

## SECOND REFRACTIVITY VIRIAL COEFFICIENTS FOR GAS MIXTURES

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The present paper brings calculations of the second refractivity virial coefficient  $B_R = \sum_i \sum_j x_i x_j B_R^{(ij)}$  for a mixture of quadrupole and dipole gases. In addition to the influence of anisotropy in the polarizability on  $B_R^{(ij)}$ , the effects of hyperpolarizability of the quadrupole or dipole molecules on  $B_R^{(ij)}$  was taken into account. In carrying out the calculations, the intermolecular central forces, the anisotropic dispersion forces, quadrupole-quadrupole and dipole-dipole interactions, as well as the induction interactions occurring between spherical, quadrupole and dipole molecules of the gas mixture were taken into consideration. Numerical evaluations for the gases  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{CHCl}_3$ , and  $\text{CH}_3\text{F}$  and their mixtures are given. These evaluations establish the importance of the particular contributions to  $B_R$ .

## 1. Introduction

The molecular refraction, or Lorentz-Lorenz function, is defined as

$$R_m = \frac{n^2 - 1}{n^2 + 2} V, \quad (1)$$

where  $n$  is the refractive index and  $V$  the molar volume of a substance.

In the case of a perfect gas,  $R_m$  is expressed by the mean polarizability  $\alpha$  of an isolated molecule, as follows:

$$R_m^* = \frac{4\pi}{3} N\alpha, \quad (2)$$

and is independent of the density and temperature of the gas ( $N$  is Avogadro's number).

The variation of  $R_m$  with the density of imperfect gases was discussed theoretically by Mazur and Mandel (1956), Buckingham (1956) and Mazur (1959). Buckingham expanded the molecular refraction of a compressed gas in powers of  $1/V$ :

$$R_m = A_R + \frac{B_R}{V} + \frac{C_R}{V^2} + \dots, \quad (3)$$

where the expansion coefficients  $A_R$ ,  $B_R$ ,  $C_R$ , etc. are termed the first, second, third, ... refractivity virial coefficients. The first virial coefficient  $A_R$  characterizes the perfect gas

(whose molecules do not interact) and is given by Eq. (2). The coefficients  $B_R, C_R, \dots$  describe the deviations from ideal behaviour of the refractivity of the substance (*i. e.* from  $A_R$ ), and account for the interactions of two, three *etc.* molecules of an imperfect gas.

In the present paper, Buckingham's theory is extended to compressed gas mixtures. The discussion will be restricted to the virial coefficients  $A_R$  and  $B_R$  only; for a gas mixture, these are given by

$$A_R = \sum_i x_i A_R^{(i)}, \quad (4)$$

$$B_R = \sum_i \sum_j x_i x_j B_R^{(ij)}, \quad (5)$$

wherein  $x_i$  is the mole fraction of the  $i$ -th component of the mixture, and summation extends over all components. The coefficients  $A_R^{(i)}$  and  $B_R^{(ij)}$  have the form:

$$A_R^{(i)} = \frac{4\pi}{3} N \alpha_i, \quad (6)$$

$$B_R^{(ij)} = \frac{2\pi N^2}{9\Omega^2} \iiint \left\{ \frac{\partial m_\alpha^{(i)}}{\partial E_\alpha} + \frac{\partial m_\alpha^{(j)}}{\partial E_\alpha} - 3\alpha_i - 3\alpha_j \right\} e^{-\frac{u_{ij}}{kT}} d\mathbf{r}_{ij} d\omega_i d\omega_j. \quad (7)$$

Herein,

$$\alpha_i = \frac{1}{3} \alpha_{\alpha\alpha}^{(i)} = \frac{1}{3} (\alpha_{11}^{(i)} + \alpha_{22}^{(i)} + \alpha_{33}^{(i)}) \quad (8)$$

is the mean polarizability of the isolated molecule of the  $i$ -th component of the gas mixture.  $m_\alpha^{(i)}$  is the  $\alpha$ -component of the dipole moment induced in the  $i$ -th molecule by the electric field  $\mathbf{E}$  of the light wave.  $u_{ij}$  is the total potential energy of interaction between the two molecules, of species  $i$  and  $j$ ;  $\mathbf{r}_{ij}$  — denotes the vector connecting their centres, and  $\omega_i, \omega_j$  — variables describing their orientation;  $\Omega = \int d\omega_i = \int d\omega_j$ ; are integrals over the orientational coordinates.

In the subsequent Sections, the second refractivity virial coefficient  $B_R^{(ij)}$  as given by (7) will be computed for interacting anisotropic, quadrupole or dipole, unlike molecules.

## 2. Anisotropic non-dipolar molecules

The  $\alpha$ -component of the dipole moment induced in the  $i$ -th anisotropic molecule of a gas is, in the first approximation, given by

$$m_\alpha^{(i)} = \alpha_{\alpha\beta}^{(i)} (E_\beta + F_\beta^{(i)}), \quad (9)$$

where  $\alpha_{\alpha\beta}^{(i)}$  is the polarizability tensor of the isolated molecule of species  $i$  and

$$F_\alpha^{(i)} = - T_{\alpha\beta}^{(ij)} m_\beta^{(j)} \quad (10)$$

— the  $\alpha$ -component of the electric field at the centre of the  $i$ -th molecule due to the dipole moment  $m_\beta^{(j)}$  of the  $j$ -th molecule of a gas mixture. The tensor  $T_{\alpha\beta}^{(ij)}$  accounting for dipole-dipole interaction has the form

$$T_{\alpha\beta}^{(ij)} = - r_{ij}^{-3} (3\lambda_\alpha \lambda_\beta - \delta_{\alpha\beta}), \quad (11)$$

where  $\vec{\lambda} = (\lambda_1, \lambda_2, \lambda_3)$  is a unit vector in the direction of the vector  $\mathbf{r}_{ij} = \vec{\lambda} r_{ij}$ , and  $\delta_{\alpha\beta}$  — the unity tensor:

$$\delta_{\alpha\beta} = \begin{cases} 1 & \text{for } \alpha = \beta, \\ 0 & \text{for } \alpha \neq \beta. \end{cases}$$

