THE SECOND VIRIAL COEFFICIENT FOR POLAR GAS MIXTURES

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The present paper deals with the theory of the second virial coefficient $B(T) = \Sigma\Sigma x_i x_j B^{(ij)}$ of the equation of state for polar gas mixtures. General formulas for the virial coefficients $B^{(ij)}$ are derived, containing, in addition to the contribution arising from the presence of intermolecular central forces, others due to the various tensorial forces acting between polar molecules: dipole-dipole, dipole-quadrupole, dipole-octupole and quadrupole-quadrupole interaction; moreover, dipole-induced dipole and quadrupole-induced dipole inductive interaction. The formulas are given in two forms: the general form as derived by means of tensor formalism and relating to polar molecules of arbitrary symmetry and arbitrary central forces potential, and one obtained by specialization for molecules presenting the axial symmetry and a Lennard-Jones (6—12) potential. In particular, the latter formulas are applied to one-, two- and three-component gas mixtures.

1. Introduction

Kamerlingh Onnes proposed an equation of state for imperfect gases, of the form of the virial expansion

$$\frac{pV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \dots \tag{1.1}$$

wherein p, V, R and T are the pressure, molar volume, gas constant and Kelvin temperature, respectively. $B(T)$, $C(T)$, $D(T)$, etc. are the second, third, fourth, ... virial coefficient. If the values of the virial coefficients B, C and D accounting for the experimental divergences of imperfect gases from the equation of state of a perfect gas are known, statistical mechanics will provide valuable information on the intermolecular forces.

The classical theory and quantitative discussions of the second virial coefficient $B(T)$ for intermolecular forces of various types are given in papers by Lennard-Jones (1924), Stockmayer (1941), Rowlinson (1949), Pople (1954), Buckingham and Pople (1955), Stogryn and Hirschfelder (1959), and others (see, Hirschfelder et al. 1954).

The third and fourth virial coefficients, $C(T)$ and $D(T)$, are discussed by Rushbrooke and Scoins (1951), Kihara (1953), and the fourth — by Katsura (1959).

The present paper brings the theory and a discussion of the second virial coefficient for a mixture of polar gases. In computing $B(T)$, account is taken of the intermolecular central forces and of various types of directional forces, the latter being considered to represent a perturbation in the central forces. In order that the formulas be correct for molecules of arbitrary symmetry, all contributions to $B(T)$ from the directional intermolecular forces are computed by means of the tensor formalism. The general formulas thus derived for $B(T)$, which hold for arbitrary central forces, are discussed for the cases of dipole and quadrupole molecules having the axial symmetry, on the simplifying assumption of central forces given by a Lennard-Jones (6—12) potential. The latter formulas are applied to certain special cases, namely, a one-component gas, a two-component gas mixture and, finally, a three-component gas.

2. The general expression for the second virial coefficient of a mixture of gases

In the case of a gas mixture, the second virial coefficient $B(T)$ in the equation of state (1.1) is given as follows:

$$B(T) = \sum_{i=1}^{\nu} \sum_{j=1}^{\nu} x_i x_j B^{(ij)}, \tag{2.1}$$

wherein ν is the number of components of the mixture, and x_i is the mole fraction of the i-th component in the gas mixture, $\sum_{i=1}^{\nu} x_i = 1$.

Classical statistical mechanics yields $B(T)$ in the form of

$$B(T) = -\frac{N}{2\Omega^2} \iiint \left\{ e^{-\frac{u_{ij}^{(12)}}{kT}} - 1 \right\} dr_{ij}^{(12)} d\omega_i^{(1)} d\omega_j^{(2)} \tag{2.2}$$

with N denoting Avogadro's number, k — Boltzmann's constant, T — the Kelvin temperature, $u_{ij}^{(12)}$ — the total potential energy of interaction between the molecules "1" and "2" of species "i" and species "j", $r_{ij}^{(12)}$ — the vector connecting their centres, and $\omega_i^{(1)}$, $\omega_j^{(2)}$ — variables describing their orientation; $\Omega = \int d\omega_i = \int d\omega_j$.

The total potential energy can be expressed in the form

$$u_{ij}^{(12)} = u^{(0)}(r_{ij}) + V_{ij}^{(12)}(r_{ij}, \omega_i, \omega_j) \tag{2.3}$$

$u^{(0)}(r_{ij})$ being the potential energy due to the central forces (angle-independent potentials), and $V_{ij}^{(12)}$ — the energy due to the tensorial forces (angle-dependent potentials). Considering $V_{ij}^{(12)}$ to represent a perturbation in the energy $u^{(0)}(r_{ij})$, the second virial coefficient of eq. (2.2) can be put in the form of an expansion:

$$B^{(ij)} = B_0^{(ij)} + \sum_{n=1}^{\infty} B_n^{(ij)}, \tag{2.4}$$

wherein the zero term

$$B_0^{(ij)} = -2\pi N \int_0^{\infty} \left\{ e^{-\frac{u^{(0)}(r_{ij})}{kT}} - 1 \right\} r_{ij}^2 dr_{ij} \tag{2.5}$$

is the second virial coefficient for a central force field $u^{(0)}(r_{ij})$, and the subsequent terms given by

$$B_n^{(ij)} = -\frac{N}{2\Omega^2 n!} \left(-\frac{1}{kT}\right)^n \iiint \{V_{ij}^{(12)}(r_{ij}, \omega_i, \omega_j)\}^n e^{-\frac{u^{(0)}(r_{ij})}{kT}} d\mathbf{r}_{ij}^{(12)} d\omega_i^{(1)} dw_j^{(2)} \qquad (2.6)$$

are contributions thereto resulting from the tensorial (directional) forces.

For the sake of simplicity, $u^{(0)}(r_{ij})$ will be assumed throughout the present investigation to be given by the following Lennard-Jones potential (1924) (see, Hirschfelder et al. 1954):

$$u^{(0)}(r_{ij}) = 4\varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6 \right\} \qquad (2.7)$$

wherein the parameters σ_{ij} and ε_{ij}, possessing the dimensions of a length and energy, respectively, are constants characteristic of the chemical species of the interacting molecules. The force constants between unlike molecules relate to those between like molecules by the empirical combining rules

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j); \qquad \varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{\frac{1}{2}}. \qquad (2.8)$$

Applying the Lennard-Jones method (1924), and by eq. (2.7), B_0 is obtained in the form (see, Buckingham and Pople, 1955)

$$B_0^{(ij)} = \tfrac{2}{3}\pi N\sigma_{ij}^3 F(y_{ij}), \qquad (2.9)$$

wherein

$$F(y_{ij}) = \frac{1}{y_{ij}^2}\left\{ H_{12}(y_{ij}) - \frac{1}{2}H_6(y_{ij})\right\}; \qquad y_{ij}^2 = \frac{4\varepsilon_{ij}}{kT} \qquad (2.10)$$

is a function tabulated in the monograph by Hirschfelder et al. (1954), whereas

$$H_n(y_{ij}) = 12y_{ij}^4\sigma_{ij}^{n-3} \int_0^\infty r_{ij}^{-n} e^{-y_{ij}^2\left\{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right\}} r_{ij}^2 dr_{ij} = y_{ij}^{\frac{27-n}{6}} \sum_{m=0}^\infty \Gamma\left(\frac{6m+n-3}{12}\right)\frac{y_{ij}^m}{m!} \qquad (2.11)$$

are functions introduced by Pople (1954) and tabulated by Buckingham and Pople (1955) for all n and for values of y from 0.6 to 3.2.

In the subsequent sections, the terms $B_n^{(ij)}$ as given in general by eq. (2.6) will be computed for various directional forces acting between two dipole or two quadrupole molecules.

