

SECOND VIRIAL COEFFICIENTS FOR UNLIKE NON-DIPOLAR MOLECULES

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Synopsis

The present paper brings the calculation and a discussion of the second virial coefficients B_{ij} for unlike non-dipolar molecules of a gas mixture. In computing B_{ij} , account is taken of the intermolecular central forces and of various types of tensorial forces acting between two non-dipolar molecules possessing, in general, a permanent quadrupole or octopole moment. In order that the formulas shall be correct for molecules of arbitrary symmetry, all contributions to B_{ij} from the directional intermolecular forces are computed by means of the tensor formalism. The general formulas thus derived for B_{ij} are discussed for the cases of linear or planar molecules having the axial symmetry, and for that of tetrahedral molecules. The latter formulas for the Lennard-Jones (6 : 12) potential are applied to one-, two-, and three-component gas mixtures. Numerical estimations of the second virial coefficients are given for the gases He, H₂, N₂, O₂, CO₂ and CH₄, and for their mixtures.

§ 1. *Introduction.* The Kamerlingh Onnes virial expansion for the equation of state of a gas mixture is of the form:

$$\frac{pV}{RT} = \sum_{i=1}^{\nu} x_i + \frac{1}{V} \sum_{i=1}^{\nu} \sum_{j=1}^{\nu} x_i x_j B_{ij} + \frac{1}{V^2} \sum_{i=1}^{\nu} \sum_{j=1}^{\nu} \sum_{k=1}^{\nu} x_i x_j x_k C_{ijk} + \dots \quad (1)$$

Here p , V and T are the pressure, molar volume and the Kelvin temperature, respectively; x_i is the mole fraction of the i -th component of the mixture and ν the number of all components. B_{ij} is the second virial coefficient describing the interaction between two molecules of species i and species j . The third virial coefficient C_{ijk} characterizes the three-body interactions of the molecules of species i , j and k , respectively.

According to classical statistical mechanics, the second virial coefficient B_{ij} can be expanded in the form^{1) 2)}:

$$B_{ij} = B_{ij}^{\text{centr}} - \frac{N}{2\Omega^2} \sum_{n=1}^{\infty} \frac{1}{n!} \left(-\frac{1}{kT} \right)^n \iiint v_{ij}^n e^{-\frac{u(r_{ij})}{kT}} dr_{ij} d\omega_i d\omega_j, \quad (2)$$

where

$$B_{ij}^{\text{centr}} = -2\pi N \int_0^{\infty} \left\{ e^{-\frac{u(r_{ij})}{kT}} - 1 \right\} r_{ij}^2 dr_{ij} \quad (3)$$

is the second virial coefficient for a central force field $u(r_{ij})$; r_{ij} is the distance between the centres of the i -th and j -th molecules, $v_{ij} = v(r_{ij}, \omega_i, \omega_j)$ being the tensorial potential energy (angle-dependent potentials) of interaction between the two molecules of species \mathbf{i} and species \mathbf{j} , and the variables ω_i and ω_j describing their orientation; $\Omega = \int d\omega_i = \int d\omega_j$.

In the present paper we calculate the second virial coefficient B_{ij} given by (2) for non-dipolar molecules of arbitrary symmetry and possessing permanent quadrupole and octopole moments.

§ 2. *Calculation of B_{ij} for the general case.* Let us consider the case of interacting molecules of a gas mixture which, though not dipolar, possess permanent electric quadrupole and octopole moments, defined by the tensors^{2) 3)}

$$\Theta_{\alpha\beta}^{(i)} = \frac{1}{2} \sum_n e_i^{(n)} (3r_{i\alpha}^{(n)} r_{i\beta}^{(n)} - r_{in}^2 \delta_{\alpha\beta}), \quad (4)$$

$$\Omega_{\alpha\beta\gamma}^{(i)} = \frac{1}{2} \sum_n e_i^{(n)} \{ 5r_{i\alpha}^{(n)} r_{i\beta}^{(n)} r_{i\gamma}^{(n)} - r_{in}^2 (r_{i\alpha}^{(n)} \delta_{\beta\gamma} + r_{i\beta}^{(n)} \delta_{\gamma\alpha} + r_{i\gamma}^{(n)} \delta_{\alpha\beta}) \}, \quad (5)$$

where $e_i^{(n)}$ is the n -th electric charge of the molecule of species i , and $r_i^{(n)}$ – its radius vector; $\delta_{\alpha\beta}$ is the unit tensor, and $\alpha, \beta = 1, 2, 3$.

