

STATISTICAL MECHANICS OF HEXADECAPOLAR SYSTEMS

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(Received July 2, 1963)

The classical theory of the second virial coefficient of hexadecapolar gases and their mixtures with monatomic, dipolar, quadrupolar or octopolar gases is discussed. Also, a statistical theory of the molecular orientation polarization and molecular refraction of multi-component systems consisting of molecules possessing a hexadecapole moment is proposed. The formulas derived by tensor formalism hold for molecules of arbitrary symmetry and are applied to the case of molecules presenting the axial, tetrahedral or octahedral symmetry. They allow to obtain information on the value of the hexadecapole moment of octahedral molecules such as SF_6 or UF_6 .

1. Introduction

The properties of a molecular electric system are commonly characterized by its multipole (monopole, dipole, quadrupole, octopole, hexadecapole, ..., 2^n -pole) moments. The fact of a given molecule presenting the full set of consecutive multipole moments or presenting but one of them (of appropriate order) is determined by its structure and the kind of symmetry it possesses. Thus *e. g.*, in addition to the vast class of dipolar molecules, others are known which present a quadrupole moment (the linear molecules of CO_2 , CS_2 , the plane molecules of C_6H_6 *etc.*) or an octopole moment (the tetrahedral molecules of CH_4 , CF_4 *etc.*). Molecules possessing the octahedral symmetry, such as SF_6 and UF_6 , will present a hexadecapole moment but none of the lower order moments (neither a dipole, quadrupole nor octopole moment).

In the present paper we shall consider the statistical properties of systems of molecules presenting a hexadecapole moment determined quite generally by the tensor $\Phi_{\alpha\beta\gamma\delta}$. In three-dimensional space a fourth order tensor generally presents 81 elements; however, the tensor $\Phi_{\alpha\beta\gamma\delta}$ being symmetric in all indices α , β , γ and δ , its mutually independent components number but 21. The number of independent components is still further reduced — and some may vanish — according to the symmetry of the molecule: the higher the symmetry, the lesser is the number of components of the tensor $\Phi_{\alpha\beta\gamma\delta}$. Their number

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is strongly reduced if the molecule possesses the octahedral symmetry, as then the tensor of the hexadecapole moment is of the form (see Appendix B)

$$\Phi_{\alpha\beta\gamma\delta} = \frac{7}{4} h \{ \delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma} - 5(i_{\alpha}i_{\beta}i_{\gamma}i_{\delta} + j_{\alpha}j_{\beta}j_{\gamma}j_{\delta} + k_{\alpha}k_{\beta}k_{\gamma}k_{\delta}) \}, \quad (1)$$

with i, j, k denoting unit vectors along the axes x, y, z of the molecular reference system and $\delta_{\alpha\beta}$ — the unit tensor.

Molecular hexadecapole moments can neither be computed exactly nor measured directly; however, information as to their values can be obtained indirectly from an investigation of various effects of a statistical-molecular nature wherein molecular interactions of the hexadecapolar type, or mixed dipole-hexadecapole, quadrupole-hexadecapole and octopole-hexadecapole interactions come to the fore. Since effects related to the octopole moment of tetrahedral molecules (*e. g.*, CH_4 or CF_4) are accessible to measurement (see, *e. g.* Johnston *et al.* 1960), similar effects should exist in the case of substances consisting of octahedral molecules having a hexadecapole moment.

In the ensuing sections, we shall consider the theory of the second virial coefficient of the equation of state for a gas mixture and that of the molecular polarization and refraction of multi-component systems consisting of hexadecapolar molecules. The calculations are carried out by means of the tensor formalism which allows to derive general results that are applicable to molecules of arbitrary symmetry. In particular, the results are applied to octahedral and to axially symmetric molecules.

2. Second virial coefficient for hexadecapolar gases

The second virial coefficient of the Kamerlingh Onnes equation of state of a gas mixture is given by

$$B_m = \sum_{ij} x_i x_j B^{(ij)}, \quad (2)$$

where x_i is the mole fraction of the i -th component in the gas mixture. The total $B^{(ij)}$ is composed of two parts: $B_{\text{centr}}^{(ij)}$ describes central interaction between molecules of species i and j with potential $u_{ij}(r_{pq})$, and (Kielich 1962a)

$$B_{\text{noncentr}}^{(ij)} = -\frac{N}{2} \sum_{n=1}^{\infty} \frac{1}{n!} \left(-\frac{1}{kT} \right)^n \langle v_{ij}^n \rangle_{ij} \quad (3)$$

is the second part of $B^{(ij)}$ resulting from the noncentral intermolecular forces, with

$$\langle v_{ij}^n \rangle_{ij} = \frac{\iiint \{v_{ij}(r_{pq}, \omega_p, \omega_q)\}^n \exp \left\{ -\frac{u_{ij}(r_{pq})}{kT} \right\} d\mathbf{r}_{pq} d\omega_p d\omega_q}{\iint d\omega_p d\omega_q}, \quad (4)$$

where $v_{ij}(r_{pq}, \omega_p, \omega_q)$ is the potential energy of noncentral interaction dependent on the distance r_{pq} and on the orientation ω_p and ω_q of the molecules p and q ; N is Avogadro's number, k — Boltzmann's constant and T — the Kelvin temperature.

The tensorial potential energy of the interaction between two unlike hexadecapolar molecules is of the form (see Appendix A)

$$v_{ij}(r_{pq}, \omega_p, \omega_q) = -\frac{1}{11025} \Phi_{\alpha\beta\gamma\delta}^{(pi)} T_{\alpha\beta\gamma\delta\epsilon\eta\theta\chi}^{(pq)} \Phi_{\epsilon\eta\theta\chi}^{(qj)} - \frac{1}{22050} \{ \alpha_{\alpha\beta}^{(pi)} \Phi_{\gamma\delta\epsilon\eta}^{(qj)} \Phi_{\theta\chi\phi\psi}^{(qj)} + \alpha_{\alpha\beta}^{(qj)} \Phi_{\gamma\delta\epsilon\eta}^{(pi)} \Phi_{\theta\chi\phi\psi}^{(pi)} \} T_{\alpha\gamma\delta\epsilon\eta}^{(pq)} T_{\beta\theta\chi\phi\psi}^{(pq)} - \dots, \quad (5)$$

where $\alpha_{\alpha\beta}^{(pi)}$ is the electric polarizability tensor of a molecule p of species i and $T_{\alpha\beta\gamma\delta\epsilon}^{(pq)}$ and $T_{\alpha\beta\gamma\delta\epsilon\eta\theta\chi}^{(pq)}$ are the tensors characterizing the (induced) dipole-hexadecapole (r_{pq}^{-6}) and hexadecapole-hexadecapole (r_{pq}^{-9}) interactions, respectively.