3. Dipole anisotropically polarizable molecules

The potential energy of the electrostatic interaction between two unlike, dipolar, anisotropically polarizable molecules is given by the expression (cf., Barker, 1953)

$$V_{ij}^{(12)} = \mu_\alpha^{(1,i)}\mu_\beta^{(2,j)}T_{\alpha\beta}^{(ij)} - \tfrac{1}{2}(\mu_\alpha^{(1,i)}\alpha_{\beta\gamma}^{(2,j)}\mu_\delta^{(1,i)} + \mu_\alpha^{(2,j)}\alpha_{\beta\gamma}^{(1,i)}\mu_\delta^{(2,j)})T_{\alpha\beta}^{(ij)}T_{\gamma\delta}^{(ij)} +$$
$$+ \mu_\alpha^{(1,i)}\alpha_{\beta\gamma}^{(2,j)}\alpha_{\delta\varepsilon}^{(1,i)}\mu_\eta^{(2,j)}T_{\alpha\beta}^{(ij)}T_{\gamma\delta}^{(ij)}T_{\varepsilon\eta}^{(ij)} - \dots \qquad (3.1)$$

wherein $\mu_\alpha^{(i)}$ is the α-component of the permanent electric dipole moment of a molecule of species "i", and $\alpha_{\alpha\beta}^{(i)}$ is its electric polarizability tensor. The first term in the foregoing expression accounts for dipole-dipole interaction (Keesom), whereas the subsequent ones are those of dipole-induced dipole interaction (Debye, Falkenhagen). The tensor $T_{\alpha\beta}^{(ij)}$ accounting for dipole-dipole interaction is defined as follows:

$$T_{\alpha\beta}^{(ij)} = -\frac{1}{r_{ij}^5}\{3r_{ij\alpha}r_{ij\beta} - r_{ij}^2\delta_{\alpha\beta}\},\tag{3.2}$$

where $\delta_{\alpha\beta}$ is the substitution tensor, unity if $\alpha = \beta$ and zero when $\alpha \neq \beta$.

By the method explained in the Appendix, substitution of (3.1) in eq. (2.6) yields the consecutive terms of the expansion (2.4)[1] in the form:

$$B_1^{(ij)} = -\frac{N}{2kT}(\alpha_{(i)}\mu_{(j)}^2 + \mu_{(i)}^2\alpha_{(j)})\langle r_{ij}^{-6}\rangle,$$

$$B_2^{(ij)} = -\frac{\mu_{(i)}^2\mu_{(j)}^2 N}{6k^2T^2}\langle r_{ij}^{-6}\rangle,$$

$$B_3^{(ij)} = -\frac{N}{75\,k^3T^3}\{15(\alpha_{(i)}\mu_{(j)}^2 + \mu_{(i)}^2\alpha_{(j)})\,\mu_{(i)}^2\mu_{(j)}^2 + 2(3\alpha_{\alpha\beta}^{(i)}\mu_\alpha^{(i)}\mu_\beta^{(i)} -$$
$$- \alpha_{\alpha\alpha}^{(i)}\mu_\beta^{(i)}\mu_\beta^{(i)})\,\mu_{(j)}^4 + 2(3\alpha_{\alpha\beta}^{(j)}\mu_\alpha^{(j)}\mu_\beta^{(j)} - \alpha_{\alpha\alpha}^{(j)}\mu_\beta^{(j)}\mu_\beta^{(j)})\,\mu_{(i)}^4\}\langle r_{ij}^{-12}\rangle,$$

$$B_4^{(ij)} = -\frac{\mu_{(i)}^4\mu_{(j)}^4 N}{50k^4T^4}\langle r_{ij}^{-12}\rangle,$$

$$B_5^{(ij)} = -\frac{29\,\mu_{(i)}^2\mu_{(j)}^2 N}{22050k^5T^5}\{21(\alpha_{(i)}\mu_{(j)}^2 + \mu_{(i)}^2\alpha_{(j)})\,\mu_{(i)}^2\mu_{(j)}^2 +$$
$$+ 4\,(3\alpha_{\alpha\beta}^{(i)}\mu_\alpha^{(i)}\mu_\beta^{(i)} - \alpha_{\alpha\alpha}^{(i)}\mu_\beta^{(i)}\mu_\beta^{(i)})\,\mu_{(j)}^4 + 4\,(3\alpha_{\alpha\beta}^{(j)}\mu_\alpha^{(j)}\mu_\beta^{(j)} - \alpha_{\alpha\alpha}^{(j)}\mu_\beta^{(j)}\mu_\beta^{(j)})\,\mu_{(i)}^4\}\langle r_{ij}^{-18}\rangle,$$

$$B_6^{(ij)} = -\frac{29\,\mu_{(i)}^6\mu_{(j)}^6 N}{22050\,k^6T^6}\langle r_{ij}^{-18}\rangle,\dots,\tag{3.3}$$

where $\alpha_{(i)} = \frac{1}{3}\alpha_{\alpha\alpha}^{(i)}$ is the mean polarizability of a molecule of species "i", and the brackets $\langle\ \rangle$ denote the mean value dependent solely on the model of central forces, i.e.

$$\langle r_{ij}^{-n}\rangle = 4\pi\int_0^\infty r_{ij}^{-n}e^{-\frac{u^{(0)}(r_{ij})}{kT}}r_{ij}^2 dr_{ij}.\tag{3.4}$$

The expressions (3.3) are correct for a central forces potential $u^{(0)}(r_{ij})$ of arbitrary form. Assuming, for simplicity, Lennard-Jones (6—12) potentials, we have, by (2.11),

$$\langle r_{ij}^{-n}\rangle = \frac{\pi\sigma_{ij}^{3-n}}{3\,y_{ij}^4}H_n(y_{ij}),\tag{3.5}$$

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[1] In computing the expressions (3.3), of all the terms due to the energy of inductive interaction between the molecules only the ones linear in the polarizability α have been retained.

whence the second virial coefficient given by the expansion (2.4) can be written in the form

$$B^{(ij)} = B_0^{(ij)} + {}_{\text{dip-dip}} B^{(ij)} + {}_{\text{dip-ind dip}} B^{(ij)}, \tag{3.6}$$

wherein $B_0^{(ij)}$ is given by eq. (2.9).

The contribution to the second virial coefficient $B^{(ij)}$ from dipole-dipole interaction is of the form

$$_{\text{dip-dip}} B^{(ij)} = - \frac{\pi \mu_{(i)}^2 \mu_{(j)}^2 N}{288 \, \sigma_{ij}^3 \varepsilon_{ij}^2} \left\{ H_6(y_{ij}) + \frac{3 \, \mu_{(i)}^2 \mu_{(j)}^2 y_{ij}^4}{400 \, \sigma_{ij}^6 \varepsilon_{ij}^2} \, H_{12}(y_{ij}) + \right.$$
$$\left. + \frac{29 \, \mu_{(i)}^4 \mu_{(j)}^4 y_{ij}^8}{940800 \, \sigma_{ij}^{12} \varepsilon_{ij}^4} \, H_{18}(y_{ij}) + ... \right\} \tag{3.7}$$

The last contribution to $B^{(ij)}$ in (3.3) results from inductive interaction between the molecules; if these have the axial symmetry, it assumes the form

$$_{\text{dip-ind dip}} B^{(ij)} = - \frac{\pi N}{24 \, \sigma_{ij}^3 \varepsilon_{ij} y_{ij}^2} \left\{ (\alpha_{(i)} \mu_{(j)}^2 + \mu_{(i)}^2 \alpha_{(j)}) H_6(y_{ij}) + \right.$$
$$+ \frac{\mu_{(i)}^2 \mu_{(j)}^2 y_{ij}^4}{40 \, \sigma_{ij}^6 \varepsilon_{ij}^2} \left[\alpha_{(i)} \left(1 + \frac{4}{5} \, \delta_{(i)} \right) \mu_{(j)}^2 + \mu_{(i)}^2 \left(1 + \frac{4}{5} \, \delta_{(j)} \right) \alpha_{(j)} \right] H_{12}(y_{ij}) +$$
$$\left. + \frac{29 \, \mu_{(i)}^4 \mu_{(j)}^4 y_{ij}^8}{134400 \, \sigma_{ij}^{12} \varepsilon_{ij}^4} \left[\alpha_{(i)} \left(1 + \frac{8}{7} \, \delta_{(i)} \right) \mu_{(j)}^2 + \mu_{(i)}^2 \left(1 + \frac{8}{7} \, \delta_{(j)} \right) \alpha_{(j)} \right] H_{18}(y_{ij}) + ... \right\}, \tag{3.8}$$

here, the quantities

$$\alpha_{(i)} = \frac{1}{3} \, (\alpha_{\|}^{(i)} + 2\alpha_{\perp}^{(i)}) \quad \text{and} \quad \delta_{(i)} = \frac{\alpha_{\|}^{(i)} - \alpha_{\perp}^{(i)}}{3\alpha_{(i)}} \tag{3.9}$$

denote the mean polarizability and the anisotropy of electric polarizability of a molecule of species "i", respectively, $\alpha_{\|}^{(i)}$ being its polarizability along the axis of symmetry, and $\alpha_{\perp}^{(i)}$ — that perpendicular to the axis.

From (3.8), the anisotropy of polarizability of the molecule, $\delta_{(i)}$, is seen to have no bearing on the second virial coefficient in the first approximation; it plays a part in higher ones only.