The tensorial potential energy of mutual interaction of two unlike anisotropically polarizable non-dipolar molecules is given by the general expression⁴⁾:

$$\begin{aligned} v_{ij} = & -\frac{\hbar}{4} \frac{v_i v_j}{v_i + v_j} (\alpha_{\alpha\beta}^{(i)} \alpha_{\gamma\delta}^{(j)} - \alpha_i \alpha_j \delta_{\alpha\beta} \delta_{\gamma\delta}) T_{\alpha\gamma}^{(ij)} T_{\beta\delta}^{(ij)} - \frac{1}{9} \Theta_{\alpha\beta}^{(i)} \Theta_{\gamma\delta}^{(j)} T_{\alpha\beta\gamma\delta}^{(ij)} - \\ & - \frac{1}{18} (\alpha_{\alpha\beta}^{(i)} \Theta_{\gamma\delta}^{(j)} \Theta_{\epsilon\eta}^{(j)} + \alpha_{\alpha\beta}^{(j)} \Theta_{\gamma\delta}^{(i)} \Theta_{\epsilon\eta}^{(i)}) T_{\alpha\gamma\delta}^{(ij)} T_{\beta\epsilon\eta}^{(ij)} + \\ & + \frac{1}{45} (\alpha_{\alpha\beta}^{(i)} \Theta_{\gamma\delta}^{(j)} \Omega_{\epsilon\eta\lambda}^{(j)} + \alpha_{\alpha\beta}^{(j)} \Theta_{\gamma\delta}^{(i)} \Omega_{\epsilon\eta\lambda}^{(i)}) T_{\alpha\gamma\delta}^{(ij)} T_{\beta\epsilon\eta\lambda}^{(ij)} - \\ & - \frac{1}{500} (\alpha_{\alpha\beta}^{(i)} \Omega_{\gamma\delta\epsilon}^{(j)} \Omega_{\eta\lambda\mu}^{(j)} + \alpha_{\alpha\beta}^{(j)} \Omega_{\gamma\delta\epsilon}^{(i)} \Omega_{\eta\lambda\mu}^{(i)}) T_{\alpha\gamma\delta\epsilon}^{(ij)} T_{\beta\eta\lambda\mu}^{(ij)} - \dots, \quad (6) \end{aligned}$$

where $\alpha_{\alpha\beta}^{(i)}$ denotes the electric polarizability tensor of the isolated molecule of species i , and α_i and v_i – its mean polarizability and frequency of electron oscillations, respectively; \hbar is the Planck constant.

The first term in the foregoing expression determines the interaction energy resulting from the anisotropic dispersion forces; it was discussed by De Boer and Heller⁵⁾, London⁶⁾ and De Boer⁷⁾. The second term in eq. (6) accounts for the potential energy of quadrupole-quadrupole interaction (Keesom⁸⁾), whereas the subsequent ones are those of induced dipole-quadrupole (Debye⁹⁾, Keesom⁸⁾), induced dipole-octopole etc. inductive interactions. The tensors $T_{\alpha\beta}^{(ij)}$, $T_{\alpha\beta\gamma}^{(ij)}$ and $T_{\alpha\beta\gamma\delta}^{(ij)}$ characterizing the dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions are given by^{2) 10)}

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

On substitution of the expression (6) in eq. (2), and by the method used in the preceding papers^{2) 11)}, the second virial coefficient is obtained in the form:

$$B_{ij} = B_{ij}^{\text{centr}} + B_{ij}^{\text{disp}} + B_{ij}^{\text{quad-quad}} + B_{ij}^{\text{ind. dip-quad}} + B_{ij}^{\text{ind. dip-octop.}} \quad (8)$$

Here, B_{ij}^{disp} is the contribution to B_{ij} resulting from anisotropic dispersive forces and having the form

$$\begin{aligned}
B_{ij}^{\text{disp}} &= -\frac{h^2N}{14400k^2T^2} \left(\frac{v_i v_j}{v_i + v_j} \right)^2 \{10\alpha_{\alpha\alpha}^{(i)}\alpha_{\beta\beta}^{(i)}(3\alpha_{\gamma\delta}^{(j)}\alpha_{\gamma\delta}^{(j)} - \alpha_{\gamma\gamma}^{(j)}\alpha_{\delta\delta}^{(j)}) + \\
&\quad + 19(3\alpha_{\alpha\beta}^{(i)}\alpha_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)}\alpha_{\beta\beta}^{(i)})(3\alpha_{\gamma\delta}^{(j)}\alpha_{\gamma\delta}^{(j)} - \alpha_{\gamma\gamma}^{(j)}\alpha_{\delta\delta}^{(j)}) + \\
&\quad + 10(3\alpha_{\alpha\beta}^{(i)}\alpha_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)}\alpha_{\beta\beta}^{(i)})\alpha_{\gamma\gamma}^{(j)}\alpha_{\delta\delta}^{(j)}\langle r_{ij}^{-12} \rangle + \dots \quad (9)
\end{aligned}$$

where we have used the notation

$$\langle r_{ij}^{-n} \rangle = \int r_{ij}^{-n} e^{-\frac{u(r_{ij})}{kT}} d\mathbf{r}_{ij}. \quad (10)$$