From Eqs. (9) and (10) we obtain, in approximation, the following expression for the molecular electric field:

$$F_{\beta}^{(i)} = -T_{\beta\gamma}^{(ij)} \alpha_{\gamma\delta}^{(j)} E_{\delta} + T_{\beta\gamma}^{(ij)} \alpha_{\gamma\delta}^{(j)} T_{\delta\epsilon}^{(ij)} \alpha_{\epsilon\eta}^{(i)} E_{\eta} - \dots \quad (12)$$

For molecules possessing axial symmetry about the 3-axis, we can express the polarizability tensor  $\alpha_{\alpha\beta}^{(i)}$  in the following form:

$$\alpha_{\alpha\beta}^{(i)} = \alpha_i \delta_{\alpha\beta} + \alpha_i \kappa_{\alpha,i} (3s_{\alpha}^{(i)} s_{\beta}^{(i)} - \delta_{\alpha\beta}), \quad (13)$$

wherein

$$\kappa_{\alpha,i} = \frac{\alpha_{33}^{(i)} - \alpha_{11}^{(i)}}{3\alpha_i} \quad (14)$$

is a parameter describing the anisotropy of polarizability of an axially symmetric molecule of species  $i$ , and  $\mathbf{s} = (s_1, s_2, s_3)$  — a unit vector along the axis of symmetry.

With respect to eqs. (11), (12) and (13), the following result is obtained from (9) for axially symmetric molecules:

$$\begin{aligned} \left( \frac{\partial m_{\alpha}^{(i)}}{\partial E_{\alpha}} \right)_{\text{anis}} &= 3\alpha_i + 3\alpha_i \alpha_j \{ \kappa_{\alpha,i} (1 - \kappa_{\alpha,j}) (3 \cos^2 \theta_i - 1) + \\ &+ \kappa_{\alpha,j} (1 - \kappa_{\alpha,i}) (3 \cos^2 \theta_j - 1) + 3\kappa_{\alpha,i} \kappa_{\alpha,j} (3 \cos \theta_i \cos \theta_j - \cos \theta_{ij}) \cos \theta_{ij} \} r_{ij}^{-3} + \\ &+ 3\alpha_i^2 \alpha_j \{ 2(1 - \kappa_{\alpha,i})^2 (1 - \kappa_{\alpha,j}) + \kappa_{\alpha,i} (2 + \kappa_{\alpha,i}) (1 - \kappa_{\alpha,j}) (3 \cos^2 \theta_i + 1) + \\ &+ (1 - \kappa_{\alpha,i})^2 \kappa_{\alpha,j} (3 \cos^2 \theta_j + 1) + 3\kappa_{\alpha,i} \kappa_{\alpha,j} (2 + \kappa_{\alpha,i}) (3 \cos \theta_i \cos \theta_j - \cos \theta_{ij})^2 \} r_{ij}^{-6} + \dots, \end{aligned} \quad (15)$$

where we have used the notation

$$\begin{aligned} s_{\alpha}^{(i)} s_{\alpha}^{(j)} &= \cos \theta_{ij} = \cos \theta_i \cos \theta_j + \sin \theta_i \sin \theta_j \cos (\varphi_j - \varphi_i), \\ s_{\alpha}^{(i)} \lambda_{\alpha} &= \cos \theta_i, \quad s_{\beta}^{(j)} \lambda_{\beta} = \cos \theta_j, \end{aligned}$$

and  $\theta_{ij}$  is the angle between the symmetry axes of molecules  $i$  and  $j$ ,  $\theta_i$  and  $\theta_j$  are the angles formed by the respective axis and the unit vector  $\vec{\lambda}$ , while  $\varphi_i$  and  $\varphi_j$  are the angles between the planes formed by the two axes with the line of centres  $\vec{\lambda}$ .

We shall assume that  $u_{ij}$  consists of the Lennard-Jones 6:12 potential and of the energy resulting from London's anisotropic dispersive forces (see Pople 1954, Kielich 1962a):

$$\begin{aligned} u_{ij} &= 4\epsilon_{ij}^{\text{LJ}} \left\{ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} + 2\epsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \{ \kappa_{\alpha,i} + \kappa_{\alpha,j} - \\ &- 3\kappa_{\alpha,i} (1 - \kappa_{\alpha,j}) \cos^2 \theta_i - 3\kappa_{\alpha,j} (1 - \kappa_{\alpha,i}) \cos^2 \theta_j - 3\kappa_{\alpha,i} \kappa_{\alpha,j} (3 \cos \theta_i \cos \theta_j - \cos \theta_{ij})^2 \}, \end{aligned} \quad (16)$$

where  $\varepsilon_{ij}$  and  $\sigma_{ij}$  are the force constants having the dimensions of energy and length for an interacting pair of molecules of species  $i$  and  $j$ .

Substituting Eqs. (15) and (16) in (7), the second refractivity virial coefficient for two unlike axially symmetric molecules is obtained in the form of

$$B_R^{(ij)} = \frac{4\pi^2 \alpha_i \alpha_j N^2}{9\sigma_{ij}^3 y_{ij}^4} \left\{ [\alpha_i (1 + 2\kappa_{\alpha,i}^2) + \alpha_j (1 + 2\kappa_{\alpha,j}^2)] H_6(y_{ij}^{\frac{5}{2}}) + \right. \\ \left. + \frac{2}{25} \sigma_{ij}^3 y_{ij}^2 (5\kappa_{\alpha,i}^2 - \kappa_{\alpha,i}^2 \kappa_{\alpha,j}^2 + 5\kappa_{\alpha,j}^2) H_9(y_{ij}) + \dots \right\}, \quad (17)$$

where the  $H_n(y_{ij})$  are functions defined by Pople (1954) and tabulated by Buckingham and Pople (1955a);  $y_{ij} = 2(\varepsilon_{ij}/hT)^{\frac{1}{2}}$ .

In this expression, the second term multiplied by  $H_9(y_{ij})$  results from the anisotropic dispersive forces and, as will be shown later, plays an important role in all cases considered in this paper.