If, in particular, the dipolar molecules are isotropically polarizable, $\delta = 0$, eq. (3.8) reduces to

$$_{\text{dip-ind dip}} B^{(ij)} = - \frac{\pi N}{24 \, \sigma_{ij}^3 \varepsilon_{ij} y_{ij}^2} \, (\alpha_{(i)} \mu_{(j)}^2 + \mu_{(i)}^2 \alpha_{(j)}) \left\{ H_6(y_{ij}) + \right.$$
$$\left. + \frac{\mu_{(i)}^2 \mu_{(j)}^2 y_{ij}^4}{40 \, \sigma_{ij}^6 \varepsilon_{ij}^2} \, H_{12}(y_{ij}) + \frac{29 \, \mu_{(i)}^4 \mu_{(j)}^4 y_{ij}^8}{134400 \, \sigma_{ij}^{12} \varepsilon_{ij}^4} \, H_{18}(y_{ij}) + ... \right\}. \tag{3.10}$$

4. Anisotropically polarizable quadrupole molecules

In the case of a gas mixture consisting of anisotropic molecules which, though not dipolar, possess a permanent electric quadrupole moment, we have (see, Kielich 1960)

$$V_{ij}^{(12)} = - \frac{1}{9} \, \Theta_{\alpha\beta}^{(1,i)} \Theta_{\gamma\delta}^{(2,j)} T_{\alpha\beta\gamma\delta}^{(ij)} - \frac{1}{18} (\alpha_{\alpha\beta}^{(1,i)} \Theta_{\gamma\delta}^{(2,j)} \Theta_{\varepsilon\eta}^{(2,j)} + \alpha_{\alpha\beta}^{(2,j)} \Theta_{\gamma\delta}^{(1,i)} \Theta_{\varepsilon\eta}^{(1,i)}) \, T_{\alpha\gamma\delta}^{(ij)} T_{\beta\varepsilon\eta}^{(ij)} - ..., \tag{4.1}$$

here, $\Theta_{\alpha\beta}^{(i)}$ is the tensor of the quadrupole moment of the molecule of species "i", given by

$$\Theta_{\alpha\beta}^{(i)} = \tfrac{1}{2} \sum_n e_n^{(i)} (3 r_{n\alpha}^{(i)} r_{n\beta}^{(i)} - r_{ni}^2 \delta_{\alpha\beta}), \tag{4.2}$$

with $e_n^{(i)}$ denoting the n-th electric charge of the molecule of species "i", and $\boldsymbol{r}_n^{(i)}$ — its radius vector.

The first term in eq. (4.1) accounts for the potential energy of quadrupole-quadrupole interaction, whereas the second is that of quadrupole-induced dipole interaction. The respective tensors $T_{\alpha\beta\gamma}^{(ij)}$ and $T_{\alpha\beta\gamma\delta}^{(ij)}$ describing these interactions are determined by eqs. (A.10) (see, Appendix).

By eqs. (4.1) and (2.6), the consecutive terms in the second virial coefficient are obtained as follows (cf. eqs. (A.8) in Appendix):

$$B_1^{(ij)} = -\frac{N}{2kT} \{ \alpha_{(i)} \Theta_{\alpha\beta}^{(j)} \Theta_{\alpha\beta}^{(j)} + \Theta_{\alpha\beta}^{(i)} \Theta_{\alpha\beta}^{(i)} \alpha_{(j)} \} \langle r_{ij}^{-8} \rangle,$$

$$B_2^{(ij)} = -\frac{14N}{45\,k^2 T^2} \Theta_{\alpha\beta}^{(i)} \Theta_{\alpha\beta}^{(i)} \Theta_{\gamma\delta}^{(j)} \Theta_{\gamma\delta}^{(j)} \langle r_{ij}^{-10} \rangle +$$

$$+ \frac{8N}{35\,k^2 T^2} \{ \alpha_{\alpha\beta}^{(i)} \Theta_{\alpha\beta}^{(i)} \Theta_{\gamma\delta}^{(j)} \Theta_{\gamma\varepsilon}^{(j)} \Theta_{\delta\varepsilon}^{(j)} + \Theta_{\alpha\beta}^{(i)} \Theta_{\alpha\gamma}^{(i)} \Theta_{\beta\gamma}^{(i)} \alpha_{\delta\varepsilon}^{(j)} \Theta_{\delta\varepsilon}^{(j)} \} \langle r_{ij}^{-13} \rangle,$$

$$B_3^{(ij)} = \frac{64N}{245 k^3 T^3} \Theta_{\alpha\beta}^{(i)} \Theta_{\alpha\gamma}^{(i)} \Theta_{\beta\gamma}^{(i)} \Theta_{\delta\varepsilon}^{(j)} \Theta_{\delta\eta}^{(j)} \Theta_{\varepsilon\eta}^{(j)} \langle r_{ij}^{-15} \rangle, \ \dots \tag{4.3}$$

With respect to the foregoing expressions, the second virial coefficient of eq. (2.4) assumes the form

$$B^{(ij)} = B_0^{(ij)} + {}_{\text{quadr-quadr}} B^{(ij)} + {}_{\text{quadr-ind dip}} B^{(ij)}. \tag{4.4}$$

In the case of molecules possessing the axial symmetry, and for a (6—12) Lennard-Jones potential, the contributions from quadrupole-quadrupole and quadrupole-induced dipole interaction are, herein, of the form

$${}_{\text{quadr-quadr}} B^{(ij)} = -\frac{7\pi \Theta_{(i)}^2 \Theta_{(j)}^2 N}{480 \sigma_{ij}^7 \varepsilon_{ij}^2} \left\{ H_{10}(y_{ij}) - \frac{18 \Theta_{(i)} \Theta_{(j)} y_{ij}^2}{343 \sigma_{ij}^5 \varepsilon_{ij}} H_{15}(y_{ij}) + \dots \right\}, \tag{4.5}$$

$${}_{\text{quadr-ind dip}} B^{(ij)} = -\frac{\pi N}{16 \sigma_{ij}^5 \varepsilon_{ij} y_{ij}^2} \left\{ (\alpha_{(i)} \Theta_{(j)}^2 + \Theta_{(i)}^2 \alpha_{(j)}) H_8(y_{ij}) - \right.$$

$$\left. - \frac{6 \Theta_{(i)} \Theta_{(j)} y_{ij}^2}{35 \sigma_{ij}^5 \varepsilon_{ij}} (\alpha_{(i)} \delta_{(i)} \Theta_{(j)}^2 + \Theta_{(i)}^2 \alpha_{(j)} \delta_{(j)}) H_{13}(y_{ij}) + \dots \right\}, \tag{4.6}$$

$\Theta_{(i)}$ is the quadrupole moment of an axially symmetric molecule of species "i", which, by the general definition of eq. (4.2), is given by

$$\Theta_{(i)} = \Theta_{33}^{(i)} = \tfrac{1}{2} \sum_n e_n^{(i)} (3 \mathscr{Z}_{ni}^2 - r_{ni}^2), \tag{4.7}$$

where $\mathscr{Z}_{ni}$ is measured along the molecular axis, and

$$\Theta_{33}^{(i)} = -2 \Theta_{11}^{(i)} = -2 \Theta_{22}^{(i)}. \tag{4.8}$$

5. Multi-polar molecules

Let us now consider the case of interacting molecules of a gas mixture presenting, quite generally, a dipole, quadrupole and octupole moment. The potential energy of multipole interaction between two unlike polar molecules is given by the following expression (see Kielich 1960):

$$V_{ij}^{(12)} = \mu_\alpha^{(1,i)}\mu_\beta^{(2,j)}T_{\alpha\beta}^{(ij)} + \tfrac{1}{3}(\mu_\alpha^{(1,i)}\Theta_{\beta\gamma}^{(2,j)} - \Theta_{\alpha\beta}^{(1,i)}\mu_\gamma^{(2,j)})T_{\alpha\beta\gamma}^{(ij)} +$$

$$+ \tfrac{1}{45}(3\mu_\alpha^{(1,i)}\Omega_{\beta\gamma\delta}^{(2,j)} - 5\Theta_{\alpha\beta}^{(1,i)}\Theta_{\gamma\delta}^{(2,j)} + 3\Omega_{\alpha\beta\gamma}^{(1,i)}\mu_\delta^{(2,j)})T_{\alpha\beta\gamma\delta}^{(ij)} + \dots, \qquad (5.1)$$

wherein $\Omega_{\alpha\beta\gamma}^{(i)}$ is the tensor of the octupole moment of the molecule of species "i", defined as (see, Buckingham 1959)

$$\Omega_{\alpha\beta\gamma}^{(i)} = \tfrac{1}{2}\sum_n e_n^{(i)}\{5r_{n\alpha}^{(i)}r_{n\beta}^{'(i)}r_{n\gamma}^{(i)} - r_{ni}^2(r_{n\alpha}^{(i)}\delta_{\beta\gamma} + r_{n\beta}^{(i)}\delta_{\gamma\alpha} + r_{n\gamma}^{(i)}\delta_{\alpha\beta})\}. \qquad (5.2)$$

The terms in eq. (5.1) determine the potential energy of dipole-dipole (r_{ij}^{-3}), dipole-quadrupole (r_{ij}^{-4}), and, furthermore, dipole-octupole and quadrupole-quadrupole (r_{ij}^{-5}) interaction, respectively.