The remaining contributions to B_{ij} in (8), which result from quadrupole-quadrupole, induced dipole-quadrupole and induced dipole-octopole interaction, are given by the following expressions;

$$\begin{aligned}
B_{ij}^{\text{quad-quad}} &= -\frac{14N}{45k^2T^2} \Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\beta}^{(i)}\Theta_{\gamma\delta}^{(j)}\Theta_{\gamma\delta}^{(j)} \langle r_{ij}^{-10} \rangle + \\
&\quad + \frac{64N}{245k^3T^3} \Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\gamma}^{(i)}\Theta_{\beta\gamma}^{(i)}\Theta_{\delta\epsilon}^{(j)}\Theta_{\delta\eta}^{(j)}\Theta_{\epsilon\eta}^{(j)} \langle r_{ij}^{-15} \rangle - \dots, \quad (11)
\end{aligned}$$

$$\begin{aligned}
B_{ij}^{\text{ind. dip-quad}} &= -\frac{N}{2kT} (\alpha_i\Theta_{\alpha\beta}^{(j)}\Theta_{\alpha\beta}^{(j)} + \alpha_j\Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\beta}^{(i)}) \langle r_{ij}^{-8} \rangle + \\
&\quad + \frac{3hN}{25k^2T^2} \frac{v_i v_j}{v_i + v_j} \alpha_{\alpha\beta}^{(i)}\Theta_{\alpha\beta}^{(i)}\alpha_{\gamma\delta}^{(j)}\Theta_{\gamma\delta}^{(j)} \langle r_{ij}^{-11} \rangle + \\
&\quad + \frac{8N}{35k^2T^2} (\alpha_{\alpha\beta}^{(i)}\Theta_{\alpha\beta}^{(i)}\Theta_{\gamma\delta}^{(j)}\Theta_{\gamma\epsilon}^{(j)}\Theta_{\delta\epsilon}^{(j)} + \alpha_{\alpha\beta}^{(j)}\Theta_{\alpha\beta}^{(j)}\Theta_{\gamma\delta}^{(i)}\Theta_{\gamma\epsilon}^{(i)}\Theta_{\delta\epsilon}^{(i)}) \langle r_{ij}^{-13} \rangle - \dots, \quad (12)
\end{aligned}$$

$$B_{ij}^{\text{ind. dip-octop}} = -\frac{9N}{25kT} (\alpha_i\Omega_{\alpha\beta\gamma}^{(j)}\Omega_{\alpha\beta\gamma}^{(j)} + \alpha_j\Omega_{\alpha\beta\gamma}^{(i)}\Omega_{\alpha\beta\gamma}^{(i)}) \langle r_{ij}^{-10} \rangle + \dots \quad (13)$$

For linear or planar molecules having the axial symmetry, we obtain

$$\begin{aligned}
3\alpha_{\alpha\beta}^{(i)}\alpha_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)}\alpha_{\beta\beta}^{(i)} &= 18\alpha_i^2\kappa_i^2, \quad \alpha_{\alpha\beta}^{(i)}\Theta_{\alpha\beta}^{(i)} = 3\alpha_i\kappa_i\Theta_i, \\
\Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\beta}^{(i)} &= \frac{3}{2}\Theta_i^2, \quad \Theta_{\alpha\beta}^{(i)}\Theta_{\alpha\gamma}^{(i)}\Theta_{\beta\gamma}^{(i)} = \frac{3}{4}\Theta_i^3, \quad (14)
\end{aligned}$$

wherein

$$\kappa_i = \frac{\alpha_{33}^{(i)} - \alpha_{11}^{(i)}}{3\alpha_i} = \frac{\alpha_{33}^{(i)} - \alpha_{11}^{(i)}}{\alpha_{33}^{(i)} + 2\alpha_{11}^{(i)}} \quad (15)$$

denote the anisotropy of electric polarizability of the axially symmetric molecule of species i , and Θ_i - its quadrupole moment ($\Theta_i = \Theta_{33}^{(i)} = - = -2\Theta_{11}^{(i)} = -2\Theta_{22}^{(i)}$).

In the case of axially symmetrical quadrupole molecules, the expressions (9), (11) and (12) assume the following form when (14) is used:

$$B_{ij}^{\text{disp}} = -\frac{9h^2N}{400k^2T^2} \left(\frac{v_i v_j}{v_i + v_j} \right)^2 \alpha_i^2 \alpha_j^2 (5\kappa_i^2 + 5\kappa_j^2 + 19\kappa_i^2 \kappa_j^2) \langle r_{ij}^{-12} \rangle + \dots, \quad (16)$$

$$B_{ij}^{\text{quad-quad}} = -\frac{7\Theta_i^2 \Theta_j^2 N}{10k^2T^2} \left(\langle r_{ij}^{-10} \rangle - \frac{72\Theta_i \Theta_j}{343kT} \langle r_{ij}^{-15} \rangle + \dots \right), \quad (17)$$

$$B_{ij}^{\text{ind.dip-quad}} = -\frac{3N}{4kT} \left\{ (\alpha_i \Theta_j^2 + \alpha_j \Theta_i^2) \langle r_{ij}^{-8} \rangle - \right. \\ \left. - \frac{36h}{25kT} \frac{v_i v_j}{v_i + v_j} \alpha_i \kappa_i \Theta_i \alpha_j \kappa_j \Theta_j \langle r_{ij}^{-11} \rangle - \right. \\ \left. - \frac{24\Theta_i \Theta_j}{35kT} (\alpha_i \kappa_i \Theta_j^2 + \alpha_j \kappa_j \Theta_i^2) \langle r_{ij}^{-13} \rangle + \dots \right\}. \quad (18)$$