On substitution of (5) in Eq. (3), we obtain by integration over all orientational variables

$$B_{\text{id-h}}^{(ij)} = -\frac{N}{(630)^2 kT} \{ \alpha_i \Phi_{\alpha\beta\gamma\delta}^{(i)} \Phi_{\alpha\beta\gamma\delta}^{(j)} + \alpha_j \Phi_{\alpha\beta\gamma\delta}^{(i)} \Phi_{\alpha\beta\gamma\delta}^{(j)} \} \langle T_{\sigma\nu\varrho\lambda}^{(pq)} T_{\sigma\nu\varrho\lambda}^{(pq)} \rangle_{ij}, \quad (6)$$

$$B_{\text{h-h}}^{(ij)} = -\frac{N}{(198450kT)^2} \Phi_{\alpha\beta\gamma\delta}^{(i)} \Phi_{\alpha\beta\gamma\delta}^{(i)} \Phi_{\epsilon\eta\theta\chi}^{(j)} \Phi_{\epsilon\eta\theta\chi}^{(j)} \langle T_{\sigma\nu\varrho\lambda\mu\pi\omega}^{(pq)} T_{\sigma\nu\varrho\lambda\mu\pi\omega}^{(pq)} \rangle_{ij}, \quad (7)$$

where $\alpha_i = \frac{1}{3} \alpha_{\alpha\alpha}^{(i)}$ is the mean polarizability of an isolated molecule of species i . Eq. (6) represents the contribution to $B^{(ij)}$ resulting from interaction between the induced dipole moment and the hexadecapole moment of the molecule, whereas Eq. (7) is contributed by interaction between the hexadecapole moments of the molecules.

If, in particular, the molecules possess the octahedral symmetry we have, by Eq. (1), $\Phi_{\alpha\beta\gamma\delta} \Phi_{\alpha\beta\gamma\delta} = (735/8) h^2$ and on invoking the fact that (Jansen 1958)

$$T_{\sigma\nu\varrho\lambda}^{(pq)} T_{\sigma\nu\varrho\lambda}^{(pq)} = \frac{10!}{32} \frac{-12}{r_{pq}}, T_{\sigma\nu\varrho\lambda\mu\pi\omega}^{(pq)} T_{\sigma\nu\varrho\lambda\mu\pi\omega}^{(pq)} = \frac{16!}{256} \frac{-18}{r_{pq}},$$

Eqs (6) and (7) reduce to

$$B_{\text{id-h}}^{(ij)} = -\frac{105N}{4kT} (\alpha_i h_j^2 + h_i^2 \alpha_j) \langle r_{pq}^{-12} \rangle_{ij}, \quad (8)$$

$$B_{\text{h-h}}^{(ij)} = -\frac{35035N}{2k^2 T^2} h_i^2 h_j^2 \langle r_{pq}^{-18} \rangle_{ij}; \quad (9)$$

here, h_i is the hexadecapole moment of the octahedral molecule of species i .

Eqs (8) and (9) hold also for tetrahedral molecules (such as CH_4) possessing an hexadecapole moment (Kielich 1963).

For a binary gas mixture whose one component consists of spherical atoms (or molecules) and the other of octahedral molecules, we obtain by Eqs (8) and (9)

$$B^{(11)} = B_{\text{centr}}^{(11)}, \quad (10)$$

$$B^{(12)} = B_{\text{centr}}^{(12)} - \frac{105}{4kT} \alpha_1 h_2^2 N \langle r_{pq}^{-12} \rangle_{12}, \quad (11)$$

$$B^{(22)} = B_{\text{centr}}^{(22)} - \frac{105}{2kT} h_2^2 N \left\{ \alpha_2 \langle r_{pq}^{-12} \rangle_{22} + \frac{1001}{3kT} h_2^2 \langle r_{pq}^{-18} \rangle_{22} \right\}. \quad (12)$$

On using the well-known 6—12 Lennard-Jones potential for computing the radial mean values $\langle r_{pq}^{-n} \rangle_{ij}$ we obtain

$$\langle r_{pq}^{-n} \rangle_{ij} = \int r_{pq}^{-n} \exp \left\{ -\frac{u_{ij}(r_{pq})}{kT} \right\} dr_{pq} = \frac{\pi \sigma_{ij}^{3-n}}{48 \varepsilon_{ij}^2} (kT)^2 H_n \left(2 \sqrt{\frac{\varepsilon_{ij}}{kT}} \right), \quad (13)$$

wherein σ_{ij} and ε_{ij} denote parameters of the central forces and the H_n — Pople's functions (Pople 1954). Eq. (13) enables us to evaluate numerically the contributions to $B^{(ij)}$ given by Eqs (8)—(12) and to compare them with the corresponding experimental data, so that we can glean information as to the hexadecapole moment of the molecule of the gas under investigation.

3. Calculation of other noncentral contributions to $B^{(ij)}$

Let us now consider the case of a mixture of a dipole gas and a hexadecapole gas. Dipole-hexadecapole interaction is given by

$$v_{ij}(r_{pq}, \omega_p, \omega_q) = -\frac{1}{105} \{ \mu_\alpha^{(pi)} \Phi_{\beta\gamma\delta\varepsilon}^{(qj)} - \Phi_{\alpha\beta\gamma\delta}^{(pi)} \mu_\varepsilon^{(qj)} \} T_{\alpha\beta\gamma\delta\varepsilon}^{(pq)} - \dots, \quad (14)$$

where $\mu_\alpha^{(pi)}$ is the α -component of the permanent dipole moment of molecule p of species i .