Analogously, by (5.1), eq. (2.6) yields the following contributions to the second virial coefficient (see, formulas (A-9) in Appendix):

$$B_1^{(ij)} = 0,$$

$$B_2^{(ij)} = -\frac{\mu_{(i)}^2\mu_{(j)}^2 N}{6\,k^2T^2}\langle r_{ij}^{-6}\rangle - \frac{N}{6\,k^2T^2}(\mu_{(i)}^2\Theta_{\alpha\beta}^{(j)}\Theta_{\alpha\beta}^{(j)} + \Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\beta}^{(i)}\mu_{(j)}^2)\langle r_{ij}^{-8}\rangle -$$

$$- \frac{2N}{45\,k^2T^2}\{3\,\mu_{(i)}^2\Omega_{\alpha\beta\gamma}^{(j)}\Omega_{\alpha\beta\gamma}^{(j)} + 7\,\Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\beta}^{(i)}\Theta_{\gamma\delta}^{(j)}\Theta_{\gamma\delta}^{(j)} + 3\,\Omega_{\alpha\beta\gamma}^{(i)}\Omega_{\alpha\beta\gamma}^{(i)}\mu_{(j)}^2\}\langle r_{ij}^{-10}\rangle,$$

$$B_3^{(ij)} = \frac{2N}{5\,k^3T^3}\mu_\alpha^{(i)}\mu_\beta^{(i)}\Theta_{\alpha\beta}^{(i)}\Theta_{\gamma\delta}^{(j)}\mu_\gamma^{(j)}\mu_\delta^{(j)}\langle r_{ij}^{-11}\rangle +$$

$$+ \frac{8N}{35\,k^3T^3}\{\mu_\alpha^{(i)}\mu_\beta^{(i)}\Theta_{\alpha\beta}^{(i)}\Theta_{\gamma\delta}^{(j)}\Theta_{\gamma\varepsilon}^{(j)}\Theta_{\delta\varepsilon}^{(j)} + \Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\gamma}^{(i)}\Theta_{\beta\gamma}^{(i)}\mu_\delta^{(j)}\mu_\varepsilon^{(i)}\Theta_{\delta\varepsilon}^{(j)}\}\langle r_{ij}^{-13}\rangle +$$

$$+ \frac{64N}{245\,k^3T^3}\Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\gamma}^{(i)}\Theta_{\beta\gamma}^{(i)}\Theta_{\delta\varepsilon}^{(j)}\Theta_{\delta\eta}^{(j)}\Theta_{\varepsilon\eta}^{(j)}\langle r_{ij}^{-15}\rangle,$$

$$B_4^{(ij)} = -\frac{\mu_{(i)}^4\mu_{(j)}^4 N}{50\,k^4T^4}\langle r_{ij}^{-12}\rangle - \frac{6N}{175k^4T^4}\{\Omega_{\alpha\beta\gamma}^{(i)}\mu_\alpha^{(i)}\mu_\beta^{(i)}\mu_\gamma^{(i)}\mu_{(j)}^4 + \mu_{(i)}^4\Omega_{\alpha\beta\gamma}^{(j)}\mu_\alpha^{(j)}\mu_\beta^{(j)}\mu_\gamma^{(j)}\}\langle r_{ij}^{-14}\rangle - \dots$$

$$\qquad (5.3)$$

On substitution of the foregoing expressions in eq. (2.4), the second virial coefficient for polar gases is obtained in the form

$$B^{(ij)} = B_0^{(ij)} + {}_{\text{dip—dip}}B^{(ij)} + {}_{\text{dip—quadr}}B^{(ij)} + {}_{\text{quadr—quadr}}B^{(ij)} + {}_{\text{dip—octup}}B^{(ij)}, \qquad (5.4)$$

where the first, second and fourth terms are given by eqs. (2.9), (3.7) and (4.5), respectively. The two remaining ones, accounting for dipole-quadrupole and dipole-octupole interaction,

are, in the case of axially symmetrical molecules, given by the following expressions:

$$_{\text{dip—quadr}}B^{(ij)} = -\frac{\pi N}{192\sigma_{ij}^5\varepsilon_{ij}^2}\left\{(\mu_{(i)}^2\Theta_{(j)}^2 + \Theta_{(i)}^2\mu_{(j)}^2)\left[H_8(y_{ij}) -\right.\right.$$

$$\left.\left. -\frac{6\Theta_{(i)}\Theta_{(j)}y_{ij}^2}{35\sigma_{ij}^5\varepsilon_{ij}}H_{13}(y_{ij}) + ...\right] - \frac{2\mu_{(i)}^2\Theta_{(i)}\Theta_{(j)}\mu_{(j)}^2 y_{ij}^2}{5\sigma_{ij}^3\varepsilon_{ij}}H_{11}(y_{ij}) + ...\right\},\tag{5.5}$$

$$_{\text{dip-octup}}B^{(ij)} = -\frac{\pi N}{144\sigma_{ij}^7\varepsilon_{ij}^2}\left\{(\mu_{(i)}^2\Omega_{(j)}^2 + \Omega_{(i)}^2\mu_{(j)}^2)\,H_{10}(y_{ij}) +\right.$$

$$\left. + \frac{9\mu_{(i)}^3\mu_{(j)}^3 y_{ij}^4}{1400\sigma_{ij}^4\varepsilon_{ij}^2}(\mu_{(i)}\Omega_{(j)} + \Omega_{(i)}\mu_{(j)})\,H_{14}(y_{ij}) + ...\right\},\tag{5.6}$$

wherein $\Omega_{(i)}$ is the octupole moment of the axially symmetrical molecule of species "i":

$$\Omega_{(i)} = \Omega_{333}^{(i)} = \tfrac{1}{2}\sum_n e_n^{(i)}\mathscr{Z}_{ni}(5\,\mathscr{Z}_{ni}^2 - 3r_{ni}^2),\tag{5.7}$$

with

$$\Omega_{333}^{(i)} = -2\Omega_{311}^{(i)} = -2\Omega_{322}^{(i)}.\tag{5.8}$$

6. Applications to special cases

We shall now proceed to apply the formulas for $B(T)$ derived in sections 2—5 to some special cases.

(i) *One-component gas.* For a gas consisting of a single species, the contributions to the second virial coefficient computed in sections 2—5 assume the form

$$B_0 = \tfrac{2}{3}\pi\sigma^3 NF(y),\tag{6.1}$$

$$_{\text{dip—dip}}B = -\frac{\pi\mu^4 N}{288\sigma^3\varepsilon^2}\left\{H_6(y) + \frac{3\mu^4 y^4}{400\sigma^6\varepsilon^2}H_{12}(y) + \frac{29\mu^8 y^8}{940\,800\sigma^{12}\varepsilon^4}H_{18}(y) + ...\right\},\tag{6.2}$$

$$_{\text{dip—ind dip}}B = -\frac{N\alpha\mu^2 N}{12\sigma^3\varepsilon y^2}\left\{H_6(y) + \frac{\mu^4 y^4}{40\sigma^6\varepsilon^2}H_{12}(y) + \frac{29\mu^8 y^8}{134\,400\sigma^{12}\varepsilon^4}H_{18}(y) +\right.$$

$$\left. + \frac{\delta\mu^4 y^4}{50\sigma^6\varepsilon^2}\left[H_{12}(y) + \frac{29\mu^4 y^4}{2352\sigma^6\varepsilon^2}H_{18}(y) + ...\right] + ...\right\},\tag{6.3}$$

$$_{\text{quadr—quadr}}B = -\frac{7\pi\Theta^4 N}{480\sigma^7\varepsilon^2}\left\{H_{10}(y) - \frac{18\Theta^2 y^2}{343\sigma^5\varepsilon}H_{15}(y) + ...\right\},\tag{6.4}$$

$$_{\text{quadr—ind dip}}B = -\frac{\pi\alpha\Theta^2 N}{8\sigma^5\varepsilon y^2}\left\{H_8(y) - \frac{6\delta\Theta^2 y^2}{35\sigma^5\varepsilon}H_{13}(y) + ...\right\},\tag{6.5}$$

$$_{\text{dip-quadr}}B = -\frac{\pi\mu^2\Theta^2 N}{96\sigma^5\varepsilon^2}\left\{H_8(y) - \frac{\mu^2 y^2}{5\sigma^3\varepsilon}H_{11}(y) - \frac{6\Theta^2 y^2}{35\sigma^5\varepsilon}H_{13}(y) + ...\right\},\tag{6.6}$$

$$_{\text{dip-octup}}B = -\frac{\pi\mu^2\Omega N}{72\sigma^7\varepsilon^2}\left\{\Omega H_{10}(y) + \frac{9\mu^5 y^4}{1400\sigma^4\varepsilon^2}H_{14}(y) + ...\right\}.\tag{6.7}$$

The expressions (6.1), (6.2), (6.4) and (6.6) are identical with the ones derived by Buckingham and Pople (1955).