If, in particular, the molecules are isotropically polarizable,  $\kappa_{\alpha} = 0$ , Eq. (17) reduces to:

$$B_R^{(ij)} = \frac{4\pi^2 \alpha_i \alpha_j N^2}{9\sigma_{ij}^3 y_{ij}^4} (\alpha_i + \alpha_j) H_6(y_{ij}). \quad (18)$$

In the case of a gas mixture consisting of anisotropic molecules possessing a permanent electric quadrupole moment  $\Theta$ , we have (see Kielich 1962a):

$$u_{ij} = 4\varepsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} + \frac{3}{4} \Theta_i \Theta_j \{ 1 - 5 (\cos^2 \theta_i + 3 \cos^2 \theta_i \cos^2 \theta_j + \cos^2 \theta_j) + \\ + 2(5 \cos \theta_i \cos \theta_j - \cos \theta_{ij})^2 \} r_{ij}^{-5} - \frac{9}{8} \{ \alpha_i (1 - \kappa_{\alpha,i}) \Theta_j^2 (5 \cos^4 \theta_j - 2 \cos^2 \theta_j + 1) + \\ + \alpha_j (1 - \kappa_{\alpha,j}) \Theta_i^2 (5 \cos^4 \theta_i - 2 \cos^2 \theta_i + 1) + \\ + 3\alpha_i \kappa_{\alpha,i} \Theta_j^2 (5 \cos \theta_i \cos^2 \theta_j - 2 \cos \theta_{ij} \cos \theta_j - \cos \theta_{ij})^2 + \\ + 3\alpha_j \kappa_{\alpha,j} \Theta_i^2 (5 \cos^2 \theta_i \cos \theta_j - 2 \cos \theta_{ij} \cos \theta_i - \cos \theta_j)^2 \} r_{ij}^{-8} + \dots, \quad (19)$$

here, in addition to the Lennard-Jones (6:12) potential, terms accounting for the energy of electrostatic quadrupole-quadrupole ( $r_{ij}^{-5}$ ) and quadrupole-induced dipole ( $r_{ij}^{-8}$ ) interactions occur.

On substituting Eqs. (15) and (19) in (7), we obtain the following contributions to  $B_R^{(ij)}$  resulting from quadrupole-induced dipole and quadrupole-quadrupole interactions:

$$B_R^{(ij)} = \frac{4\pi^2 \alpha_i \alpha_j N^2}{1575 \sigma_{ij}^8 \varepsilon_{ij} y_{ij}^2} \left\{ [3\alpha_i \Theta_j^2 (10\kappa_{\alpha,j} + 7\kappa_{\alpha,i}^2 - 2\kappa_{\alpha,i} \kappa_{\alpha,i}^2) - \right. \\ - 7\kappa_{\alpha,i} \kappa_{\alpha,j} \Theta_i \Theta_j (2\alpha_i + 2\alpha_j + \alpha_i \kappa_{\alpha,i} + \alpha_j \kappa_{\alpha,j}) + \\ + 3\alpha_j \Theta_i^2 (10\kappa_{\alpha,i} + 7\kappa_{\alpha,j}^2 - 2\kappa_{\alpha,i} \kappa_{\alpha,i}^2)] H_{11}(y_{ij}) + \\ \left. + \frac{25y_{ij}^2 \Theta_i^2 \Theta_j^2}{28\sigma_{ij}^2 \varepsilon_{ij}} (7\kappa_{\alpha,i} - 2\kappa_{\alpha,i} \kappa_{\alpha,j} + 7\kappa_{\alpha,j}) H_{13}(y_{ij}) + \dots \right\}. \quad (20)$$

### 3. The influence of hyperpolarizability on $B_R$

In measuring the refraction, we are dealing with a weak electric field of the light beam. Essentially, such a weak field  $\mathbf{E}$  can only give rise to linear polarization of a molecule, as described by equation (9). However, a compressed gas generally presents a very strong molecular field  $\mathbf{F}_0$  developing a nonlinear deformation of the molecule. In this case, instead of (9), we have the following expansion:

$$m_{\alpha}^{(i)} = \{\alpha_{\alpha\beta}^{(i)} + \beta_{\alpha\beta:\gamma}^{(i)} F_{0\gamma}^{(i)} + \frac{1}{2} \gamma_{\alpha\beta:\gamma\delta}^{(i)} F_{0\gamma}^{(i)} F_{0\delta}^{(i)} + \dots\} \{E_{\beta} + F_{\beta}^{(i)}\}, \quad (21)$$

where  $\beta_{\alpha\beta:\gamma}^{(i)}$  and  $\gamma_{\alpha\beta:\gamma\delta}^{(i)}$  are the hyperpolarizability tensors describing the change in polarizability of the molecule  $i$  caused by the electric field  $\mathbf{F}_0$  of the neighbouring molecule (at  $E = 0$ ).

For molecules with centres of inversion,  $\beta_{\alpha\beta:\gamma}^{(i)} = 0$ , while the tensor  $\gamma_{\alpha\beta:\gamma\delta}^{(i)}$  (if the molecule possesses axial symmetry) is of the form

$$\begin{aligned} \gamma_{\alpha\beta:\gamma\delta}^{(i)} = & \frac{1}{3} \gamma_i (1 - \kappa_{\gamma,i}) (\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) + \frac{1}{2} \gamma_i \kappa_{\gamma,i} (\delta_{\alpha\beta} s_{\gamma}^{(i)} s_{\delta}^{(i)} + \delta_{\alpha\gamma} s_{\beta}^{(i)} s_{\delta}^{(i)} + \\ & + \delta_{\alpha\delta} s_{\beta}^{(i)} s_{\gamma}^{(i)} + \delta_{\beta\gamma} s_{\alpha}^{(i)} s_{\delta}^{(i)} + \delta_{\beta\delta} s_{\alpha}^{(i)} s_{\gamma}^{(i)} + \delta_{\gamma\delta} s_{\alpha}^{(i)} s_{\beta}^{(i)}), \end{aligned} \quad (22)$$

wherein the quantities

$$\kappa_{\gamma,i} = \frac{\gamma_{33\ 33}^{(i)} - \gamma_{11\ 11}^{(i)}}{3\gamma_i}; \quad \gamma_i = \frac{1}{3} (\gamma_{33\ 33}^{(i)} + 2\gamma_{11\ 11}^{(i)}) \quad (23)$$

yield a measure of the anisotropy of hyperpolarizability and the mean hyperpolarizability of a molecule of species  $i$ , respectively.