Regular tetrahedral molecules (e.g., CH₄, CCl₄) have a single octopole moment component $\Omega = \Omega_{123}$, where 1, 2, 3, refer to the three axes of a cube whose three diagonals from a corner form the sides of the tetrahedron. For molecules of this type, the contributions to B_{ij} given by eqs. (9), (11) and (12) vanish, whereas

$$\Omega_{\alpha\beta\gamma} \Omega_{\alpha\beta\gamma} = 6\Omega_{123}^2 = 6\Omega^2 \quad (19)$$

and (13) reduces to:

$$B_{ij}^{\text{ind.dip-octop}} = -\frac{54N}{25kT} (\alpha_i \Omega_j^2 + \alpha_j \Omega_i^2) \langle r_{ij}^{-10} \rangle + \dots \quad (20)$$

§ 3. *Applications to some special cases.* The expressions for B_{ij} derived in § 2 are correct for a central forces potential $u(r_{ij})$ of arbitrary form. Assuming, for simplicity, the Lennard-Jones potential in the form¹²⁾

$$u(r_{ij}) = 4\varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\}, \quad (21)$$

we have by the Lennard-Jones method^{13) 14)}:

$$\int_0^\infty \left\{ e^{-\frac{u(r_{ij})}{kT}} - 1 \right\} r_{ij}^2 dr_{ij} = -\frac{1}{3} \sigma_{ij}^3 F(y_{ij}), \quad (22)$$

$$\langle r_{ij}^{-n} \rangle = 4\pi \int_0^\infty r_{ij}^{2-n} e^{-\frac{u(r_{ij})}{kT}} dr_{ij} = \frac{\pi \sigma_{ij}^{3-n}}{3y_{ij}^4} H_n(y_{ij}). \tag{23}$$

Herein, ϵ_{ij} and σ_{ij} are the well-known central forces parameters having the dimensions of energy and length, and $y_{ij} = 2(\epsilon_{ij}/kT)^{\frac{1}{2}}$. The function

$$F(y_{ij}) = \frac{1}{y_{ij}^2} \{H_{12}(y_{ij}) - \frac{1}{2}H_8(y_{ij})\} \tag{24}$$

is tabulated in the monograph by Hirschfelder *et al*¹²), and

$$H_n(y_{ij}) = y_{ij}^{(27-n)/6} \sum_{m=0}^\infty \Gamma\left(\frac{6m+n-3}{12}\right) \frac{y_{ij}^m}{m!} \tag{25}$$

are functions introduced by Pople¹) and tabulated by Buckingham and Pople¹⁴).

By eq. (22), the central-force second virial coefficient (3) assumes the form^{12) 14)}

$$B_{ij}^{\text{centr}} = \frac{2}{3}\pi N \sigma_{ij}^3 F(y_{ij}) = b_{ij} F(y_{ij}), \tag{26}$$

wherein we have used the notation:

$$b_{ij} = \frac{2}{3}\pi N \sigma_{ij}^3. \tag{27}$$

For anisotropic molecules possessing the axial symmetry, eqs. (16), (17) and (18) yield, with the Lennard-Jones (6:12) potential:

$$B_{ij}^{\text{disp}} = -b_{ij} \{0.025 (\kappa_i^2 + \kappa_j^2) + 0.095 \kappa_i^2 \kappa_j^2\} H_{12}(y_{ij}), \tag{28}$$

$$B_{ij}^{\text{quad-quad}} = -\frac{7b_{ij}}{320} \left(\frac{\Theta_i \Theta_j}{\sigma_{ij}^5 \epsilon_{ij}}\right)^2 \left\{ H_{10}(y_{ij}) - \frac{18y_{ij}^2}{343} \left(\frac{\Theta_i \Theta_j}{\sigma_{ij}^5 \epsilon_{ij}}\right) H_{15}(y_{ij}) \right\}, \tag{29}$$

$$B_{ij}^{\text{ind. dip-quad}} = -\frac{3b_{ij}}{32} \left\{ \frac{\alpha_i \Theta_j^2 + \alpha_j \Theta_i^2}{\sigma_{ij}^8 \epsilon_{ij} y_{ij}^2} H_8(y_{ij}) - \frac{24}{25} \left(\frac{\Theta_i \Theta_j}{\sigma_{ij}^5 \epsilon_{ij}}\right) \left[\kappa_i \kappa_j H_{11}(y_{ij}) + \frac{5}{28} \frac{\alpha_i \kappa_i \Theta_j^2 + \alpha_j \kappa_j \Theta_i^2}{\sigma_{ij}^8 \epsilon_{ij}} H_{13}(y_{ij}) \right] \right\}. \tag{30}$$