In an earlier paper (Kielich 1960), the second virial coefficient B_S of the molecular constant of light scattering was computed for the molecular models considered in the foregoing Sections; for molecules of constant polarizability, the isotropic contribution to B_S is related to $B(T)$ by the formula

$$B_S^{is} = - \frac{16\,\pi^4\alpha^2 N}{\lambda^4}\, B(T), \tag{6.8}$$

wherein λ is the light wavelength.

(ii) Binary gas mixture. By eq. (2.1), the second virial coefficient of a binary gas mixture is of the form

$$B(T) = x_1^2 B^{(11)} + 2\,x_1 x_2 B^{(12)} + x_2^2 B^{(22)}. \tag{6.9}$$

In particular, the molecules of one component of the mixture being spherical and those of the other quadrupolar, the expressions derived in Sections 2—5 assume the form

$$B = \tfrac{2}{3}\pi\sigma_{11}^3 N F(y_{11}), \tag{6.10}$$

$$B^{(12)} = \frac{2}{3}\,\pi\sigma_{12}^3 N \left\{ F(y_{12}) - \frac{3\,\alpha_{(1)}\Theta_{(2)}^2}{32\,\sigma_{12}^8 \varepsilon_{12} y_{12}^2}\, H_8(y_{12}) \right\}, \tag{6.11}$$

$$B^{(22)} = \frac{2}{3}\,\pi\sigma_{22}^3 N \left\{ F(y_{22}) - \frac{3\,\alpha_{(2)}\Theta_{(2)}^2}{16\,\sigma_{22}^8 \varepsilon_{22} y_{22}^2} \left[H_8(y_{22}) - \frac{6\,\delta_{(2)}\Theta_{(2)}^2 y_{22}^2}{35\,\sigma_{22}^5 \varepsilon_{22}}\, H_{13}(y_{22}) \right] - \right.$$
$$\left. - \frac{7\Theta_{(2)}^4}{320\,\sigma_{22}^{10}\varepsilon_{22}^2} \left[H_{10}(y_{22}) - \frac{18\,\Theta_{(2)}^2 y_{22}^2}{343\,\sigma_{22}^5 \varepsilon_{22}}\, H_{15}(y_{22}) \right] \right\}. \tag{6.12}$$

Eq. (6.11) was derived previously and applied to an argon-carbon dioxide mixture by Buckingham (1959).

(iii) Ternary gas mixture. In the case of a gas mixture consisting of three unlike components, the second virial coefficient has the form

$$B(T) = x_1^2 B^{(11)} + x_2^2 B^{(22)} + x_3^2 B^{(33)} + 2(x_1 x_2 B^{(12)} + x_1 x_3 B^{(13)} + x_2 x_3 B^{(23)}). \tag{6.13}$$

E.g. assume the molecules of component 1 to be spherical ($\alpha_{(1)} \neq 0$, $\mu_{(1)} = \Theta_{(1)} = 0$), those of component 2 to be quadrupolar ($\mu_{(2)} = 0$, $\Theta_{(2)} \neq 0$), and those of component 3 — dipolar ($\mu_{(3)} \neq 0$, $\Theta_{(3)} = 0$). The expressions derived in sections 2—5 for $B^{(11)}$, $B^{(12)}$ and $B^{(22)}$ once more yield eqs. (6.10), (6.11) and (6.12), whereas those for $B^{(13)}$, $B^{(23)}$ and $B^{(33)}$ lead to the following formulas:

$$B^{(13)} = \frac{2}{3}\,\pi\sigma_{13}^3 N \left\{ F(y_{13}) - \frac{\alpha_{(1)}\mu_{(3)}^2}{16\,\sigma_{13}^3 \varepsilon_{13} y_{13}^2}\, H_6(y_{13}) \right\}, \tag{6.14}$$

$$B^{(23)} = \frac{2}{3}\,\pi\sigma_{23}^3 N \left\{ F(y_{23}) - \frac{\alpha_{(2)}\mu_{(3)}^2}{16\,\sigma_{23}^6 \varepsilon_{23} y_{23}^2}\, H_6(y_{23}) - \right.$$
$$\left. - \frac{3\Theta_{(2)}^2}{32\sigma_{23}^8 \varepsilon_{23} y_{23}^2} \left[\alpha_{(3)} + \frac{\mu_{(3)}^2 y_{23}^2}{12\varepsilon_{23}} \right] H_8(y_{23}) \right\}, \tag{6.15}$$

$$B^{(33)} = \frac{2}{3}\pi\sigma_{33}^3 N \left\{ F(y_{33}) - \frac{\alpha_{(3)}\mu_{(3)}^2}{8\sigma_{33}^6\varepsilon_{33}y_{33}^2} \left[H_6(y_{33}) + \frac{\mu_{(3)}^4 y_{33}^4}{40\sigma_{33}^6\varepsilon_{33}^2} \left(1 + \frac{4}{5}\delta_{(3)} \right) H_{12}(y_{33}) + \right. \right.$$

$$\left. + \frac{29\mu_{(3)}^8 y_{33}^8}{134400\sigma_{33}^{12}\varepsilon_{33}^8} \left(1 + \frac{8}{7}\delta_{(3)} \right) H_{18}(y_{33}) + \dots \right] - \frac{\mu_{(3)}^4}{192\sigma_{33}^6\varepsilon_{33}^2} \left[H_6(y_{33}) + \right.$$

$$\left. \left. + \frac{3\mu_{(3)}^4 y_{33}^4}{400\sigma_{33}^6\varepsilon_{33}^2} H_{12}(y_{33}) + \frac{29\mu_{(3)}^8 y_{33}^8}{940800\sigma_{33}^{12}\varepsilon_{33}^4} H_{18}(y_{33}) + \dots \right] + \dots \right\}. \qquad (6.16)$$

The expressions derived in sections 2—6 for the second virial coefficient can be easily applied to more complex gas mixtures. We refrain here, however, from considering these special cases.

APPENDIX

The method of isotropic averageing of V_{ij}^n

In order to compute the terms in $B_n^{(ij)}$ as given by eq. (2.6), it is convenient to carry out integration over all possible configurations of the molecules first, i.e. to compute the mean isotropic values of the respective powers of their tensorial interaction energy:

$$\overline{V_{ij}^n} = \frac{1}{\Omega^2} \int\int \{V_{ij}^{(12)}(r_{ij}, \omega_i, \omega_j)\}^n d\omega_i d\omega_j. \qquad (A.1)$$

On inspection of the various forms of the energy V_{ij} in sections 3—5, it will be seen that computation of $\overline{V_{ij}^n}$ implies averageing of the respective products of the tensors μ_α, $\alpha_{\alpha\beta}$, $\Theta_{\alpha\beta}$ and $\Omega_{\alpha\beta\gamma}$. This can be effected as follows: Let $T_{\alpha\beta}...$ be a tensor of arbitrary order, given in a fixed coordinate system in three-dimensional space (X_α), $\alpha = 1, 2, 3$, and $T_{\sigma\tau\nu}...$ — one given in a coordinate system in motion with respect to the first one, (X_σ), $\sigma = 1, 2, 3$. The tensors are related by the transformation formula

$$T_{\sigma\tau\nu} \dots = \omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma} \dots T_{\alpha\beta\gamma} \dots , \qquad (A.2)$$

wherein, for rectangular coordinate systems (X_σ) and (X_α), the transformation coefficients $\omega_{\sigma\alpha}$, ... have the meaning of cosines of the angles subtended by the respective coordinate axes of the systems. The directional cosines $\omega_{\sigma\alpha}$ and $\omega_{\tau\beta}$ fulfill the conditions of normalization and orthogonality:

$$\omega_{\sigma\alpha}\omega_{\sigma\beta} = \delta_{\alpha\beta}, \quad \omega_{\sigma\alpha}\omega_{\tau\alpha} = \delta_{\sigma\tau}. \qquad (A.3)$$