Since the square of electric field,  $F_{0\alpha}^{(i)} F_{0\beta}^{(i)}$ , at the centre of molecule  $i$  arising from anisotropic dispersive forces is of the form

$$\begin{aligned} F_{0\alpha}^{(i)} F_{0\beta}^{(i)} = & \frac{2\varepsilon_{ij}}{3\alpha_i} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \{ (1 - \kappa_{\alpha,j}) (3\lambda_{\alpha} \lambda_{\beta} + \delta_{\alpha\beta}) + \\ & + 3\kappa_{\alpha,j} (9\lambda_{\alpha} \lambda_{\beta} \cos^2 \theta_j - 3\lambda_{\alpha} s_{\beta}^{(j)} \cos \theta_j - 3s_{\alpha}^{(j)} \lambda_{\beta} \cos \theta_j + s_{\alpha}^{(j)} s_{\beta}^{(j)}) \}, \end{aligned} \quad (24)$$

the expansion (21) yields,

$$\left( \frac{\partial m_{\alpha}^{(i)}}{\partial E_{\alpha}} \right)_{\text{total}} = \left( \frac{\partial m_{\alpha}^{(i)}}{\partial E_{\alpha}} \right)_{\text{anis}} + \left( \frac{\partial m_{\alpha}^{(i)}}{\partial E_{\alpha}} \right)_{\text{hyp-disp}}, \quad (25)$$

where the first term is given by Eq. (15) and the second one by (26):

$$\begin{aligned} \left( \frac{\partial m_{\alpha}^{(i)}}{\partial E_{\alpha}} \right)_{\text{hyp-disp}} = & \frac{1}{2} \gamma_{\alpha\alpha:\beta\gamma}^{(i)} F_{0\beta}^{(i)} F_{0\gamma}^{(i)} + \dots \\ & + \frac{\varepsilon_{ij}}{6} \left( \frac{\gamma_i}{\alpha_i} \right) \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \{ (10 - 7\kappa_{\gamma,i}) [2(1 - \kappa_{\alpha,j}) + \kappa_{\alpha,j}(3 \cos^2 \theta_j + 1)] + \\ & + 7\kappa_{\gamma,i} [(1 - \kappa_{\alpha,j}) (3 \cos^2 \theta_j + 1) + 3\kappa_{\alpha,j}(3 \cos \theta_j \cos \theta_j - \cos \theta_{ij}^2)] \} + \dots \end{aligned} \quad (26)$$

Substitution of the foregoing in Eq. (7), with the potential of Eq. (16), yields

$$\begin{aligned}
 B_R^{(ij)} = & \frac{20\pi^2 N^2}{81y_{ij}^4} \varepsilon_{ij} \sigma_{ij}^3 \left\{ \left( \frac{\gamma_i}{\alpha_i} + \frac{\gamma_j}{\alpha_j} \right) H_6(y_{ij}) + \right. \\
 & + \frac{y_{ij}^2}{250} \left[ \frac{\gamma_i}{\alpha_i} (50\kappa_{\alpha,j}^2 + 35\kappa_{\alpha,i}\kappa_{\gamma,i} + 133\kappa_{\alpha,i}\kappa_{\gamma,i}\kappa_{\alpha,j}^2) + \right. \\
 & \left. \left. + \frac{\gamma_j}{\alpha_j} (50\kappa_{\alpha,i}^2 + 35\kappa_{\alpha,j}\kappa_{\gamma,j} + 133\kappa_{\alpha,j}\kappa_{\gamma,j}\kappa_{\alpha,i}^2) \right] H_{12}(y_{ij}) + \dots \right\}. \quad (27)
 \end{aligned}$$

In the case of quadrupole molecules, the electric field  $F_{0\alpha}^{(i)}$  at the centre of the  $i$ -th molecule due to the quadrupole of the  $j$ -th molecule is given by

$$F_{0\alpha}^{(i)} = \frac{3}{2} \Theta_j r_{ij}^{-4} \{ (5 \cos^2 \theta_j - 1) \lambda_\alpha - 2s_\alpha^{(j)} \cos \theta_j \}, \quad (28)$$

and

$$\begin{aligned}
 \left( \frac{\partial m_\alpha^{(i)}}{\partial E_\alpha} \right)_{\text{hyp-quadr}} = & \frac{3}{16} \gamma_i \Theta_j^2 r_{ij}^{-8} \{ (10 - 7\kappa_{\gamma,i}) (5 \cos^4 \theta_j - 2 \cos^2 \theta_j + 1) + \\
 & + 21\kappa_{\gamma,i} (5 \cos \theta_i \cos^2 \theta_j - 2 \cos \theta_{ij} \cos \theta_j - \cos \theta_i)^2 \} + \dots \quad (29)
 \end{aligned}$$

From (7), (19) and (29), we therefore find on neglecting terms of order  $\alpha\gamma$ :

$$\begin{aligned}
 B_R^{(ij)} = & \frac{5\pi^2 N^2}{27\sigma_{ij}^5 y_{ij}^4} \left\{ (\gamma_i \Theta_j^2 + \Theta_i^2 \gamma_j) H_8(y_{ij}) - \right. \\
 & \left. - \frac{3y_{ij}^2 \Theta_i \Theta_j}{25\varepsilon_{ij} \sigma_{ij}^5} (\gamma_i \kappa_{\gamma,i} \Theta_j^2 + \Theta_i^2 \gamma_j \kappa_{\gamma,j}) H_{12}(y_{ij}) + \dots \right\}. \quad (30)
 \end{aligned}$$

In the first approximation, the anisotropy of hyperpolarizability of the molecules can be neglected,  $\kappa_\gamma = 0$ , and (27) and (30) reduce to simpler form

$$\begin{aligned}
 B_R^{(ij)} = & \frac{20\pi^2 N^2}{81y_{ij}^4} \varepsilon_{ij} \sigma_{ij}^3 \left\{ \left( \frac{\gamma_i}{\alpha_i} \right) \left[ H_6(y_{ij}) + \frac{1}{5} y_{ij}^2 \kappa_{\alpha,j}^2 H_{12}(y_{ij}) + \dots \right] + \right. \\
 & \left. + \left( \frac{\gamma_j}{\alpha_j} \right) \left[ H_6(y_{ij}) + \frac{1}{5} y_{ij}^2 \kappa_{\alpha,i}^2 H_{12}(y_{ij}) + \dots \right] \right\}, \quad (31)
 \end{aligned}$$

$$B_R^{(ij)} = \frac{5\pi^2 N^2}{27\sigma_{ij}^5 y_{ij}^4} (\gamma_i \Theta_j^2 + \Theta_i^2 \gamma_j) H_8(y_{ij}) + \dots \quad (32)$$

The formula (32) corresponds to the result which could be obtained for quadrupole liquids on the basis of Onsager's model (see Kielich 1960, 1961).

