\{ \alpha_2 \langle r_{pq}^{-6} \rangle_{12} + \frac{8}{5kT} \Omega_2^2 \langle r_{pq}^{-10} \rangle_{12} \right\}, \quad (25)$$

wherein the first term represents the contribution from interaction between the permanent dipole moment μ_1 and the induced dipole moment of the tetrahedral molecule (the second term in Eq. (24)), whereas the second term is contributed by interaction between the dipole μ_1 and the octopole Ω_2 (the first term in (24)).

With the potential of Eq. (3), we now have by (25)

$$B_{\text{non-centr}}^{(12)} = - \frac{b_{12}}{16\gamma_{12}^2} \left(\frac{\mu_1^2}{\sigma_{12}^3 \epsilon_{12}} \right) \left\{ \left(\frac{\alpha_2}{\sigma_{12}^3} \right) H_6(\gamma_{12}) + \frac{2}{5} \gamma_{12}^2 \left(\frac{\Omega_2^2}{\sigma_{12}^7 \epsilon_{12}} \right) H_{10}(\gamma_{12}) \right\}. \quad (26)$$

The expressions derived here allow to determine the octopole moment of a tetrahedral molecule not only from measurements on the pure gas, but moreover from the investigation of gaseous mixtures whose one component consists of the tetrahedral molecules for which Ω is to be determined, whereas the other component is either atomic (*e.g.* argon), dipolar or quadrupolar.

3. Determination of the octopole moment from other molecular effects

Obviously, it is desirable to possess more data on the octopole moment, since the possibility is then given of establishing a reasonable value of Ω for the molecule in question by comparing the various results. Having this in mind, we shall now proceed to discuss in brief the chances of determining Ω from other effects accessible to measurement in real gases.

Dielectric polarization and molecular refraction. Generalizing the theory of Buckingham and Raab [18] to a mixture of gases consisting of tetrahedral molecules, we obtain the second dielectric virial coefficient (strictly — its orientational part) in the form

$$B_D^{(ij)} = \frac{32\pi N^2}{15kT} \{ \alpha_i^2 \Omega_j^2 + \Omega_i^2 \alpha_j^2 \} \langle r_{pq}^{-10} \rangle_{ij}. \quad (27)$$

For a gas consisting of tetrahedral molecules of a single species admitting of the 6-12 Lennard-Jones potential, Eq. (27) yields [2, 3]

$$B_D^* = \frac{64\pi N^2}{15kT} \alpha^2 \Omega^2 \langle r_{pq}^{-10} \rangle = \frac{4b^2}{5y^2} \left(\frac{\alpha}{\sigma^3} \right)^2 \left(\frac{\Omega^2}{\sigma^7 \varepsilon} \right) H_{10}(y). \quad (28)$$

More information on the octopole moment of tetrahedral molecules can be derived from the second refractivity virial coefficient which, in the present case, is of the form

$$B_R^{(ij)} = \frac{4\pi}{3} N^2 \left\{ \alpha_i \alpha_j (\alpha_i + \alpha_j) \langle r_{pq}^{-6} \rangle_{ij} + \frac{4}{3} (\gamma_i \Omega_j^2 + \Omega_i^2 \gamma_j) \langle r_{pq}^{-10} \rangle_{ij} \right\}, \quad (29)$$

with γ_i denoting the hyperpolarizability induced in a molecule of species i by the electric field of the octopole Ω_j peculiar to the molecule of species j . In the present investigation, we refrain from distinguishing between the optical and electric polarizability of a molecule.

For a one-component gas and the potential of Eq. (3), the relation (29) reduces to [3, 5]

$$B_R^* = 2 \frac{b^2}{y^4} \left\{ \left(\frac{\alpha}{\sigma^3} \right)^3 H_6(y) + \frac{4}{3} \left(\frac{\varepsilon \gamma}{\sigma^6} \right) \left(\frac{\Omega^2}{\sigma^7 \varepsilon} \right) H_{10}(y) \right\}. \quad (30)$$

In particular, for molecules presenting no octopole moment, Eq. (30) reduces to the equation derived by Buckingham [4].

Molecular light scattering. Quite generally, we can distinguish an isotropic and an anisotropic component in Rayleighian light scattering, as characterized by the molecular constants F_{is} and F_{anis} , respectively, which can be expressed by Rayleigh's ratio R and the depolarization ratio D as follows [8]:

$$F_{\text{is}} = \frac{81\lambda^4 VR}{8\pi^4(n^2 + 2)^2} \frac{6 - 7D}{6 + 6D}, \quad F_{\text{anis}} = \frac{135\lambda^4 VR}{16\pi^4(n^2 + 2)^2} \frac{D}{1 + D}, \quad (31)$$

with λ denoting the wavelength and n — the refractive index.