Thus, the problem of averageing the tensor $T_{\sigma\tau\nu}$ ...reduces to that of averageing the corresponding functions of the directional cosines over all possible orientations of the system (X_σ) with respect to (X_α). Tensorial summation over the indices $\sigma, \tau \nu, \dots$ leads to the following mean values of the functions of the directional cosines:

$$\overline{\omega_{\sigma\alpha}\omega_{\tau\beta}} = \tfrac{1}{3}\delta_{\alpha\beta}\delta_{\sigma\tau},$$

$$\overline{\omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\omega_{\varrho\delta}} = \tfrac{1}{30}\{(4\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma})\delta_{\sigma\tau}\delta_{\nu\varrho} +$$

$$+ (4\delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma} - \delta_{\alpha\beta}\delta_{\gamma\delta})\delta_{\sigma\nu}\delta_{\tau\varrho} + (4\delta_{\alpha\delta}\delta_{\beta\gamma} - \delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\gamma}\delta_{\beta\delta})\delta_{\sigma\varrho}\delta_{\tau\nu}\},$$

$$\omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\omega_{\varrho\delta}\omega_{\lambda\varepsilon}\omega_{\mu\eta} = \tfrac{1}{210}\{x_1\delta_{\sigma\tau}\delta_{\nu\varrho}\delta_{\lambda\mu} + x_2\delta_{\sigma\tau}\delta_{\nu\lambda}\delta_{\varrho\mu} + x_3\delta_{\sigma\tau}\delta_{\nu\mu}\delta_{\lambda\varrho} + x_4\delta_{\nu\varrho}\delta_{\sigma\lambda}\delta_{\tau\mu} +$$
$$+\, x_5\delta_{\nu\varrho}\delta_{\sigma\mu}\delta_{\tau\lambda} + x_6\delta_{\lambda\mu}\delta_{\sigma\nu}\delta_{\tau\varrho} + x_7\delta_{\lambda\mu}\delta_{\sigma\varrho}\delta_{\tau\nu} + x_8\delta_{\sigma\nu}\delta_{\tau\lambda}\delta_{\varrho\mu} + x_9\delta_{\sigma\nu}\delta_{\tau\mu}\delta_{\lambda\varrho} + x_{10}\delta_{\tau\nu}\delta_{\sigma\lambda}\delta_{\varrho\mu} +$$
$$+\, x_{11}\delta_{\tau\nu}\delta_{\sigma\mu}\delta_{\varrho\lambda} + x_{12}\delta_{\sigma\varrho}\delta_{\tau\lambda}\delta_{\nu\mu} + x_{13}\delta_{\sigma\varrho}\delta_{\tau\mu}\delta_{\nu\lambda} + x_{14}\delta_{\tau\varrho}\delta_{\sigma\lambda}\delta_{\nu\mu} + x_{15}\delta_{\tau\varrho}\delta_{\sigma\mu}\delta_{\nu\lambda}\}, \qquad (A.4)$$

with the notation

$$x_1 = 16a_1 - 5(a_2 + a_3 + a_4 + a_5 + a_6 + a_7) + 2(a_8 + a_9 + a_{10} + a_{11} + a_{12} + a_{13} + a_{14} + a_{15}),$$
$$x_2 = 16a_2 - 5(a_1 + a_3 + a_8 + a_{10} + a_{13} + a_{15}) + 2(a_4 + a_5 + a_6 + a_7 + a_9 + a_{11} + a_{12} + a_{14}),$$
$$x_3 = 16a_3 - 5(a_1 + a_2 + a_9 + a_{11} + a_{12} + a_{14}) + 2(a_4 + a_5 + a_6 + a_7 + a_8 + a_{10} + a_{13} + a_{15}),$$
$$x_4 = 16a_4 - 5(a_1 + a_5 + a_9 + a_{10} + a_{13} + a_{14}) + 2(a_2 + a_3 + a_6 + a_7 + a_8 + a_{11} + a_{12} + a_{15}),$$
$$x_5 = 16a_5 - 5(a_1 + a_4 + a_8 + a_{11} + a_{12} + a_{15}) + 2(a_2 + a_3 + a_6 + a_7 + a_9 + a_{10} + a_{13} + a_{14}),$$
$$x_6 = 16a_6 - 5(a_1 + a_7 + a_8 + a_9 + a_{14} + a_{15}) + 2(a_2 + a_3 + a_4 + a_5 + a_{10} + a_{11} + a_{12} + a_{13}),$$
$$x_7 = 16a_7 - 5(a_1 + a_6 + a_{10} + a_{11} + a_{12} + a_{13}) + 2(a_2 + a_3 + a_4 + a_5 + a_8 + a_9 + a_{14} + a_{15}),$$
$$x_8 = 16a_8 - 5(a_2 + a_5 + a_6 + a_9 + a_{10} + a_{12}) + 2(a_1 + a_3 + a_4 + a_7 + a_{11} + a_{13} + a_{14} + a_{15}),$$
$$x_9 = 16a_9 - 5(a_3 + a_4 + a_6 + a_8 + a_{11} + a_{13}) + 2(a_1 + a_2 + a_5 + a_7 + a_{10} + a_{12} + a_{14} + a_{15}),$$
$$x_{10} = 16a_{10} - 5(a_2 + a_4 + a_7 + a_8 + a_{11} + a_{14}) + 2(a_1 + a_3 + a_5 + a_6 + a_9 + a_{12} + a_{13} + a_{15}),$$
$$x_{11} = 16a_{11} - 5(a_3 + a_5 + a_7 + a_9 + a_{10} + a_{15}) + 2(a_1 + a_2 + a_4 + a_6 + a_8 + a_{12} + a_{13} + a_{14}),$$
$$x_{12} = 16a_{12} - 5(a_3 + a_5 + a_7 + a_8 + a_{13} + a_{14}) + 2(a_1 + a_2 + a_4 + a_6 + a_9 + a_{10} + a_{11} + a_{15}),$$
$$x_{13} = 16a_{13} - 5(a_2 + a_4 + a_7 + a_9 + a_{12} + a_{15}) + 2(a_1 + a_3 + a_5 + a_6 + a_8 + a_{10} + a_{11} + a_{14}),$$
$$x_{14} = 16a_{14} - 5(a_3 + a_4 + a_6 + a_{10} + a_{12} + a_{15}) + 2(a_1 + a_2 + a_5 + a_7 + a_8 + a_9 + a_{11} + a_{13}),$$
$$x_{15} = 16a_{15} - 5(a_2 + a_5 + a_6 + a_{11} + a_{13} + a_{14}) + 2(a_1 + a_3 + a_4 + a_7 + a_8 + a_9 + a_{10} + a_{12}), \quad (A.5)$$

and

$$a_1 = \delta_{\alpha\beta}\delta_{\gamma\delta}\delta_{\varepsilon\eta}, \quad a_2 = \delta_{\alpha\beta}\delta_{\gamma\varepsilon}\delta_{\delta\eta}, \quad a_3 = \delta_{\alpha\beta}\delta_{\gamma\eta}\delta_{\delta\varepsilon},$$
$$a_4 = \delta_{\gamma\delta}\delta_{\alpha\varepsilon}\delta_{\beta\eta}, \quad a_5 = \delta_{\gamma\delta}\delta_{\alpha\eta}\delta_{\beta\varepsilon}, \quad a_6 = \delta_{\varepsilon\eta}\delta_{\alpha\gamma}\delta_{\beta\delta},$$
$$a_7 = \delta_{\varepsilon\eta}\delta_{\alpha\delta}\delta_{\beta\gamma}, \quad a_8 = \delta_{\alpha\gamma}\delta_{\beta\varepsilon}\delta_{\delta\eta}, \quad a_9 = \delta_{\alpha\gamma}\delta_{\beta\eta}\delta_{\delta\varepsilon},$$
$$a_{10} = \delta_{\alpha\varepsilon}\delta_{\beta\gamma}\delta_{\delta\eta}, \quad a_{11} = \delta_{\alpha\eta}\delta_{\beta\gamma}\delta_{\delta\varepsilon}, \quad a_{12} = \delta_{\alpha\delta}\delta_{\beta\varepsilon}\delta_{\gamma\eta},$$
$$a_{13} = \delta_{\alpha\delta}\delta_{\beta\eta}\delta_{\gamma\varepsilon}, \quad a_{14} = \delta_{\alpha\varepsilon}\delta_{\gamma\eta}\delta_{\beta\delta}, \quad a_{15} = \delta_{\alpha\eta}\delta_{\gamma\varepsilon}\delta_{\beta\delta}. \qquad (A.6)$$

With the formulas (A.4), the mean isotropic values of the respective powers of the energy V_{ij} given in sections 3—5 are readily computed.