#### 4. Dipole molecules

Let us now calculate  $B_R^{(ij)}$  for the case of a gas mixture consisting of molecules endowed with a permanent dipole moment  $\mu$ . The total potential energy of interaction between two

unlike dipole molecules is given by (Kielich 1962a)

$$u_{ij} = 4\epsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} - \mu_i \mu_j (3 \cos \theta_i \cos \theta_j - \cos \theta_{ij}) r_{ij}^{-3} - \\ - \frac{1}{2} \{ \alpha_i (1 - \kappa_{\alpha,i}) \mu_j^2 (3 \cos^2 \theta_j + 1) + \alpha_j (1 - \kappa_{\alpha,j}) \mu_i^2 (3 \cos^2 \theta_i + 1) + \\ + 3(\alpha_i \kappa_{\alpha,i} \mu_j^2 + \mu_i^2 \alpha_j \kappa_{\alpha,j}) (3 \cos \theta_i \cos \theta_j - \cos \theta_{ij})^2 \} r_{ij}^{-6} + \dots \quad (33)$$

Besides the Lennard-Jones (6:12) potential there are included also terms representing dipole-dipole ( $r_{ij}^{-3}$ ) and dipole-induced dipole ( $r_{ij}^{-6}$ ) interactions.

On substitution of (15) and (33) in Eq. (7), we obtain

$$B_R^{(ij)} = \frac{2\pi^2 \alpha_i \alpha_j N^2}{225 \sigma_{ij}^6 \epsilon_{ij}^2 y_{ij}^2} \left\{ [\alpha_i \mu_j^2 (5\kappa_{\alpha,j} + 5\kappa_{\alpha,i} - \kappa_{\alpha,j} \kappa_{\alpha,i}) + \alpha_j \mu_i^2 (5\kappa_{\alpha,i} + 5\kappa_{\alpha,j} - \kappa_{\alpha,i} \kappa_{\alpha,j})] H_9(y_{ij}) + \right. \\ + \frac{\mu_i^2 \mu_j^2 y_{ij}^2}{24 \sigma_{ij}^3 \epsilon_{ij}} [\alpha_i (5 + 2\kappa_{\alpha,i} + 11\kappa_{\alpha,i}^2) (5 + \kappa_{\alpha,i}) + 18\kappa_{\alpha,i} \kappa_{\alpha,j} (2\alpha_i + 2\alpha_j + \alpha_i \kappa_{\alpha,i} + \alpha_j \kappa_{\alpha,j}) + \\ + \alpha_j (5 + 2\kappa_{\alpha,j} + 11\kappa_{\alpha,j}^2) (5 + \kappa_{\alpha,j})] H_{12}(y_{ij}) + \dots \\ + \frac{\mu_i^2 \mu_j^2 y_{ij}^2}{12 \epsilon_{ij}} (5\kappa_{\alpha,i} - \kappa_{\alpha,i} \kappa_{\alpha,j} + 5\kappa_{\alpha,j}) H_9(y_{ij}) + \\ \left. + \frac{\mu_i^4 \mu_j^4 y_{ij}^6}{1176 \sigma_{ij}^6 \epsilon_{ij}^3} (7\kappa_{\alpha,i} + \kappa_{\alpha,i} \kappa_{\alpha,j} + 7\kappa_{\alpha,j}) H_{15}(y_{ij}) + \dots \right\}. \quad (34)$$

We now calculate, moreover the further contributions to  $B_R^{(ij)}$  resulting from the effect of hyperpolarizability of the dipole molecules. For dipole molecules exhibiting the axial symmetry we have, in addition to Eqs. (13) and (22),

$$\mu_{\alpha}^{(i)} = \mu_i s_{\alpha}^{(i)}, \quad \beta_{\alpha\beta:\gamma}^{(i)} = \beta_i (1 - \kappa_{\beta,i}) \delta_{\alpha\beta} s_{\gamma}^{(i)} + 3 \beta_i \kappa_{\beta,i} s_{\alpha}^{(i)} s_{\beta}^{(i)} s_{\gamma}^{(i)}, \quad (35)$$

where

$$\kappa_{\beta,i} = \frac{\beta_{33:3}^{(i)} - \beta_{11:3}^{(i)}}{3\beta_i}, \quad \beta_i = \frac{1}{3} (\beta_{33:3}^{(i)} + 2\beta_{11:3}^{(i)}) \quad (36)$$

are the anisotropy and mean hyperpolarizability of the dipole molecules of species  $i$ , respectively.

In the present case, account should be taken of the electric field given rise to at the centre of the  $i$ -th molecule by the dipole of the  $j$ -th one:

$$F_{0\alpha}^{(i)} = \mu_j r_{ij}^{-3} (3\lambda_{\alpha} \cos \theta_j - s_{\alpha}^{(j)}), \quad (37)$$

thus, by formulas (22) and (35), Eq. (21) yields (terms of order  $\alpha\beta$  and  $\alpha\gamma$  are omitted):

$$\left( \frac{\partial m_{\alpha}^{(i)}}{\partial E_{\alpha}} \right)_{\text{hyp-dip}} = \beta_{\alpha\alpha:\beta}^{(i)} F_{0\beta}^{(i)} + \frac{1}{2} \gamma_{\alpha\alpha:\beta\gamma}^{(i)} F_{0\beta}^{(i)} F_{0\gamma}^{(i)} + \dots \\ = 3 \beta_{ii} \mu_j r_{ij}^{-3} (3 \cos \theta_i \cos \theta_j - \cos \theta_{ij}) + \\ + \frac{1}{12} \gamma_i \mu_j^2 r_{ij}^{-6} \{ (10 - 7\kappa_{\gamma,i}) (3 \cos^2 \theta_j + 1) + 21\kappa_{\gamma,i} (3 \cos \theta_i \cos \theta_j - \cos \theta_{ij})^2 \} + \dots \quad (38)$$