The first virial coefficient of light scattering amounts to $A_{\text{is}}^{(ij)} = 9\alpha_i \alpha_j N$, whereas the second one, $B_{\text{is}}^{(ij)}$, for a gas consisting of tetrahedral molecules, is given by

$$B_{\text{is}}^{(ij)} = -18\alpha_i \alpha_j N B^{ij} + \frac{27}{2\pi} (\alpha_i + \alpha_j) B_R^{(ij)}, \quad (32)$$

wherein $B^{(ij)}$ is the total second virial coefficient of the equation of state of real gases and, in the case of tetrahedral molecules, is the sum of the terms (2), (11) and (12); $B_R^{(ij)}$ is given by Eq. (29).

In the case now under consideration, the first virial coefficient of anisotropic scattering vanishes, $A_{\text{anis}}^{(ij)} = 0$, whereas the second coefficient, $B_{\text{anis}}^{(ij)}$, is given as

$$B_{\text{anis}}^{(ij)} = 18N^2 \left\{ \alpha_i^2 \alpha_j^2 \langle r_{pq}^{-6} \rangle_{ij} + \frac{4}{35} (7\beta_i^2 \Omega_j^2 + 6\beta_i \beta_j \Omega_i \Omega_j + 7\Omega_i^2 \beta_j^2) \langle r_{pq}^{-10} \rangle_{ij} \right\}, \quad (33)$$

$\beta_i = \beta_{xyz}^{(i)}$ being the hyperpolarizability of the tetrahedral molecule of species i induced therein by the electric field of the octopole Ω_j of a molecule of species j .

Electric and magnetic birefringence. The theory of the second virial coefficient of the molecular Kerr constant K_m of dipolar and quadrupolar gases is due to Buckingham [9] and an analogous theory of the molecular Cotton-Mouton constant C_m has been evolved by the present author [10]. On applying these theories to gases consisting of tetrahedral molecules, we obtain for C_m

$$B_C^{(ij)} = \frac{4\pi N^2}{5kT} \left\{ (\alpha_i^2 \chi_i^2 + \chi_i^2 \alpha_j^2) \langle r_{pq}^{-6} \rangle_{ij} + \frac{8}{35} [7\beta_i \xi_i \Omega_j^2 + 3(\beta_i \xi_j + \xi_i \beta_j) \Omega_i \Omega_j + 7\Omega_i^2 \beta_j \xi_j] \langle r_{pq}^{-10} \rangle_{ij} \right\}, \quad (34)$$

and for K_m

$$B_K^{(ij)} = \frac{4\pi}{45kT} B_{\text{anis}}^{(ij)} + \frac{32\pi N^2}{35k^2 T^2} \alpha_i \alpha_j (\alpha_i^2 \Omega_j^2 + \Omega_i^2 \alpha_j^2) \langle r_{pq}^{-13} \rangle_{ij}, \quad (35)$$

with χ_i denoting the mean magnetic polarizability of a molecule of species i and $\xi_i = \xi_{xyz}^{(i)}$ — its magnetic hyperpolarizability, $B_{\text{anis}}^{(ij)}$ being given by Eq. (33).

4. Discussion and results

We now proceed to apply the expressions of the various second virial coefficients derived in Sections 2 and 3 for evaluating numerically the octopole moment of the methane molecule.

With the following values for CH_4 : [11] $\epsilon/k = 137^\circ\text{K}$, $\sigma = 3.882 \text{ \AA}$, $\alpha = 2.6 \times 10^{-24} \text{ cm}^3$ and [19] $B_{\text{exp}} = -44.5 \text{ cm}^3/\text{mole}$ at $T = 295^\circ\text{K}$, we obtain by Eq. (18) $\Omega_{\text{CH}_4} = 5 \times 10^{-34} \text{ e.s.u.}$

The value of Ω can also be determined from Eq. (17) by applying it to a mixture of argon and methane, for which Thomaes *et al.* [19] found experimentally $B_{\text{CH}_4-\text{A}} = -26.9 \text{ cm}^3/\text{mole}$ at $T = 295^\circ\text{K}$. Assuming the preceding values for CH_4 and [11] $\epsilon/k = 122^\circ\text{K}$, $\sigma = 3.4 \text{ \AA}$, $\alpha = 1.63 \times 10^{-24} \text{ cm}^3$ for argon with the well-known relations $\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{\frac{1}{2}}$ and $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$, we obtain by (17) a value of $\Omega_{\text{CH}_4} = 8 \times 10^{-34} \text{ e.s.u.}$

Similarly, it would be possible to use Eqs. (23) and (26) for computing Ω_{CH_4} ; however, no measurements of $B^{(12)}$ were available to the present author.