Hence, if the interaction potential energy of a pair of dipolar molecules is given by eq. (3.1), the following mean values result (in computing the terms accounting for the part of the energy due to inductive interaction, only the ones linear in α have been retained):

$$\overline{V_{ij}} = -\tfrac{1}{6}(\alpha_{(i)}\mu_{(j)}^2 + \mu_{(i)}^2\alpha_{(j)})\, T_{\sigma\tau}^{(ij)}T_{\sigma\tau}^{(ij)},$$

$$\overline{V_{ij}^2} = \tfrac{1}{9}\mu_{(i)}^2\mu_{(j)}^2 T_{\sigma\tau}^{(ij)}T_{\sigma\tau}^{(ij)},$$

$$\overline{V_{ij}^3} = -\tfrac{1}{450}\{15(\alpha_{(i)}\mu_{(j)}^2 + \mu_{(i)}^2\alpha_{(j)})\mu_{(i)}^2\mu_{(j)}^2 + 2(3\alpha_{\alpha\beta}^{(i)}\mu_\alpha^{(i)}\mu_\beta^{(i)} - \alpha_{\alpha\alpha}^{(i)}\mu_\beta^{(i)}\mu_\beta^{(i)})\mu_{(j)}^4 +$$
$$+\, 2(3\alpha_{\alpha\beta}^{(j)}\mu_\alpha^{(j)}\mu_\beta^{(j)} - \alpha_{\alpha\alpha}^{(j)}\mu_\beta^{(j)}\mu_\beta^{(j)})\mu_{(i)}^4\}\, \{T_{\sigma\tau}^{(ij)}T_{\sigma\tau}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\nu\varrho}^{(ij)} + 2T_{\sigma\tau}^{(ij)}T_{\tau\nu}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\varrho\sigma}^{(ij)}\},$$

$$\overline{V_{ij}^4} = \tfrac{1}{75}\,\mu_{(i)}^4\mu_{(j)}^4\,\{T_{\sigma\tau}^{(ij)}T_{\sigma\tau}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\nu\varrho}^{(ij)} + 2T_{\sigma\tau}^{(ij)}T_{\tau\nu}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\varrho\sigma}^{(ij)}\},$$

$$\overline{V_{ij}^5} = -\,\frac{\mu_{(i)}^2\mu_{(j)}^2}{4410}\,\{21\,(\alpha_{(i)}\mu_{(j)}^2 + \mu_{(i)}^2\alpha_{(j)})\,\mu_{(i)}^2\mu_{(j)}^2\,+$$

$$+\;4(3\alpha_{\alpha\beta}^{(i)}\mu_{\alpha}^{(i)}\mu_{\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)}\mu_{\beta}^{(i)}\mu_{\beta}^{(i)})\mu_{(j)}^4 + 4(3\alpha_{\alpha\beta}^{(j)}\mu_{\alpha}^{(j)}\mu_{\beta}^{(j)}\,-$$

$$-\;\alpha_{\alpha\alpha}^{(j)}\mu_{\beta}^{(j)}\mu_{\beta}^{(j)})\mu_{(i)}^4\}\,\{T_{\sigma\tau}^{(ij)}T_{\sigma\tau}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\lambda\mu}^{(ij)}T_{\lambda\mu}^{(ij)}\,+$$

$$+\;6T_{\sigma t}^{(ij)}T_{\sigma\tau}^{(ij)}T_{\nu\varrho}^{'(ij)}T_{\varrho\lambda}^{(ij)}T_{\lambda\mu}^{(ij)}T_{\mu\nu}^{(ij)} + 8T_{\sigma\tau}^{(ij)}T_{\tau\nu}^{(ij)}T_{\nu\varrho}^{'(ij)}T_{\varrho\lambda}^{(ij)}T_{\lambda\mu}^{(ij)}T_{\mu\sigma}^{(ij)}\},$$

$$\overline{V_{ij}^6} = \frac{\mu_{(i)}^6\mu_{(j)}^6}{735}\,\{T_{\sigma\tau}^{(ij)}T_{\sigma\tau}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\lambda\mu}^{(ij)}T_{\lambda\mu}^{(ij)}\,+$$

$$+\;6T_{\sigma\tau}^{(ij)}T_{\sigma\tau}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\varrho\lambda}^{(ij)}T_{\lambda\mu}^{(ij)}T_{\mu\nu}^{(ij)} + 8T_{\sigma\tau}^{(ij)}T_{\tau\nu}^{(ij)}T_{\nu\varrho}^{(ij')}T_{\varrho\lambda}^{(ij)}T_{\lambda\mu}^{(ij)}T_{\mu\sigma}^{(ij)}\}. \tag{A.7}$$

Likewise, for quadrupole molecules, eq. (4.1) yields

$$\overline{V}_{ij} = -\,\tfrac{1}{90}\,\{\alpha_{(i)}\Theta_{\alpha\beta}^{(j)}\Theta_{\alpha\beta}^{(j)} + \Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\beta}^{(i)}\alpha_{(j)}\}\,T_{\sigma\tau\nu}^{(ij)}T_{\sigma\tau\nu}^{(ij)},$$

$$\overline{V}_{ij}^2 = \tfrac{1}{2025}\,\Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\beta}^{(i)}\Theta_{\gamma\delta}^{(j)}\Theta_{\gamma\delta}^{(j)}T_{\sigma\tau\nu\varrho}^{(ij)}T_{\sigma\tau\nu\varrho}^{(ij)}\,+$$

$$+\,\tfrac{4}{4725}\,\{\alpha_{\alpha\beta}^{(i)}\Theta_{\alpha\beta}^{(i)}\Theta_{\gamma\delta}^{(j)}\Theta_{\gamma\varepsilon}^{(j)}\Theta_{\delta\varepsilon}^{(j)} + \Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\gamma}^{(i)}\Theta_{\beta\gamma}^{(i)}\alpha_{\delta\varepsilon}^{(j)}\Theta_{\delta\varepsilon}^{(j)}\}\,T_{\sigma\sigma\lambda}^{(ij)}T_{\nu\varrho\lambda}^{(ij)}T_{\sigma\tau\nu\varrho}^{(ij)},$$

$$\overline{V}_{ij}^3 = -\,\tfrac{16}{99225}\,\Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\gamma}^{(i)}\Theta_{\beta\gamma}^{(i)}\Theta_{\delta\varepsilon}^{(j)}\Theta_{\delta\eta}^{(j)}\Theta_{\varepsilon\eta}^{(j)}T_{\sigma\tau\nu\varrho}^{(ij)}T_{\nu\varrho\lambda\mu}^{(ij)}T_{\lambda\mu\sigma\tau}^{(ij)}. \tag{A.8}$$