By the foregoing expression and by (33) and (7), the following result is obtained for the contribution to  $B_R^{(ij)}$  arising from the hyperpolarizability of dipole molecules:

$$\begin{aligned}
 B_R^{(ij)} = & \frac{2\pi^2 N^2}{81\sigma_{ij}^3 \gamma_{ij}^4} \left\{ 5(\gamma_i \mu_j^2 + \mu_i^2 \gamma_j) H_6(\gamma_{ij}) + \right. \\
 & + \frac{\mu_i^2 \mu_j^2 \gamma_{ij}^4}{200\sigma_{ij}^6 \epsilon_{ij}^2} [\gamma_i (25 + 14\kappa_{\gamma,ij}) \mu_j^2 + \mu_i^2 \gamma_j (25 + 14\kappa_{\gamma,ij})] H_{12}(\gamma_{ij}) + \\
 & + \frac{29 \mu_i^4 \mu_j^4 \gamma_{ij}^8}{134400 \sigma_{ij}^{12} \epsilon_{ij}^4} [\gamma_i (5 + 4\kappa_{\gamma,ij}) \mu_j^2 + \mu_i^2 \gamma_j (5 + 4\kappa_{\gamma,ij})] H_{18}(\gamma_{ij}) + \dots \\
 & + \frac{3\gamma_{ij}^2}{2\epsilon_{ij}} (\beta_{ij} u_i u_j^2 + \mu_i^2 \mu_j \beta_j) \left[ H_6(\gamma_{ij}) + \frac{3\mu_i^2 \mu_j^2 \gamma_{ij}^4}{200\sigma_{ij}^6 \epsilon_{ij}^2} H_{12}(\gamma_{ij}) + \right. \\
 & \left. + \frac{29 \mu_i^4 \mu_j^4 \gamma_{ij}^8}{313600 \sigma_{ij}^{12} \epsilon_{ij}^4} H_{18}(\gamma_{ij}) + \dots \right] + \dots \left. \right\}. \quad (39)
 \end{aligned}$$

### 5. One-component gases

In the case of a one-component gas, the contributions to the second refractivity virial coefficient given by Eqs. (17), (18), (20) and (34) assume the form

$$B_R^{is} = \frac{8\pi^2 \alpha^3 N^2}{9\sigma^3 \gamma^4} H_6(\gamma), \quad (40)$$

$$B_R^{anis} = \frac{16\pi^2 \alpha^3 N^2}{9\sigma^3 \gamma^4} \kappa_\alpha^2 H_6(\gamma) = 2\kappa_\alpha^2 B_R^{is}, \quad (41)$$

$$B_R^{anis-disp} = \frac{8\pi^2 \alpha^2 N^2}{225\gamma^2} \kappa_\alpha^2 (10 - \kappa_\alpha^2) H_9(\gamma), \quad (42)$$

$$B_R^{quadr-ind.dip} = \frac{8\pi^2 \alpha^3 N^2}{1575\sigma^8 \epsilon \gamma^2} \kappa_\alpha \Theta^2 (30 + 7\kappa_\alpha - 13\kappa_\alpha^2) H_{11}(\gamma), \quad (43)$$

$$B_R^{quadr-quadr} = \frac{2\pi^2 \alpha^2 N^2}{441\sigma^{10} \epsilon^2} \kappa_\alpha \Theta^4 (7 - \kappa_\alpha) H_{13}(\gamma), \quad (44)$$

$$\begin{aligned}
 B_R^{dip-ind.dip} = & \frac{4\pi^2 \alpha^3 \mu^2 N^2}{225\sigma^6 \epsilon \gamma^2} \left\{ \kappa_\alpha (5 + 5\kappa_\alpha - \kappa_\alpha^2) H_9(\gamma) + \right. \\
 & \left. + \frac{\mu^2 \gamma^2}{24\sigma^3 \epsilon} (25 + 15\kappa_\alpha + 93\kappa_\alpha^2 + 29\kappa_\alpha^3) H_{12}(\gamma) \right\}, \quad (45)
 \end{aligned}$$

$$B_R^{dip-dip} = \frac{\pi^2 \alpha^2 N^2}{1350 \sigma^6 \epsilon^2} \mu^4 \kappa_\alpha \left\{ (10 - \kappa_\alpha) H_9(\gamma) + \frac{\mu^4 \gamma^4}{98 \sigma^6 \epsilon^2} (14 + \kappa_\alpha) H_{15}(\gamma) + \dots \right\}. \quad (46)$$

The expressions (40), (44) and (46) were derived previously by Buckingham (1956).

In Table I, the various contributions to  $B_R$ , calculated for some gases on the basis of formulas (40)–(46), are shown. The latter prove immediately that the principal contribu-



TABLE I  
Calculated contributions to  $B_R$  in  $\text{cm}^6 \text{mol}^{-2}$  for  $T = 298.2^\circ\text{K}$ .

Gases	$\text{CH}_4$	$\text{N}_2$	$\text{O}_2$	$\text{CO}_2$	$\text{CHCl}_3$	$\text{CH}_3\text{F}$
$\epsilon/k^\circ\text{K}$	137.0 <sup>1)</sup>	91.5 <sup>1)</sup>	113.0 <sup>1)</sup>	190.0 <sup>1)</sup>	327.0 <sup>1)</sup>	196.0 <sup>2)</sup>
$\sigma(\text{\AA})$	3.882 <sup>1)</sup>	3.681 <sup>1)</sup>	3.433 <sup>1)</sup>	3.996 <sup>1)</sup>	5.430 <sup>1)</sup>	3.370 <sup>2)</sup>
$\alpha \times 10^{24} (\text{cm}^3)$	2.60 <sup>1)</sup>	1.76 <sup>1)</sup>	1.60 <sup>1)</sup>	2.92 <sup>3)</sup>	8.23 <sup>1)</sup>	2.60 <sup>3)</sup>
$\alpha$	0	0.18	0.24	0.27	-0.09	0.11
$\mu \times 10^{18} (\text{e.s.u.})$	0	0	0	0	1.05	1.82
$\Theta \times 10^{26} (\text{e.s.u.})$	0	1.8 <sup>4)</sup>	1.9 <sup>4)</sup>	5.0 <sup>4)</sup>	0	0
$B_R^{\text{is}}$	5.7	2.0	1.8	8.8	87.0	8.4
$B_R^{\text{anis}}$	0	0.1	0.2	1.3	1.6	0.2
$B_R^{\text{anis-disp}}$	0	0.6	1.0	7.6	16.2	0.9
$B_R^{\text{quadr-ind.dip}}$	0	0.01	0.03	0.5	0	0
$B_R^{\text{quadr-quadr}}$	0	0.02	0.1	3.4	0	0
$B_R^{\text{dip-ind.dip}}$	0	0	0	0	1.0	10.9
$B_R^{\text{dip-dip}}$	0	0	0	0	0.4	6.3
$B_R^{\text{total}}$	5.7	2.73	3.13	21.6	106.2	26.7

<sup>1</sup> Hirschfelder, J. O., Curtiss, Ch. F. and Bird, R. B., *Molecular Theory of Gases and Liquids* (J. Wiley & Sons, Inc., New York, 1954).