Analogously, by (23), eq. (20) yields for tetrahedral molecules:

$$B_{ij}^{\text{ind. dip-octop}} = -\frac{27b_{ij}}{100y_{ij}^2} \left(\frac{\alpha_i \Omega_j^2 + \alpha_j \Omega_i^2}{\sigma_{ij}^{10} \epsilon_{ij}}\right) H_{10}(y_{ij}). \tag{31}$$

(i) One-component gas. In the case of a one-component gas the virial expansion (1) reduces to:

$$\frac{pV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots, \tag{32}$$

and the contributions to the second virial coefficient given by eqs. (26)–(31) assume the form:

$$B^{\text{centr}} = bF(y), \quad b = \frac{2}{3}\pi N\sigma^3, \quad (33)$$

$$B^{\text{disp}} = -b\kappa^2(0.05 + 0.095\kappa^2) H_{12}(y), \quad (34)$$

$$B^{\text{quad-quad}} = -\frac{7b}{320} \left(\frac{\Theta^2}{\sigma^5 \varepsilon} \right)^2 \left\{ H_{10}(y) - \frac{18y^2}{343} \left(\frac{\Theta^2}{\sigma^5 \varepsilon} \right) H_{15}(y) \right\}, \quad (35)$$

$$B^{\text{ind. dip-quad}} = -\frac{3b}{16} \left(\frac{\Theta^2}{\sigma^5 \varepsilon} \right) \left\{ \frac{1}{y^2} \left(\frac{\alpha}{\sigma^3} \right) H_8(y) - \frac{1}{25} \kappa^2 H_{11}(y) - \frac{6}{35} \kappa \left(\frac{\alpha}{\sigma^3} \right) \left(\frac{\Theta^2}{\sigma^5 \varepsilon} \right) H_{13}(y) \right\}, \quad (36)$$

$$B^{\text{ind. dip-octop}} = -\frac{27b}{50y^2} \left(\frac{\alpha}{\sigma^3} \right) \left(\frac{\Omega^2}{\sigma^7 \varepsilon} \right) H_{10}(y). \quad (37)$$

The expressions (33), (34) and (35) were derived previously by Pople¹ (see also ref. 14).

(ii) Binary gas mixture. For a binary gas mixture, the equation of state (1) is of the form:

$$\frac{pV}{RT} = 1 + (x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22}) V^{-1} + (x_1^3 C_{111} + 3x_1^2 x_2 C_{112} + 3x_1 x_2^2 C_{122} + x_2^3 C_{222}) V^{-2} + \dots \quad (38)$$

If, in particular, the molecules of one component of the gas mixture are spherical and those of the other tetrahedral, we obtain, by the expressions (26) and (31):

$$B_{11} = b_{11} F(y_{11}), \quad (39)$$

$$B_{12} = B_{21} = b_{12} \left\{ F(y_{12}) - \frac{27}{100y_{12}^2} \left(\frac{\alpha_1}{\sigma_{12}^3} \right) \left(\frac{\Omega_2^2}{\sigma_{12}^7 \varepsilon_{12}} \right) H_{10}(y_{12}) \right\}, \quad (40)$$

$$B_{22} = b_{22} \left\{ F(y_{22}) - \frac{27}{50y_{22}^2} \left(\frac{\alpha_2}{\sigma_{22}^3} \right) \left(\frac{\Omega_2^2}{\sigma_{22}^7 \varepsilon_{22}} \right) H_{10}(y_{22}) \right\}. \quad (41)$$

In the case of a collision between a spherical molecule 1 and a quadrupolar molecule 2 we obtain from eqs. (26)–(30):

$$B_{12} = b_{12} \left\{ F(y_{12}) - 0.025\kappa_2^2 H_{12}(y_{12}) - \frac{3}{32y_{12}^2} \left(\frac{\alpha_1}{\sigma_{12}^3} \right) \left(\frac{\Theta_2^2}{\sigma_{12}^5 \varepsilon_{12}} \right) H_8(y_{12}) \right\}. \quad (42)$$

For a mixture of a quadrupole gas with an other quadrupole gas, the expressions (26)–(30) assume the form:

$$\begin{aligned}
B_{11} = b_{11} \left\{ F(y_{11}) - \kappa_1^2(0.05 + 0.095\kappa_1^2) H_{12}(y_{11}) - \right. \\
- \frac{7}{320} \left(\frac{\Theta_1^2}{\sigma_{11}^5 \epsilon_{11}} \right)^2 \left[H_{10}(y_{11}) - \frac{18y_{11}^2}{343} \left(\frac{\Theta_1^2}{\sigma_{11}^5 \epsilon_{11}} \right) H_{15}(y_{11}) \right] - \\
- \frac{3}{16} \left(\frac{\Theta_1^2}{\sigma_{11}^5 \epsilon_{11}} \right) \left[\frac{1}{y_{11}^2} \left(\frac{\alpha_1}{\sigma_{11}^3} \right) H_8(y_{11}) - \frac{12}{25} \kappa_1^2 H_{11}(y_{11}) - \right. \\
\left. \left. - \frac{6}{35} \kappa_1 \left(\frac{\alpha_1}{\sigma_{11}^3} \right) \left(\frac{\Theta_1^2}{\sigma_{12}^5 \epsilon_{12}} \right) H_{13}(y_{11}) \right] \right\}, \quad (43)
\end{aligned}$$