For the case of polar molecules we have, by eqs. (5.1) and (A.4),

$$\overline{V}_{ij} = 0,$$

$$\overline{V}_{ij}^2 = \tfrac{1}{9}\,\mu_{(i)}^2\mu_{(j)}^2 T_{\sigma\tau}^{(ij)}T_{\sigma\tau}^{(ij)} + \tfrac{1}{135}\,(\mu_{(i)}^2\Theta_{\alpha\beta}^{(j)}\Theta_{\alpha\beta}^{(j)} + \Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\beta}^{(i)}\mu_{(j)}^2)\,T_{\sigma\tau\nu}^{(ij)}T_{\sigma\tau\nu}^{(ij)}\,+$$

$$+\,\tfrac{1}{14175}\,\{3\mu_{(i)}^2\Omega_{\alpha\beta\gamma}^{(j)}\Omega_{\alpha\beta\gamma}^{(j)} + 7\Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\beta}^{(i)}\Theta_{\gamma\delta}^{(j)}\Theta_{\gamma\delta}^{(j)}\,+$$

$$+\,3\Omega_{\alpha\beta\gamma}^{(i)}\Omega_{\alpha\beta\gamma}^{(i)}\mu_{(j)}^2\}\,T_{\sigma\tau\nu\varrho}^{(ij)}T_{\sigma\tau\nu\varrho}^{'(ij)},$$

$$\overline{V}_{ij}^3 = -\,\tfrac{1}{75}\,\mu_{\alpha}^{(i)}\mu_{\beta}^{(i)}\Theta_{\alpha\beta}^{(i)}\Theta_{\gamma\delta}^{(j)}\mu_{\gamma}^{(j)}\mu_{\delta}^{(j)}\{T_{\sigma\tau}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\sigma\tau\nu\varrho}^{(ij)} + 2\,T_{\sigma\tau}^{(ij)}T_{\sigma\nu\varrho}^{(ij)}T_{\tau\nu\varrho}^{(ij)}\}\,-$$

$$-\,\tfrac{4}{1575}\,\{\mu_{\alpha}^{(i)}\mu_{\beta}^{(i)}\Theta_{\alpha\beta}^{(i)}\Theta_{\gamma\delta}^{(j)}\Theta_{\gamma\varepsilon}^{(j)}\Theta_{\delta\varepsilon}^{(j)} + \Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\gamma}^{(i)}\Theta_{\beta\gamma}^{(i)}\mu_{\delta}^{(j)}\mu_{\varepsilon}^{(j)}\Theta_{\delta\varepsilon}^{(j)}\}\,T_{\sigma\tau\lambda}^{(ij)}T_{\nu\varrho\lambda}^{(ij)}T_{\sigma\tau\nu\varrho}^{(ij)}\,-$$

$$-\,\tfrac{16}{99225}\,\Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\gamma}^{(i)}\Theta_{\beta\gamma}^{(i)}\Theta_{\delta\varepsilon}^{(j)}\Theta_{\delta\eta}^{(j)}\Theta_{\varepsilon\eta}^{(j)}T_{\sigma\tau\nu\varrho}^{(ij)}T_{\nu\varrho\lambda\mu}^{(ij)}T_{\lambda\mu\sigma\tau}^{(ij)},$$

$$\overline{V}_{ij}^4 = \tfrac{1}{75}\,\mu_{(i)}^4\mu_{(i)}^4\{T_{\sigma\tau}^{(ij)}T_{\sigma\tau}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\nu\varrho}^{(ij)} + 2\,T_{\sigma\tau}^{(ij)}T_{\tau\nu}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\varrho\sigma}^{(ij)}\}\,+$$

$$+\,\tfrac{4}{525}\,\{\Omega_{\alpha\beta\gamma}^{(i)}\mu_{\alpha}^{(i)}\mu_{\beta}^{(i)}\mu_{\gamma}^{(i)}\mu_{(j)}^4 + \mu_{(i)}^4\Omega_{\alpha\beta\gamma}^{(j)}\mu_{\alpha}^{(j)}\mu_{\beta}^{(j)}\mu_{\gamma}^{(j)}\}T_{\sigma\tau}^{(ij)}T_{\nu\lambda}^{(ij)}T_{\varrho\lambda}^{(ij)}T_{\sigma\tau\nu\varrho}^{(ij)} + \dots \tag{A.9}$$

The tensors $T_{\sigma\tau}^{(ij)}$, $T_{\sigma\tau\nu}^{(ij)}$ and $T_{\sigma\tau\nu\varrho}^{(ij)}$ appearing in the foregoing expressions and characterizing dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interaction, respectively, are defined as follows (see, Pople 1952):

$$T_{\sigma\tau}^{(ij)} = -\,\frac{1}{r_{ij}^5}\,\{3\,r_{ij\sigma}r_{ij\tau} - r_{ij}^2\delta_{\sigma\tau}\},$$

$$T_{\sigma\tau\nu}^{(ij)} = \frac{3}{r_{ij}^7} \{5\, r_{ij\sigma}r_{ij\tau}r_{ij\nu} - r_{ij}^2 \left(r_{ij\sigma}\delta_{\tau\nu} + r_{ij\tau}\delta_{\nu\sigma} + r_{ij\nu}\delta_{\sigma\tau}\right)\},$$

$$T_{\sigma\tau\nu\varrho}^{(ij)} = -\frac{3}{r_{ij}^9} \{35\, r_{ij\sigma}r_{ij\tau}r_{ij\nu}r_{ij\varrho} - 5\, r_{ij}^2 \left(r_{ij\sigma}r_{ij\tau}\delta_{\nu\varrho} + \right.$$

$$+ r_{ij\sigma}r_{ij\nu}\delta_{\tau\varrho} + r_{ij\sigma}r_{ij\varrho}\delta_{\nu\tau} + r_{ij\tau}r_{ij\nu}\delta_{\varrho\sigma} + r_{ij\tau}r_{ij\varrho}\delta_{\sigma\nu} +$$

$$+ \left. r_{ij\nu}r_{ij\varrho}\delta_{\sigma\tau}\right) + r_{ij}^4 (\delta_{\sigma\tau}\delta_{\nu\varrho} + \delta_{\sigma\nu}\delta_{\tau\varrho} + \delta_{\sigma\varrho}\delta_{\nu\tau})\}. \tag{A.10}$$

With the foregoing definitions, we have, for the various products of the tensors $T_{\sigma\tau}^{(ij)}$, $T_{\sigma\tau\nu}^{(ij)}$ and $T_{\sigma\tau\nu\varrho}^{(ij)}$ appearing in eqs. (A.7) — (A.9),

$$T_{\sigma\tau}^{(ij)}T_{\sigma\tau}^{(ij)} = 6r_{ij}^{-6}, \qquad T_{\sigma\tau}^{(ij)}T_{\tau\nu}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\varrho\sigma}^{(ij)} = 18r_{ij}^{-12},$$

$$T_{\sigma\tau}^{(ij)}T_{\tau\nu}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\varrho\lambda}^{(ij)}T_{\lambda\mu}^{(ij)}T_{\mu\sigma}^{(ij)} = 66r_{ij}^{-18}, \qquad T_{\sigma\tau\nu}^{(ij)}T_{\sigma\tau\nu}^{(ij)} = 90r_{ij}^{-8},$$

$$T_{\sigma\tau}^{(ij)}T_{\sigma\nu\varrho}^{(ij)}T_{\tau\nu\varrho}^{(ij)} = -72r_{ij}^{-11}, \qquad T_{\sigma\tau}^{(ij)}T_{\nu\varrho}^{(ij)}T_{\sigma\tau\nu\varrho}^{(ij)} = -216r_{ij}^{-11},$$

$$T_{\sigma\tau\nu\varrho}^{(ij)}T_{\sigma\tau\nu\varrho}^{(ij)} = 2520r_{ij}^{-10}, \qquad T_{\sigma\tau\lambda}^{(ij)}T_{\nu\varrho\lambda}^{(ij)}T_{\sigma\tau\nu\varrho}^{(ij)} = -1080r_{ij}^{-13},$$

$$T_{\sigma\tau}^{(ij)}T_{\nu\lambda}^{(ij)}T_{\varrho\lambda}^{(ij)}T_{\sigma\tau\nu\varrho}^{(ij)} = 216r_{ij}^{-14},$$

$$T_{\sigma\tau\nu\varrho}^{(ij)}T_{\nu\varrho\lambda\mu}^{(ij)}T_{\lambda\mu\sigma\tau}^{(ij)} = -19440r_{ij}^{-15}. \tag{A.11}$$

In applying the expressions of eqs. (A.7) — (A.9) to molecules having the axial symmetry, use is made of the following identities:

$$3\alpha_{\alpha\beta}\mu_{\alpha}\mu_{\beta} - \alpha_{\alpha\alpha}\mu_{\beta}\mu_{\beta} = 6\alpha\delta\mu^2,$$

$$\alpha_{\alpha\beta}\Theta_{\alpha\beta} = 3\alpha\delta\Theta, \qquad \Theta_{\alpha\beta}\Theta_{\alpha\beta} = \tfrac{3}{2}\Theta^2,$$

$$\mu_{\alpha}\mu_{\beta}\Theta_{\alpha\beta} = \mu^2\Theta, \qquad \Theta_{\alpha\beta}\Theta_{\alpha\gamma}\Theta_{\beta\gamma} = \tfrac{3}{4}\Theta^3,$$

$$\mu_{\alpha}\mu_{\beta}\mu_{\gamma}\Omega_{\alpha\beta\gamma} = \mu^3\Omega, \qquad \Omega_{\alpha\beta\gamma}\Omega_{\alpha\beta\gamma} = \tfrac{5}{2}\Omega^2. \tag{A.12}$$

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