<sup>2</sup> Buckingham, A. D. and Pople, J. A., *Trans. Faraday Soc.*, **51**, 1173 (1955).

<sup>3</sup> Le Fevre, C. G. and Le Fevre, R. J. W., *Revs. pure and appl. Chem.*, **5**, 261 (1955).

<sup>4</sup> Kielich, S., *Physica*, **28**, 511 (1962).

tion to  $B_R$  for all gases considered is related to  $B_R^{\text{is}}$ , which should be calculated on the assumptions that the molecules are isotropically polarizable and interact with central forces only. It is also seen from Table I that the influence of anisotropy in the polarizability on the second refractivity virial coefficient given by

$$\frac{B_R^{\text{anis}}}{B_R^{\text{is}}} = 2\alpha^2 = 2 \left( \frac{\alpha_{33} - \alpha_{11}}{\alpha_{33} + 2\alpha_{11}} \right)^2, \quad (47)$$

is in general small and attains, at the most (*e. g.*,  $\text{CO}_2$ ), 15% of the values of  $B_R^{\text{is}}$ . Let us draw attention to the interesting fact that the anisotropy alone plays no role whatsoever in some cases (*e. g.*  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{F}$ ); nevertheless, in connection with the anisotropic-dispersive forces it yields peculiarly great contributions to  $B_R$  amounting in the case of  $\text{CHCl}_3$  to 18%, and in that of  $\text{CO}_2$  — to as much as 94% of the value of  $B_R^{\text{is}}$ . The contributions to  $B_R$  resulting from the quadrupole-induced dipole and quadrupole-quadrupole interactions are negligible, except for the case of molecules possessing a very great quadrupole moment (*e. g.*  $\text{CO}_2$ ). Dipole-induced dipole and dipole-dipole interactions yield important contributions to  $B_R$  in the case of  $\text{CH}_3\text{F}$  molecules.

We now proceed discuss the influence of hyperpolarizability on  $B_R$ . In the case of tetrahedral molecules (*e. g.*,  $\text{CH}_4$  and  $\text{CCl}_4$ ), the hyperpolarizability of the molecule could

be caused by the electric field,  $F \sim \Omega_{123} r^{-5}$ , due to the octopole moment  $\Omega_{123}$  of the neighbouring molecule. In this case, in addition to Eq. (40), we obtain the following contribution to  $B_R$ :

$$B_R^{\text{hyp-octop}} = \frac{32\pi^2 N^2}{27\sigma^7 y^4} \gamma \Omega_{123}^2 H_{10}(y). \quad (48)$$

For methane, we have from Kerr's constant (Buckingham and Pople 1955b)  $\gamma = 2.6 \times 10^{-36}$  e. s. u. and from second virial data (Kielich 1962b)  $\Omega_{123} = 12 \times 10^{-34}$  e. s. u.; hence, Eq. (48) yields (at  $T = 298.2^\circ\text{K}$ )  $B_R^{\text{hyp-octop}} = 0.3 \text{ cm}^6 \text{ mol}^{-2}$ , which amounts to 5% of the value of  $B_R^{\text{is}}$ .

On the other hand the formula (31) yields for isotropically polarizable molecules of one kind (see Buckingham 1956):

$$B_R^{\text{hyp-disp}} = \frac{40\pi^2 N^2}{81y^4} \varepsilon \sigma^3 \left( \frac{\gamma}{\alpha} \right) H_6(y), \quad (49)$$

hence for  $\text{CH}_4$  molecule:  $B_R^{\text{hyp-disp}} = 11.4 \text{ cm}^6 \text{ mol}^{-2} = 2B_R^{\text{is}}$ .

Thus the contribution from hyperpolarizability induced in the molecules by the field of dispersion forces has an important influence on the  $B_R$ ; this conclusion was reached earlier by Buckingham (1956).

If in Eq. (39) the anisotropy of hyperpolarizability is neglected,  $\alpha_\gamma = 0$ , the Buckingham (1956) formula is obtained:

$$\begin{aligned} B_R^{\text{hyp-dip}} = & \frac{2\pi^2 N^2}{81\sigma^3 y^4} \left\{ 10\gamma\mu^2 \left[ H_6(y) + \frac{\mu^4 y^4}{80\sigma^6 \varepsilon^2} H_{12}(y) + \right. \right. \\ & \left. \left. + \frac{29\mu^8 y^8}{268800\sigma^{12} \varepsilon^4} H_{18}(y) \right] + \frac{3\beta\mu^3 y^2}{\varepsilon} \left[ H_6(y) + \frac{3\mu^4 y^4}{200\sigma^6 \varepsilon^2} H_{12}(y) + \right. \right. \\ & \left. \left. + \frac{29\mu^8 y^8}{313600\sigma^{12} \varepsilon^4} H_{18}(y) + \dots \right] \right\}. \quad (50) \end{aligned}$$

From molecular light scattering data, we have (Kielich 1962a)  $\beta = 11.2 \times 10^{-29}$  e. s. u. for the chloroform molecule and obtain on the basis of (50) by neglecting of the terms with  $\gamma$ ,  $B_R^{\text{hyp-dip}} = 158 \text{ cm}^6 \text{ mol}^{-2}$ . This result shows that, in the case of dipole molecules, the hyperpolarizability  $\beta$  yields a far greater contribution to  $B_R$  (see also Buckingham 1956).

## 6. Two-component gases

By Eq. (5), the second refractivity virial coefficient of a binary gas mixture is of the form

$$B_R = x_1^2 B_R^{(11)} + 2x_1 x_2 B_R^{(12)} + x_2^2 B_R^{(22)}, \quad (51)$$

where  $x_1 + x_2 = 1$ .