$$\begin{aligned}
B_{12} = b_{12} \left\{ F(y_{12}) - [0.025(\kappa_1^2 + \kappa_2^2) + 0.095\kappa_1^2\kappa_2^2] H_{12}(y_{12}) - \right. \\
- \frac{7}{320} \left(\frac{\Theta_1\Theta_2}{\sigma_{12}^5 \epsilon_{12}} \right)^2 \left[H_{10}(y_{12}) - \frac{18y_{12}^2}{343} \left(\frac{\Theta_1\Theta_2}{\sigma_{12}^5 \epsilon_{12}} \right) H_{15}(y_{12}) \right] - \\
- \frac{3}{32} \left[\frac{\alpha_1\Theta_2^2 + \alpha_2\Theta_1^2}{\sigma_{12}^8 \epsilon_{12} y_{12}^2} H_8(y_{12}) - \frac{24}{25} \left(\frac{\Theta_1\Theta_2}{\sigma_{12}^5 \epsilon_{12}} \right) (\kappa_1\kappa_2 H_{11}(y_{12}) + \right. \\
\left. \left. + \frac{5}{28} \frac{\alpha_1\kappa_1\Theta_2^2 + \alpha_2\kappa_2\Theta_1^2}{\sigma_{12}^8 \epsilon_{12}} H_{13}(y_{12})) \right] \right\}, \quad (44)
\end{aligned}$$

$$\begin{aligned}
B_{22} = b_{22} \left\{ F(y_{22}) - \kappa_2^2(0.05 + 0.095\kappa_2^2) H_{12}(y_{22}) - \right. \\
- \frac{7}{320} \left(\frac{\Theta_2^2}{\sigma_{22}^5 \epsilon_{22}} \right)^2 \left[H_{10}(y_{22}) - \frac{18y_{22}^2}{343} \left(\frac{\Theta_2^2}{\sigma_{22}^5 \epsilon_{22}} \right) H_{15}(y_{22}) \right] \\
- \frac{3}{16} \left(\frac{\Theta_2^2}{\sigma_{22}^5 \epsilon_{22}} \right) \left[\frac{1}{y_{22}^2} \left(\frac{\alpha_2}{\sigma_{22}^3} \right) H_8(y_{22}) - \frac{12}{25} \kappa_2^2 H_{12}(y_{22}) - \right. \\
\left. \left. - \frac{6}{35} \kappa_2 \left(\frac{\alpha_2}{\sigma_{22}^3} \right) \left(\frac{\Theta_2^2}{\sigma_{22}^5 \epsilon_{22}} \right) H_{13}(y_{22}) \right] \right\}. \quad (45)
\end{aligned}$$

(iii) Ternary gas mixture. In the case of a three-component dilute gas mixture the equation of state, on the basis of (1), is given by the following series:

$$\begin{aligned}
\frac{pV}{RT} = 1 + \{x_1^2 B_{11} + x_2^2 B_{22} + x_3^2 B_{33} + \\
+ 2(x_1 x_2 B_{12} + x_1 x_3 B_{13} + x_2 x_3 B_{23})\} V^{-1} + \dots \quad (46)
\end{aligned}$$

We assume the molecules of component 1 to be spherical, those of component 2 to be tetrahedral, and those of component 3-quadrupolar. In this case, the coefficients B_{11} , B_{12} and B_{22} in (46) are again given by (39), (40) and (41), whereas for B_{13} , B_{23} and B_{33} we have the following formulas:

$$B_{13} = b_{13} \left\{ F(y_{13}) - 0.025\kappa_3^2 H_{12}(y_{13}) - \frac{3}{32y_{13}^2} \left(\frac{\alpha_1}{\sigma_{13}^3} \right) \left(\frac{\Theta_3^2}{\sigma_{13}^5 \epsilon_{13}} \right) H_8(y_{13}) \right\}, \quad (47)$$

$$B_{23} = b_{23} \left\{ F(y_{23}) - 0.025 \kappa_3^2 H_{12}(y_{23}) - \frac{3}{32 y_{23}^2} \left(\frac{\alpha_2}{\sigma_{23}^3} \right) \left(\frac{\Theta_3^2}{\sigma_{23}^5 \epsilon_{23}} \right) H_8(y_{23}) - \right. \\ \left. - \frac{27}{100 y_{23}^2} \left(\frac{\alpha_3}{\sigma_{23}^3} \right) \left(\frac{\Omega_2^2}{\sigma_{23}^7 \epsilon_{23}} \right) H_{10}(y_{23}) \right\}, \quad (48)$$