Applying Eq. (14), we obtain from (3)

$$B_{d-h}^{(ij)} = -\frac{2N}{21 k^2 T^2} \{ \mu_i^2 \Phi_{\alpha\beta\gamma\delta}^{(j)} \Phi_{\alpha\beta\gamma\delta}^{(j)} + \Phi_{\alpha\beta\gamma\delta}^{(i)} \Phi_{\alpha\beta\gamma\delta}^{(i)} \mu_j^2 \} \langle r_{pq}^{-12} \rangle_{ij}. \quad (15)$$

For the interaction between a dipolar molecule of species 1 with an octahedral molecule of species 2, this expression yields

$$B_{d-h}^{(12)} = -\frac{35N}{4k^2 T^2} \mu_1^2 h_2^2 \langle r_{pq}^{-12} \rangle_{12}. \quad (16)$$

In the case of molecules possessing an electric quadrupole and hexadecapole moment, we have for the tensorial energy of quadrupole-hexadecapole interaction

$$v_{ij}(r_{pq}, \omega_p, \omega_q) = -\frac{1}{315} \{ \Theta_{\alpha\beta}^{(pi)} \Phi_{\gamma\delta\varepsilon\eta}^{(qj)} + \Phi_{\alpha\beta\gamma\delta}^{(pi)} \Theta_{\varepsilon\eta}^{(qj)} \} T_{\alpha\beta\gamma\delta\varepsilon\eta}^{(pq)} - \dots, \quad (17)$$

where $\Theta_{\alpha\beta}^{(pi)}$ is the tensor of the quadrupole moment of a molecule p of species i .

Thus, from (3) and (17), we get

$$B_{q-h}^{(ij)} = -\frac{44N}{105k^2 T^2} \{ \Theta_{\alpha\beta}^{(i)} \Theta_{\alpha\beta}^{(i)} \Phi_{\gamma\delta\varepsilon\eta}^{(j)} \Phi_{\gamma\delta\varepsilon\eta}^{(j)} + \Phi_{\alpha\beta\gamma\delta}^{(i)} \Phi_{\alpha\beta\gamma\delta}^{(i)} \Theta_{\varepsilon\eta}^{(j)} \Theta_{\varepsilon\eta}^{(j)} \} \langle r_{pq}^{-14} \rangle_{ij}. \quad (18)$$

If, in particular, the component 1 of a binary gas mixture consists of quadrupole molecules which are symmetric about the z -axis with quadrupole moment Θ_1 and the molecules of component 2 possess the octahedral symmetry, we obtain from (18)

$$B_{q-h}^{(12)} = -\frac{231N}{4k^2 T^2} \Theta_1^2 h_2^2 \langle r_{pq}^{-14} \rangle_{12}. \quad (19)$$

We now assume that the molecules of one component of the mixture possess an octopole moment described by the tensor $\Omega_{\alpha\beta\gamma}$ and those of the other component to be again hexadecapolar. In this case the general expression of the tensorial energy of octopolar-hexadecapolar interaction is of the form

$$v_{ij}(r_{pq}, \omega_p, \omega_q) = -\frac{1}{1575} \{ \Omega_{\alpha\beta\gamma}^{(pi)} \Phi_{\delta\epsilon\eta\theta}^{(qj)} - \Phi_{\alpha\beta\gamma\delta}^{(pi)} \Omega_{\epsilon\eta\theta}^{(qj)} \} T_{\alpha\beta\gamma\delta\epsilon\eta\theta}^{(pq)} - \dots, \quad (20)$$

and Eq. (3) yields

$$B_{o-h}^{(ij)} = -\frac{572N}{525 k^2 T^2} \{ \Omega_{\alpha\beta\gamma}^{(i)} \Omega_{\alpha\beta\gamma}^{(j)} \Phi_{\delta\epsilon\eta\theta}^{(j)} \Phi_{\delta\epsilon\eta\theta}^{(j)} + \Phi_{\alpha\beta\gamma\delta}^{(i)} \overline{\Phi_{\alpha\beta\gamma\delta}^{(i)}} \Omega_{\epsilon\eta\theta}^{(j)} \Omega_{\epsilon\eta\theta}^{(j)} \} \langle r_{pq}^{-16} \rangle_{ij}. \quad (21)$$

Using this expression, we obtain for the contribution to $B^{(12)}$ arising from interaction between a tetrahedral molecule of species 1 with octopole moment $o_1 = o_{xyx}^{(1)}$ and an octahedral molecule of species 2

$$B_{o-h}^{(12)} = -\frac{15015}{4k^2 T^2} O_1^2 h_2^2 \langle r_{pq}^{-16} \rangle_{12}. \quad (22)$$

4. Molecular orientation polarization

Classical statistical theory yields for the molecular orientation polarization of a multi-component system with N_i molecules of species i the following equation (Kielich 1962b):

$$P_m^0 = \frac{4\pi}{9kT} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} m_{\alpha}^{(pi)} m_{\alpha}^{(qj)} \right\rangle, \quad (23)$$

in which the brackets $\langle \rangle$ denote the statistical average in the absence of an external electric field ($E = 0$).

We consider a multi-component system in which the molecules have neither permanent dipole, quadrupole nor octopole moments, but possess a permanent hexadecapole moment. For simplicity, we assume that at zero external field only a dipole moment can be induced in a molecule p of species i by the electric field $F_0^{(pi)}$ due to the other hexadecapoles in the system. We now have

$$m_{\alpha}^{(pi)} = \alpha_{\alpha\beta}^{(pi)} F_{0\beta}^{(pi)}, \quad (24)$$

where (see Appendix A)

$$F_{0\beta}^{(pi)} = -\frac{1}{105} \sum_k \sum_{r=1}^{N_k} T_{\beta\gamma\delta\epsilon\eta}^{(pr)} \Phi_{\gamma\delta\epsilon\eta}^{(rk)} \quad (25)$$

is the electric field at molecule p of species i due to the hexadecapole moments of all the other molecules of the system.