With the result of $B_D = 9.0 \text{ cm}^6/\text{mole}^2$ at $T = 242^\circ\text{K}$ obtained for methane by Johnston *et al.* [2], Eq. (28) yields a value of $\Omega_{\text{CH}_4} = 6 \times 10^{-34} \text{ e.s.u.}$ For comparison, it should be stated that Parr (cited from [2]), using a one-centre wave-function with Slater orbitals, obtained $\Omega_{\text{CH}_4} = 6.5 \times 10^{-34} \text{ e.s.u.}$

Since the hyperpolarizability of the methane molecule is known to amount to $\gamma = 2.6 \times 10^{-36} \text{ e.s.u.}$ as determined by Buckingham and Pople [20] from Kerr's molecular constant, Eqs. (30) and (32) will be of direct use in determining Ω_{CH_4} as soon as the values of B_R and B_{1s} become available experimentally.

Obviously, our problem can be restated to gain information on the values of the hyperpolarizabilities β , γ and ξ by means of Eqs. (29), (32), (33), (34) and (35) if the octopole moment of methane is known, say, from measurements of B and B_D or of the free energy [16]

or from phase transitions in the solid state [21]. Clearly, such data will rather be of an orientational character as, on the one hand, the measurements of the respective quantities must unavoidably present considerable difficulties and involve error and, on the other, our computations are of an approximative nature, albeit containing the most essential of the possible contributions.

In concluding it can be said that, once it becomes possible to measure the entire set of quantities discussed above, we shall obtain information not only on the value of the octopole moment of the tetrahedral molecule of the gas considered, but moreover on the values of its hyperpolarizabilities β , γ and ξ . Despite the many difficulties which will have to be overcome, further research in this direction can be fruitful and will surely bring much interesting information concerning the electric and magnetic properties of tetrahedral molecules and the nature and magnitude of the forces with which they interact.

The discussion of the present paper can be easily extended to the case of gases consisting of octahedral molecules such as SF_6 possessing a hexadecapolar moment given in general by a tensor $\Phi_{\alpha\beta\gamma\delta}$ of order 4 (see, [22]).

The author wishes to thank Professor A. Piekara for his discussion of the results. The author is indebted to K. Flatau, M. Sci., for the English translation of this paper.

REFERENCES

1. Buckingham, A. D. and Pople, J. A., *Faraday Society Discussions*, **22**, 17 (1956).
2. Johnston, D. R., Oudemans, G. J. and Cole, R. H., *J. chem. Phys.*, **33**, 1310 (1960).
3. Kielich, S., *Bull. Acad. Polon. Sci., Sér. Sci. math. astr. phys.*, **10**, 657 (1962).
4. Buckingham, A. D., *Trans Faraday Soc.*, **52**, 747, 1035 (1956).
5. Kielich, S., *Acta phys. Polon.*, **22**, 477 (1962).
6. Benoit, H. and Stockmayer, W. H., *J. Phys. Radium*, **17**, 21 (1956).
7. Buckingham, A. D. and Stephen, M. J., *Trans Faraday Soc.*, **53**, 384 (1957).
8. Kielich, S., *Acta phys. Polon.*, **19**, 149, 711 (1960).
9. Buckingham, A. D., *Proc. Phys. Soc. (London)*, **A68**, 910 (1955).
10. Kielich, S., *Acta phys. Polon.*, **22**, 65, 299 (1962).
11. Hirschfelder, J. O., Curtiss, Ch. F. and Bird, R. B., *Molecular theory of gases and liquids*, J. Wiley and Sons, Inc., New York 1954.
12. Pople, J. A., *Proc. Roy. Soc. (London)* **A221**, 508 (1954).
13. Debye, P., *Phys. Z.*, **21**, 178 (1920); **22**, 302 (1921); Keesom, W. H., *Phys. Z.*, **22**, 129 (1921); Falkenhagen, H., *Phys. Z.*, **23**, 87 (1922); London, F., *Trans Faraday Soc.*, **33**, 8 (1937); Stockmayer, W. H., *J. chem. Phys.*, **9**, 398 (1941); Rowlinson, J. S., *Trans Faraday Soc.*, **45**, 984 (1949); Castle, B. J., Jansen, L. and Dawson, J. M., *J. chem. Phys.*, **24**, 1078 (1956), Barker; J. A. and Smith, F., *Austral. J. Chem.*, **13**, 171 (1960).
14. Buckingham, A. D. and Pople, J. A., *Trans Faraday Soc.*, **51**, 1173 (1955).
15. Kielich, S., *Acta phys. Polon.*, **20**, 433 (1961); *Physica*, **28**, 511 (1962).
16. Parsonage, N. G. and Scott, R. L., *J. chem. Phys.*, **37**, 304 (1962).
17. Buckingham, A. D., *Quart. Revs. (London)*, **13**, 183 (1959).
18. Buckingham, A. D. and Raab, *Trans Faraday Soc.*, **54**, 623 (1958).
19. Thomaes, G., van Steenwinkel, R. and Stone, W., *Mol. Phys.*, **5**, 301 (1962).
20. Buckingham, A. D. and Pople, J. A., *Proc. Phys. Soc. (London)*, **A68**, 905 (1955).
21. James, H. M. and Keenan, T. A., *J. chem. Phys.*, **31**, 12 (1959).
22. Kielich, S., *Acta phys. Polon.* (in press).