$$B_{33} = b_{33} \left\{ F(y_{33}) - \kappa_3^2 (0.05 + 0.095 \kappa_3^2) H_{12}(y_{33}) - \right. \\ \left. - \frac{7}{320} \left(\frac{\Theta_3^2}{\sigma_{33}^5 \epsilon_{33}} \right)^2 \left[H_{10}(y_{33}) - \frac{18 y_{33}^2}{343} \left(\frac{\Theta_3^2}{\sigma_{33}^3 \epsilon_{33}} \right) H_{15}(y_{33}) \right] - \right. \\ \left. - \frac{3}{16} \left(\frac{\Theta_3^2}{\sigma_{33}^5 \epsilon_{33}} \right) \left[\frac{1}{y_{33}^2} \left(\frac{\alpha_3}{\sigma_{33}^3} \right) H_8(y_{33}) - \frac{12}{25} \kappa_3^2 H_{11}(y_{33}) - \right. \right. \\ \left. \left. - \frac{6}{35} \kappa_3 \left(\frac{\alpha_3}{\sigma_{33}^3} \right) \left(\frac{\Theta_3^2}{\sigma_{33}^5 \epsilon_{33}} \right) H_{13}(y_{33}) \right] \right\}, \quad (49)$$

which can be deduced from eqs. (26)–(31).

Similarly one can apply eqs. (26)–(31) to more complicated gas mixtures.

§ 4. *Discussion.* The second virial coefficients of some imperfect gases are evaluated numerically on the basis of formulas (33)–(36) and compared with the available experimental data in Table II. The latter prove immediately that the principal contribution to the total value of B for all gases considered is related to the central forces. The anisotropic dispersive forces play no rôle altogether in some cases (e.g. in H_2), while in others (e.g. N_2 , O_2 , CO_2) they may give such great contributions to B that one cannot neglect them in comparison with the contributions resulting from the quadrupole-quadrupole interactions. It is obvious that the latter interaction will prevail in the case of a very great quadrupole moment of the molecules (e.g. CO_2). For H_2 and N_2 , the contributions to B from inductive interactions of the molecules are comparable to the contributions from quadrupole-quadrupole interactions.

Assuming a value of $\Omega = -12 \times 10^{-34}$ e.s.u. for the CH_4 molecule, and in addition of the molecular data in Table I, formulas (33) and (37) yield, at $T = 298.2^\circ K$:

$$B^{centr} = -36.9 \text{ cm}^3/\text{mol}, \quad B^{ind. dip-octop} = -5.9 \text{ cm}^3/\text{mol}.$$

The total second virial coefficient of methane calculated above is $B_{calc} = -42.8 \text{ cm}^3/\text{mol}$, which is in good agreement to the observed value¹⁸⁾ $-B_{exper} = -43.3 \text{ cm}^3/\text{mol}$. The octopole moment of CH_4 assumed above is certainly exaggerated with compared to the value of $\Omega = -1.1 \times 10^{-34}$ e.s.u., as calculated by Buckingham and Stephen¹⁹⁾. For that value of Ω , the induced dipole-octopole interaction yields a contribution $B^{ind. dip-octop} = -0.05 \text{ cm}^3/\text{mol}$, and so plays practically no rôle at all.

TABLE I

Molecular data for some gases*)					
gas	ϵ/k °K	σ Å	$\alpha \times 10^{24}$ cm ³	κ	$\Theta \cdot 10^{26}$ e.s.u.
He	10.22	2.576	0.22	0	0
H ₂	33.3	2.968	0.79	0.09	0.95
N ₂	91.5	3.681	1.76	0.18	1.80
O ₂	113.0	3.433	1.60	0.24	1.90
CO ₂	190.0	3.996	2.92	0.27	5.00
CH ₄	137.0	3.882	2.60	0	0

*) We used for the force constants ϵ/k , and σ values determined from viscosity measurements tabulated in the monograph of Hirschfelder and al¹²⁾, and values of α , and $\kappa = (\alpha_{||} - \alpha_{\perp})/3\alpha$ given in the Landolt-Börnstein Tables¹⁵⁾. The values of quadrupole moments of molecules were assumed to have the appropriate magnitude in order to get a satisfactory agreement between the calculated and experimentally obtained values for the second virial coefficient.