On substitution of (24) and (25) in Eq. (23), and by the method used in our preceding papers (Kielich 1962b, c), P_m^0 can be represented in the form

$$P_m^0 = \sum_{ij} x_i x_j P_m^{(ij)} + \sum_{ijk} x_i x_j x_k P_m^{(ijk)} + \dots, \quad (26)$$

where

$$P_m^{(ij)} = \frac{2\pi\rho^2}{2679075 kT} \{ \alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(j)} \Phi_{\gamma\delta\epsilon\eta}^{(j)} \Phi_{\gamma\delta\epsilon\eta}^{(j)} + \Phi_{\alpha\beta\gamma\delta}^{(i)} \Phi_{\alpha\beta\gamma\delta}^{(i)} \alpha_{\epsilon\eta}^{(j)} \alpha_{\epsilon\eta}^{(j)} \} \iint T_{\sigma\nu\rho\lambda}^{(pq)} T_{\sigma\nu\rho\lambda}^{(pq)} g_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q \quad (27)$$

$$P_m^{(ijk)} = \frac{4\pi\rho^3}{893025 kT} \alpha_i \alpha_j \Phi_{\alpha\beta\gamma\delta}^{(k)} \Phi_{\alpha\beta\gamma\delta}^{(k)} \iiint T_{\sigma\nu\rho\lambda}^{(pq)} T_{\sigma\nu\rho\lambda}^{(qr)} g_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) d\mathbf{r}_p d\mathbf{r}_q d\mathbf{r}_r \quad (28)$$

In the foregoing expressions, $\rho = N/V$ is the number density of the system of volume V , $g_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q)$ and $g_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r)$ are the binary and ternary correlation functions, respectively, and $\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r, \dots$ are the position vectors of the p -th, q -th, ... molecules.

For octahedral molecules, Eq. (27) reduces to

$$P_m^{(ij)} = \frac{70\pi\rho^2}{3kT} \{ \alpha_i^2 h_j^2 + h_i^2 \alpha_j^2 \} \iint r_{pq}^{-12} g_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q \quad (29)$$

In the case of a system at low densities, Eq. (27) as well as (29) can be expressed as

$$P_m^{(ij)} = \rho \{ B_P^{(ij)} + 0(\rho) \}, \quad (30)$$

where

$$B_P^{(ij)} = \frac{70\pi N}{3kT} \{ \alpha_i^2 h_j^2 + h_i^2 \alpha_j^2 \} \int r_{pq}^{-12} \exp \left\{ -\frac{u_{ij}(r_{pq})}{kT} \right\} d\mathbf{r}_{pq} \quad (31)$$

is the second orientation polarization virial coefficient for octahedral molecules and characterizes the hexadecapole-induced dipole effect.

The foregoing results can moreover be applied to the case of a binary gas mixture wherein the one component is monatomic and the other consists of octahedral molecules. Namely we have by Eqs (26), (30) and (31)

$$P_m = \rho x_2 \{ 2x_1 B_P^{(12)} + x_2 B_P^{(22)} \}, \quad (32)$$

where

$$B_P^{(12)} = \frac{70\pi N}{3kT} \alpha_1^2 h_2^2 \langle r_{pq}^{-12} \rangle_{12}, \quad (33)$$

$$B_P^{(22)} = \frac{140\pi N}{3kT} \alpha_2^2 h_2^2 \langle r_{pq}^{-12} \rangle_{22}. \quad (34)$$

5. Molecular refraction

The Lorentz-Lorenz function or molecular refraction of a multicomponent system is given by (Kielich 1962c)

$$R_m = \frac{4\pi}{9} \sum_i \left\langle \sum_{p=1}^{N_i} \frac{\partial m_\alpha^{(pi)}}{\partial E_\alpha} \right\rangle. \quad (35)$$

We discuss here this equation for the case when the differential polarizability of the molecule p of species i with a centre of inversion is of the form

$$\frac{\partial m_{\alpha}^{(pi)}}{\partial E_{\alpha}} = \left\{ \alpha_{\alpha\beta}^{(pi)} + \frac{1}{2} \gamma_{\alpha\beta\gamma\delta}^{(pi)} F_{0\gamma}^{(pi)} F_{0\delta}^{(pi)} + \dots \right\} \left\{ \delta_{\beta\alpha} + \frac{\partial F_{\beta}^{(pi)}}{\partial E_{\alpha}} \right\}, \quad (36)$$

where $\gamma_{\alpha\beta\gamma\delta}$ is the hyperpolarizability tensor describing the direct effect of the molecular field (25) on the polarizability of the molecule immersed in the dense medium.

With respect to expansion (36) and by

$$\frac{\partial F_{\beta}^{(pi)}}{\partial E_{\alpha}} = - \sum_j \sum_{q=1}^{N_j} T_{\beta\gamma}^{(pq)} \alpha_{\gamma\alpha}^{(q)} + \sum_{jk} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} T_{\beta\gamma}^{(pq)} \alpha_{\gamma\delta}^{(q)} T_{\delta\epsilon}^{(qr)} \alpha_{\epsilon\alpha}^{(rk)} - \dots \quad (37)$$

the following result is obtained from Eq. (35):

$$R_m = \sum_i x_i R_m^{(i)} + \sum_{ij} x_i x_j R_m^{(ij)} + \sum_{ijk} x_i x_j x_k R_m^{(ijk)} + \dots, \quad (38)$$

where

$$R_m^{(i)} = \frac{4\pi}{3} N \alpha_i, \quad (39)$$

$$R_m^{(ij)} = \frac{2\pi\varrho^2}{27} \iint \left\{ (\alpha_i \alpha_{\alpha\beta}^{(j)} \alpha_{\alpha\beta}^{(i)} + \alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(j)} \alpha_i) T_{\sigma\tau}^{(pq)} T_{\sigma\tau}^{(pq)} + \right. \\ \left. + \frac{1}{39690} (\gamma_i \Phi_{\alpha\beta\gamma\delta}^{(j)} \Phi_{\alpha\beta\gamma\delta}^{(i)} + \Phi_{\alpha\beta\gamma\delta}^{(i)} \Phi_{\alpha\beta\gamma\delta}^{(j)} \gamma_j) T_{\sigma\tau\nu\lambda}^{(pq)} T_{\sigma\tau\nu\lambda}^{(pq)} + \dots \right\} g_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q \quad (40)$$