TABLE II

Comparison of calculated and experimental values of B in cm ³ /mol.						
$T = 298.2^\circ\text{K}$						
gas	B_{centr}	B_{disp}	$B_{\text{quad-quad}}$	$B_{\text{ind. dip-quad}}$	B_{calc}	B_{exper}
H ₂	14.52	-0.01	-0.46	-0.33	13.72	13.70 ¹⁶⁾
N ₂	-3.0	-0.5	-0.8	-0.4	-4.7	-4.71 ¹⁶⁾
O ₂	-12.8	-1.0	-1.8	-0.1	-15.7	-15.0 ¹⁷⁾
CO ₂	-88.6	-6.0	-29.7	2.2	-122.1	-123.6 ¹⁶⁾

TABLE III

Calculated and experimental values of B_{12} in cm ³ /mol						
$T = 298.2^\circ\text{K}$						
Mixtures	B_{12}^{centr}	B_{12}^{disp}	$B_{12}^{\text{quad-quad}}$	$B_{12}^{\text{ind. dip-quad}}$	$B_{12, \text{calc}}$	$B_{12, \text{exper}}$
He-N ₂	16.56	-0.02	0	-0.07	16.43	12.5 ¹²⁾
H ₂ -N ₂	12.8	-0.1	-0.6	-0.5	11.6	11.1 ¹⁶⁾ 12.8 ¹⁶⁾
H ₂ -CO ₂	3.6	-0.4	-3.0	-1.8	-1.6	-1.1 ¹⁶⁾
N ₂ -CO ₂	-32.6	-1.7	-5.4	-1.5	-41.2	-42.6 ¹⁶⁾
O ₂ -CO ₂	-39.6	-0.8	-7.5	-0.6	-48.5	-58.3 ¹²⁾

Table III brings the various contributions to the second virial coefficients for collisions between two unlike non-dipolar molecules, calculated on the basis of eqs. (42) and (44) with help of the molecular data given in table I, and with the combining laws for the force constants¹²⁾:

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \quad \epsilon_{ij} = (\epsilon_i \epsilon_j)^{\frac{1}{2}}. \quad (50)$$

As it can be seen in table III, the contributions to B_{12} arising from directional molecular interactions are, in some cases, so large that they cannot be

neglected compared to the contribution from central intermolecular forces.

In conclusions a sufficiently good agreement between the theoretically computed and measured second virial coefficients may be obtained, as it follows from tables II and III, when the numerical values of the molecular quadrupole moments for H₂, N₂, O₂ and CO₂ are assumed to be:

$$\begin{aligned}\Theta_{\text{H}_2} &= 0.95 \times 10^{-26} \text{ e.s.u.}, \quad \Theta_{\text{N}_2} = 1.80 \times 10^{-26} \text{ e.s.u.}, \\ \Theta_{\text{O}_2} &= 1.90 \times 10^{-26} \text{ e.s.u.}, \quad \Theta_{\text{CO}_2} = 5.00 \times 10^{-26} \text{ e.s.u.}\end{aligned}$$

The numerical values of quadrupole moments of N₂ and CO₂ molecules deduced from microwave pressure-broadening data are ²⁰):

$$\Theta_{\text{N}_2} = 1.50 \times 10^{-26} \text{ e.s.u.}, \quad \Theta_{\text{CO}_2} = 3.10 \times 10^{-26} \text{ e.s.u.}$$

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REFERENCES

- 1) Pople, J. A., Proc. roy. Soc., **A221** (1954) 508.
- 2) Kielich, S., Acta phys. Polonica, **20** (1961) 433.
- 3) Buckingham, A. D., Quarterly Reviews **13** (1959) 183.
- 4) Kielich, S., Acta phys. Polonica, (in press).
- 5) De Boer, J. H. and Heller, G., Physica **4** (1937) 1045.
- 6) London, F., J. phys. Chem. **46** (1942) 305.
- 7) De Boer, J., Physica **9** (1942) 363.
- 8) Keesom, W. H., Physikal. Z., **22** (1921) 129, 643; **23** (1922) 225.
- 9) Debye, P., Physikal. Z. **21** (1920) 178.
- 10) Pople, J. A., Proc. roy. Soc. **A 215** (1952) 67.
- 11) Kielich, S., Acta phys. Polonica **19** (1960) 711.
- 12) Hirschfelder, J. O., Curtiss, Ch. F. and Bird, R. B., *Molecular theory of gases and liquids* (New York, 1954).
- 13) Lennard-Jones, J. E., Proc. roy. Soc. **A 106** (1924) 441.
- 14) Buckingham, A. D. and Pople, J. A., Trans. Farad. Soc. **51** (1955) 1173.
- 15) Landolt-Börnstein Tables, Vol. I part 3 (J. Springer, 1951).
- 16) Lunbeck, R. J. and Boerboom, J. H., Physica **17** (1951) 76.
- 17) Holborn, L. and Otto, J., Zeits. f. Phys. **10** (1922) 367.
- 18) Michels, A. and Nederbragt, G. W., Physica **3** (1936) 569.
- 19) Buckingham, A. D. and Stephen, M. J., Trans. Farad. Soc. **53** (1957) 884.
- 20) Gordy, W., Smith, W. V. and Trambarulo, R. F., *Microwave Spectroscopy*, Wiley, New York (1953).

ERRATUM

Second virial coefficients for unlike non-dipolar molecules,

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by S. KIELICH

In eq. (6) the factor preceding the last term, describing the induced dipole-octopole interaction, should be $1/450$ instead of $1/500$. Thus, all terms in eqs (13), (20), (31), (37), (40) and (41) proportional to the square of the octopole moment have to be multiplied by $10/9$.