$$R_m^{(ijk)} = \frac{4\pi\varrho^3}{9} \alpha_i \alpha_j \alpha_k \iiint T_{\sigma\tau}^{(pq)} T_{\sigma\tau}^{(qr)} g_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) d\mathbf{r}_p d\mathbf{r}_q d\mathbf{r}_r, \quad (41)$$

with $\gamma_i = \frac{1}{3} \gamma_{\alpha\alpha\beta\beta}^{(i)}$ denoting the mean hyperpolarizability of a molecule of species i .

For molecules having the octahedral symmetry, Eq. (40) yields

$$R_m^{(ij)} = \frac{4\pi\varrho^2}{3} \iint \left\{ \alpha_i \alpha_j (\alpha_i + \alpha_j) r_{pq}^{-6} + \right. \\ \left. + \frac{175}{12} (\gamma_i h_j^2 + h_i^2 \gamma_j) r_{pq}^{-12} \right\} g_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p^2 d\mathbf{r}_q^2. \quad (42)$$

In the case of a one-component system consisting of spherical molecules ($h = 0$), Eq. (42) reduces to the result of De Boer, Van der Maesen and Ten Seldam (1953).

6. The quantities $B_m^{(i)}$, $P_m^{(i)}$ and $R_m^{(i)}$ for the case of axially symmetric molecules

The contributions to $B_m^{(i)}$ from various non-central interactions, as computed in Sections 2 and 3, go over into the following expressions for the case of axially symmetric molecules,

on applying the formulas (B.5) given in Appendix B:

$$B_{\text{id-h}}^{(ij)} = -\frac{5N}{4kT} (\alpha_i \Phi_j^2 + \Phi_i^2 \alpha_j) \langle r_{pq}^{-12} \rangle_{ij}, \quad (43)$$

$$B_{\text{d-h}}^{(ij)} = -\frac{5N}{12k^2T^2} (\mu_i^2 \Phi_j^2 + \Phi_i^2 \mu_j^2) \langle r_{pq}^{-12} \rangle_{ij}, \quad (44)$$

$$B_{\text{q-h}}^{(ij)} = -\frac{11N}{4k^2T^2} (\Theta_i^2 \Phi_j^2 + \Phi_i^2 \Theta_j^2) \langle r_{pq}^{-14} \rangle_{ij}, \quad (45)$$

$$B_{\text{o-h}}^{(ij)} = -\frac{143N}{12k^2T^2} (\Omega_i^2 \Phi_j^2 + \Phi_i^2 \Omega_j^2) \langle r_{pq}^{-16} \rangle_{ij}, \quad (46)$$

$$B_{\text{h-h}}^{(ij)} = -\frac{715N}{18k^2T^2} \Phi_i^2 \Phi_j^2 \langle r_{pq}^{-18} \rangle_{ij}. \quad (47)$$

Eqs (27) and (39), when applied to systems of hexadecapolar axially-symmetric molecules, become

$$P_m^{(ij)} = \frac{10\pi\varrho^2}{9kT} \{ \alpha_i^2(1 + 2\kappa_i^2) \Phi_j^2 + \Phi_i^2 \alpha_j^2(1 + 2\kappa_j^2) \} \iint r_{pq}^{-12} g_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (48)$$

$$R_m^{(ij)} = \frac{4\pi}{3} \varrho^2 \iint \left\{ \alpha_i \alpha_j [\alpha_i(1 + 2\kappa_i^2) + \alpha_j(1 + 2\kappa_j^2)] r_{pq}^{-6} + \dots \right. \\ \left. + \frac{25}{36} (\gamma_i \Phi_j^2 + \Phi_i^2 \gamma_j) r_{pq}^{-12} + \dots \right\} g_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (49)$$

wherein $\kappa_i = (\alpha_{zz}^{(i)} - \alpha_{xx}^{(i)})/3\alpha_i$ is the anisotropy of polarizability of the molecule of species i .

For a one-component system with molecules possessing the axial symmetry but no hexadecapole moment ($h = 0$), Eq. (49) yields the result of Mazur and Postma (1959).

To conclude, it should be stated that research work aimed at obtaining knowledge of the second virial coefficient of the equation of state for gases as well as of molecular polarization and refraction can provide information concerning the value of the hexadecapole moment of octahedral molecules.

The author would like to thank Professor A. Piekara for his valuable discussions.

APPENDIX A

Tensorial intermolecular energy of two unlike polar molecules

The tensors of the dipolar, quadrupolar, octopolar and hexadecapolar moments of a molecular electric system of species i are defined, respectively, as (Kielich 1962d)

$$\mu_\alpha^{(i)} = \sum_n e_n^{(i)} r_{n\alpha},$$

$$\Theta_{\alpha\beta}^{(i)} = \frac{1}{2} (3q_{\alpha\beta}^{(i)} - \delta_{\alpha\beta} q_{\gamma\gamma}^{(i)}),$$

$$\begin{aligned}\Omega_{\alpha\beta\gamma}^{(i)} &= \frac{1}{2} (5o_{\alpha\beta\gamma}^{(i)} - \sum_3 \delta_{\alpha\beta} o_{\gamma\delta\delta}^{(i)}), \\ \Phi_{\alpha\beta\gamma\delta}^{(i)} &= \frac{1}{8} (35h_{\alpha\beta\gamma\delta}^{(i)} - 5 \sum_6 \delta_{\alpha\beta} h_{\gamma\delta\epsilon\epsilon}^{(i)} + h_{\epsilon\epsilon\eta\eta}^{(i)} \sum_3 \delta_{\alpha\beta} \delta_{\gamma\delta}),\end{aligned}\quad (\text{A.1})$$

with

$$\begin{aligned}q_{\alpha\beta}^{(i)} &= \sum_n e_n^{(i)} r_{n\alpha} r_{n\beta}, \\ o_{\alpha\beta\gamma}^{(i)} &= \sum_n e_n^{(i)} r_{n\alpha} r_{n\beta} r_{n\gamma}, \\ h_{\alpha\beta\gamma\delta}^{(i)} &= \sum_n e_n^{(i)} r_{n\alpha} r_{n\beta} r_{n\gamma} r_{n\delta},\end{aligned}\quad (\text{A.2})$$

wherein $e_n^{(i)}$ is the n -th electric charge of the molecule of species i , r_n — the respective radius vector and $\sum_3 \delta_{\alpha\beta} o_{\gamma\delta\delta}^{(i)}$ denotes the sum of the three terms $\delta_{\alpha\beta} o_{\gamma\delta\delta}^{(i)} + \delta_{\beta\gamma} o_{\alpha\delta\delta}^{(i)} + \delta_{\gamma\alpha} o_{\beta\delta\delta}^{(i)}$, the sums $\sum_3 \delta_{\alpha\beta} \delta_{\gamma\delta}$ and $\sum_6 \delta_{\alpha\beta} h_{\gamma\delta\epsilon\epsilon}^{(i)}$ being defined analogically.

In a system of two unlike molecule, each presenting in general the electric moments defined above, the potential energy of (electrostatic) interaction is given by the expression

$$\begin{aligned}v_{ij}(r_{pq}, \omega_p, \omega_q) &= \mu_{\alpha}^{(pi)} T_{\alpha\beta}^{(pq)} \mu_{\beta}^{(qj)} - \frac{1}{3} (\mu_{\alpha}^{(pi)} \Theta_{\beta\gamma}^{(qj)} - \Theta_{\alpha\beta}^{(pi)} \mu_{\gamma}^{(qj)}) T_{\alpha\beta\gamma}^{(pq)} + \\ &+ \frac{1}{45} (3\mu_{\alpha}^{(pi)} \Omega_{\beta\gamma\delta}^{(qj)} - 5\Theta_{\alpha\beta}^{(pi)} \Theta_{\gamma\delta}^{(qj)} + 3\Omega_{\alpha\beta\gamma}^{(pi)} \mu_{\delta}^{(qj)}) T_{\alpha\beta\gamma\delta}^{(pq)} - \\ &- \frac{1}{315} (3\mu_{\alpha}^{(pi)} \Phi_{\beta\gamma\delta\epsilon}^{(qj)} - 3\Phi_{\alpha\beta\gamma\delta}^{(pi)} \mu_{\epsilon}^{(qj)} - 7\Theta_{\alpha\beta}^{(pi)} \Omega_{\gamma\delta\epsilon}^{(qj)} + 7\Omega_{\alpha\beta\gamma}^{(pi)} \Theta_{\delta\epsilon}^{(qj)}) T_{\alpha\beta\gamma\delta\epsilon}^{(pq)} - \\ &- \frac{1}{1575} (5\Theta_{\alpha\beta}^{(pi)} \Phi_{\gamma\delta\epsilon\eta}^{(qj)} - 7\Omega_{\alpha\beta\gamma}^{(pi)} \Omega_{\delta\epsilon\eta}^{(qj)} + 5\Phi_{\alpha\beta\gamma\delta}^{(pi)} \Theta_{\epsilon\eta}^{(qj)}) T_{\alpha\beta\gamma\delta\epsilon\eta}^{(pq)} - \\ &- \frac{1}{1575} (\Omega_{\alpha\beta\gamma}^{(pi)} \Phi_{\delta\epsilon\eta\theta}^{(qj)} - \Phi_{\alpha\beta\gamma\delta}^{(pi)} \Omega_{\epsilon\eta\theta}^{(qj)}) T_{\alpha\beta\gamma\delta\epsilon\eta\theta}^{(pq)} - \\ &- \frac{1}{11025} \Phi_{\alpha\beta\gamma\delta}^{(pi)} T_{\alpha\beta\gamma\delta\epsilon\eta\theta\chi}^{(pq)} \Phi_{\epsilon\eta\theta\chi}^{(qj)} - \dots\end{aligned}\quad (\text{A.3})$$

The tensors $T_{\alpha\beta\gamma}^{(pq)}$, ... characterizing the respective multipolar interaction of the molecules are defined as $T_{\alpha\beta\gamma}^{(pq)} = -\nabla_{\alpha} \nabla_{\beta} \nabla_{\gamma} (1/r_{pq})$, wherein ∇_{α} is the differential Hamilton operator.

Denoting for simplicity $r_{pq} \equiv r$ and taking into account that

$$\nabla_{\alpha} \left(\frac{1}{r^k} \right) = -\frac{k r_{\alpha}}{r^{k+2}}, \quad \nabla_{\beta} \left(\frac{r_{\alpha}}{r^k} \right) = \frac{\delta_{\alpha\beta} r^k - k r_{\alpha} r_{\beta} r^{k-2}}{r^{2k}},$$

we have

$$\begin{aligned}T_{\alpha\beta} &= -r^{-5} (3r_{\alpha} r_{\beta} - r^2 \delta_{\alpha\beta}), \\ T_{\alpha\beta\gamma} &= 3r^{-7} (5r_{\alpha} r_{\beta} r_{\gamma} - r^2 \sum_3 r_{\alpha} \delta_{\beta\gamma}), \\ T_{\alpha\beta\gamma\delta} &= -3r^{-9} (35r_{\alpha} r_{\beta} r_{\gamma} r_{\delta} - 5r^2 \sum_6 r_{\alpha} r_{\beta} \delta_{\gamma\delta} + r^4 \sum_3 \delta_{\alpha\beta} \delta_{\gamma\delta}),\end{aligned}$$

$$\begin{aligned}
T_{\alpha\beta\gamma\delta\epsilon} &= 15r^{-11}(63r_{\alpha}r_{\beta}r_{\gamma}r_{\delta}r_{\epsilon}-7r^2\sum_{10}r_{\alpha}r_{\beta}r_{\gamma}\delta_{\delta\epsilon}+r^4\sum_{15}r_{\alpha}\delta_{\beta\gamma}\delta_{\delta\epsilon}), \\
T_{\alpha\beta\gamma\delta\epsilon\eta} &= -15r^{-13}(693r_{\alpha}r_{\beta}r_{\gamma}r_{\delta}r_{\epsilon}r_{\eta}-63r^2\sum_{15}r_{\alpha}r_{\beta}r_{\gamma}r_{\delta}\delta_{\epsilon\eta}+ \\
&\quad +7r^4\sum_{45}r_{\alpha}r_{\beta}\delta_{\gamma\delta}\delta_{\epsilon\eta}-r^6\sum_{15}\delta_{\alpha\beta}\delta_{\gamma\delta}\delta_{\epsilon\eta}), \\
T_{\alpha\beta\gamma\delta\epsilon\eta\theta} &= 105r^{-15}\{1287r_{\alpha}r_{\beta}r_{\gamma}r_{\delta}r_{\epsilon}r_{\eta}r_{\theta}-99r^2\sum_{21}r_{\alpha}r_{\beta}r_{\gamma}r_{\delta}r_{\epsilon}\delta_{\eta\theta}+ \\
&\quad +9r^4\sum_{105}r_{\alpha}r_{\beta}r_{\gamma}\delta_{\delta\epsilon}\delta_{\eta\theta}-r^6\sum_{105}r_{\alpha}\delta_{\beta\gamma}\delta_{\delta\epsilon}\delta_{\eta\theta}\}, \\
T_{\alpha\beta\gamma\delta\epsilon\eta\theta\chi} &= -105r^{-17}\{19305r_{\alpha}r_{\beta}r_{\gamma}r_{\delta}r_{\epsilon}r_{\eta}r_{\theta}r_{\chi}-1287r^2\sum_{28}r_{\alpha}r_{\beta}r_{\gamma}r_{\delta}r_{\epsilon}r_{\eta}\delta_{\theta\chi}+ \\
&\quad +99r^4\sum_{210}r_{\alpha}r_{\beta}r_{\gamma}r_{\delta}\delta_{\epsilon\eta}\delta_{\theta\chi}-9r^6\sum_{420}r_{\alpha}r_{\beta}\delta_{\gamma\delta}\delta_{\epsilon\eta}\delta_{\theta\chi}+r^8\sum_{105}\delta_{\alpha\beta}\delta_{\gamma\delta}\delta_{\epsilon\eta}\delta_{\theta\chi}\}. \quad (\text{A.4})
\end{aligned}$$

In the course of the present investigation we make use of products of these interaction tensors, which yield (Jansen 1958)

$$\begin{aligned}
T_{\alpha\beta}T_{\alpha\beta} &= 6r^{-6}, & T_{\alpha\beta\gamma}T_{\alpha\beta\gamma} &= 90r^{-8}, & T_{\alpha\beta\gamma\delta}T_{\alpha\beta\gamma\delta} &= 2520r^{-10}, \\
T_{\alpha\beta\gamma\delta\epsilon}T_{\alpha\beta\gamma\delta\epsilon} &= \frac{10!}{32}r^{-12}, & T_{\alpha\beta\gamma\delta\epsilon\eta}T_{\alpha\beta\gamma\delta\epsilon\eta} &= \frac{12!}{64}r^{-14}, \\
T_{\alpha\beta\gamma\delta\epsilon\eta\theta}T_{\alpha\beta\gamma\delta\epsilon\eta\theta} &= \frac{14!}{128}r^{-16}, & T_{\alpha\beta\gamma\delta\epsilon\eta\theta\chi}T_{\alpha\beta\gamma\delta\epsilon\eta\theta\chi} &= \frac{16!}{256}r^{-18}. \quad (\text{A.5})
\end{aligned}$$

To the energy of electrostatic interaction of the two polar molecules as computed above we have to add the energy of their inductive interaction; to within the dipolar approximation, the latter amounts to

$$v_{ij}^{\text{ind}} = -\frac{1}{2}(\alpha_{\alpha\beta}^{(pi)}F_{\alpha}^{(pi)}F_{\beta}^{(pi)} + \alpha_{\alpha\beta}^{(qj)}F_{\alpha}^{(qj)}F_{\beta}^{(qj)}), \quad (\text{A.6})$$

wherein

$$F_{\alpha}^{(pi)} = -T_{\alpha\beta}^{(pq)}\mu_{\beta}^{(qj)} + \frac{1}{3}T_{\alpha\beta\gamma}^{(pq)}\Theta_{\beta\gamma}^{(qj)} - \frac{1}{15}T_{\alpha\beta\gamma\delta}^{(pq)}\Omega_{\beta\gamma\delta}^{(qj)} + \frac{1}{105}T_{\alpha\beta\gamma\delta\epsilon}^{(pq)}\Phi_{\beta\gamma\delta\epsilon}^{(qj)} - \dots \quad (\text{A.7})$$

is the electric field of the multipoles of molecule q of species j acting on molecule p of species i to give rise therein to the induced dipole moment $m_{\alpha}^{(pi)} = \alpha_{\alpha\beta}^{(pi)}F_{\beta}^{(pi)}$.

APPENDIX B

The tensors of multipole moments for special cases

For the case of molecules possessing the regular octahedral symmetry (class O_h , see Fig. 1b), the tensors (A.2) assume the form

$$\mu_{\alpha} = o_{\alpha\beta\gamma} = 0, \quad q_{\alpha\beta} = \delta_{\alpha\beta}q_{xx} = \frac{1}{3}\delta_{\alpha\beta}q_{\gamma\gamma},$$

$$h_{\alpha\beta\gamma\delta} = h_{xxxx}(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) + (h_{xxxx} - 3h_{xxxx})(i_{\alpha}i_{\beta}i_{\gamma}i_{\delta} + j_{\alpha}j_{\beta}j_{\gamma}j_{\delta} + k_{\alpha}k_{\beta}k_{\gamma}k_{\delta}). \quad (\text{B.1})$$

Consequently, the tensor components of the dipole, quadrupole and octopole moments vanish, whereas those of the hexadecapolar tensor $\Phi_{\alpha\beta\gamma\delta}$ reduce to the single quantity $h = \frac{1}{2}(3h_{xxxx} - h_{xxxx})$ as given by Eq. (1). In particular, for molecules presenting the spherical symmetry, we have $h_{xxxx} = 3h_{xxxx}$ and in Eq. (1) $h = 0$; in this case, all multipole moments (A.1) of the system vanish.

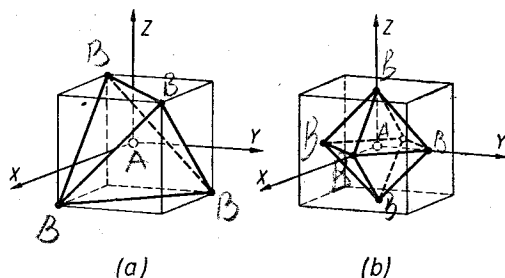


Fig. 1. (a) A molecule of the type AB_4 of tetrahedral class T_d symmetry; the four atoms B (or groups of atoms) are situated in vertices of the cube possessing no edges in common, while the atom A is at the centre of the cube which is simultaneously the centre of the regular tetrahedron thus formed. (b) A molecule of the type AB_6 of octahedral class O_h symmetry; the atom A is at the centre of the cube, the six atoms B being situated at the centres of its faces. The regular octahedron inscribed in the cube presents the elements of symmetry of the cube.

For the case of molecules possessing the tetrahedral symmetry (class T_d , see Fig. 1a), the components of the octopole moment tensor are given as follows (Kielich 1963):

$$\Omega_{\alpha\beta\gamma} = \frac{5}{2} o_{xyz} \{i_\alpha(j_\beta k_\gamma + j_\gamma k_\beta) + j_\alpha(k_\beta i_\gamma + k_\gamma i_\beta) + k_\alpha(i_\beta j_\gamma + i_\gamma j_\beta)\} \quad (\text{B. 2})$$

and the components of the hexadecapole moment tensor are given by Eq. (1).

For the case of molecules symmetric with respect to the molecular z -axis, we have

$$\begin{aligned} \mu_\alpha &= \mu_z k_\alpha, & q_{\alpha\beta} &= \delta_{\alpha\beta} q_{xx} + (q_{zz} - q_{xx}) k_\alpha k_\beta, \\ o_{\alpha\beta\gamma} &= (k_\alpha \delta_{\beta\gamma} + k_\beta \delta_{\gamma\alpha} + k_\gamma \delta_{\alpha\beta}) o_{xxx} + (o_{zzz} - 3o_{xxx}) k_\alpha k_\beta k_\gamma, \\ h_{\alpha\beta\gamma\delta} &= \frac{1}{3} h_{xxxx} \sum_3 \delta_{\alpha\beta} \delta_{\gamma\delta} + \frac{1}{3} (3h_{xxxx} - h_{xxxx}) \sum_6 \delta_{\alpha\beta} k_\gamma k_\delta + \\ &+ (h_{zzzz} - 6h_{xxxx} + h_{xxxx}) k_\alpha k_\beta k_\gamma k_\delta, \end{aligned} \quad (\text{B. 3})$$

and, consequently, the components of the tensors (A.1) are of the form

$$\begin{aligned} \mu_\alpha &= \mu k_\alpha, & \Theta_{\alpha\beta} &= \frac{1}{2} \Theta (3k_\alpha k_\beta - \delta_{\alpha\beta}), \\ \Omega_{\alpha\beta\gamma} &= \frac{1}{2} \Omega (5k_\alpha k_\beta k_\gamma - \sum_3 k_\alpha \delta_{\beta\gamma}), \\ \Phi_{\alpha\beta\gamma\delta} &= \frac{1}{8} \Phi (35k_\alpha k_\beta k_\gamma k_\delta - 5 \sum_6 k_\alpha k_\beta \delta_{\gamma\delta} + \sum_3 \delta_{\alpha\beta} \delta_{\gamma\delta}), \end{aligned} \quad (\text{B. 4})$$

wherein the quantities $\mu = \mu_z$, $\Theta = q_{zz} - q_{xx}$, $\Omega = o_{zzz} - 3o_{xxx}$, $\Phi = h_{zzzz} - 6h_{xxxx} + h_{xxxx}$ denote the dipole, quadrupole, octopole and hexadecapole moments of the axially symmetric molecule, respectively. From the above expressions we have

$$\begin{aligned} \mu_\alpha \mu_\alpha &= \mu^2, & \Theta_{\alpha\beta} \Theta_{\alpha\beta} &= \frac{3}{2} \Theta^2, \\ \Omega_{\alpha\beta\gamma} \Omega_{\alpha\beta\gamma} &= \frac{5}{2} \Omega^2, & \Phi_{\alpha\beta\gamma\delta} \Phi_{\alpha\beta\gamma\delta} &= \frac{35}{8} \Phi^2. \end{aligned} \quad (\text{B.5})$$

REFERENCES

- De Boer, J., Van der Maesen, F. and Ten Seldam, C. A., *Physica*, **19**, 265 (1953).
 Jansen, L., *Phys. Rev.*, **110**, 661 (1958).
 Johnston, D. R., Oudemans, G. I. and Cole, R. H., *J. chem. Phys.*, **33**, 1310 (1960).
 Kielich, S., *Physica*, **28**, 511 (1962a); *Bull. Acad. Polon. Sci. Ser. Sci. math. astron. phys.*, **10**, 485, 493, 657 (1962b); *Physica*, **28**, 1116 (1962c); *Acta phys. Polon.*, **22**, 65 (1962d); **24**, 399 (1963).
 Mazur, P. and Postma, B. J., *Physica*, **25**, 251 (1959).
 Pople, J. A., *Proc. Roy. Soc. (London)*, A **215**, 67 (1952); **221**, 508 (1954).