We shall now discuss the second refractivity virial coefficient  $B_R^{(12)}$  corresponding to the interactions of two unlike molecules of components 1 and 2.

If, in particular, the interacting molecules of one component of the mixture are spherical and those of the other quadrupolar, we obtain by Eqs. (17), (20), (31) and (32):

$$\begin{aligned}
 B_R^{(12)} = & \frac{4\pi^2\alpha_1\alpha_2N^2}{9\sigma_{12}^3\gamma_{12}^4} \left\{ (\alpha_1 + \alpha_2 + 2\alpha_2\kappa_{\alpha,2}^2) H_6(\gamma_{12}) + \frac{2}{5} \sigma_{12}^3\gamma_{12}^2\kappa_{\alpha,2}^2 H_9(\gamma_{12}) + \right. \\
 & \left. + \frac{6\alpha_1\kappa_{\alpha,2}\Theta_2^2\gamma_{12}^2}{35\sigma_{12}^3\epsilon_{12}} H_{11}(\gamma_{12}) \right\} + \frac{20\pi^2N^2}{81\gamma_{12}^4} \epsilon_{12}\sigma_{12}^3 \left\{ \left( \frac{\gamma_1}{\alpha_1} \right) \left[ H_6(\gamma_{12}) + \right. \right. \\
 & \left. \left. + \frac{1}{5} \gamma_{12}^2\kappa_{\alpha,2}^2 H_{12}(\gamma_{12}) \right] + \left( \frac{\gamma_2}{\alpha_2} \right) H_6(\gamma_{12}) + \frac{3\gamma_1\Theta_2^2}{4\sigma_{12}^3\epsilon_{12}} H_8(\gamma_{12}) \right\}. \quad (52)
 \end{aligned}$$

Assuming the well known rules:  $\sigma_{12} = (\sigma_1 + \sigma_2)/2$  and  $\epsilon_{12} = (\epsilon_1 \epsilon_2)^{1/2}$ , and using the molecular data from Table I, and  $\gamma_2 = 3 \times 10^{-36}$  e. s. u., we obtain for a  $\text{CH}_4\text{--CO}_2$  mixture by (52):

$$B_R^{(12)} = (3.1 + 0.5 + 2.8 + 0.2 + 15.6) \text{ cm}^6 \text{ mol}^{-2} = 22.2 \text{ cm}^6 \text{ mol}^{-2}.$$

It will be seen that important contributions to  $B_R^{(12)}$  arise from anisotropic dispersive forces (the third figure in the brackets) and from the effect of hyperpolarizability (the value of 15.6).

In the case of collisions between a spherical molecule 1 and a dipole molecule 2, expressions (17), (31), (34) and (39) yield:

$$\begin{aligned}
 B_R^{(12)} = & \frac{4\pi^2\alpha_1\alpha_2N^2}{9\sigma_{12}^3\gamma_{12}^4} \left\{ (\alpha_1 + \alpha_2 + 2\alpha_2\kappa_{\alpha,2}^2) H_6(\gamma_{12}) + \frac{2}{5} \sigma_{12}^3\gamma_{12}^2\kappa_{\alpha,2}^2 H_9(\gamma_{12}) + \right. \\
 & \left. + \frac{\alpha_1\kappa_{\alpha,2}\mu_2^2\gamma_{12}^2}{10\sigma_{12}^3\epsilon_{12}} H_9(\gamma_{12}) \right\} + \frac{20\pi^2N^2}{81\gamma_{12}^4} \epsilon_{12}\sigma_{12}^3 \left\{ \left( \frac{\gamma_1}{\alpha_1} \right) \left[ H_6(\gamma_{12}) + \right. \right. \\
 & \left. \left. + \frac{1}{5} \gamma_{12}^2\kappa_{\alpha,2}^2 H_{12}(\gamma_{12}) \right] + \left( \frac{\gamma_2}{\alpha_2} \right) H_6(\gamma_{12}) + \frac{\gamma_1\mu_2^2}{2\sigma_{12}^3\epsilon_{12}} H_6(\gamma_{12}) \right\}. \quad (53)
 \end{aligned}$$

For a mixture containing a quadrupole gas ( $\mu_1 = 0$ ,  $\Theta_1 \neq 0$ ) and a dipole gas ( $\mu_2 \neq 0$ ,  $\Theta_2 = 0$ ), on the basis of previously calculated results, we get

$$\begin{aligned}
 B_R^{(12)} = & \frac{4\pi^2\alpha_1\alpha_2N^2}{9\sigma_{12}^3\gamma_{12}^4} \left\{ [\alpha_1(1 + 2\kappa_{\alpha,1}^2) + \alpha_2(1 + 2\kappa_{\alpha,2}^2)] H_6(\gamma_{12}) + \right. \\
 & \left. + \frac{2}{5} \sigma_{12}^3\gamma_{12}^2(5\kappa_{\alpha,1}^2 - \kappa_{\alpha,1}^2\kappa_{\alpha,2}^2 + 5\kappa_{\alpha,2}^2) H_9(\gamma_{12}) + \right. \\
 & \left. + \frac{3\alpha_2\Theta_1^2\gamma_{12}^2}{175\sigma_{12}^5\epsilon_{12}} (10\kappa_{\alpha,1} + 7\kappa_{\alpha,2}^2 - 2\kappa_{\alpha,1}\kappa_{\alpha,2}^2) H_{11}(\gamma_{12}) + \right. \\
 & \left. + \frac{\alpha_1\mu_2^2\gamma_{12}^2}{50\sigma_{12}^3\epsilon_{12}} (5\kappa_{\alpha,2} + 5\kappa_{\alpha,1}^2 - \kappa_{\alpha,2}\kappa_{\alpha,1}^2) H_9(\gamma_{12}) \right\} + \\
 & + \frac{20\pi^2N^2}{81\gamma_{12}^4} \epsilon_{12}\sigma_{12}^3 \left\{ \left( \frac{\gamma_1}{\alpha_1} \right) \left[ H_6(\gamma_{12}) + \frac{1}{5} \gamma_{12}^2\kappa_{\alpha,2}^2 H_{12}(\gamma_{12}) \right] + \right.
 \end{aligned}$$

$$\begin{aligned}
& + \left( \frac{\gamma_2}{\alpha_2} \right) \left[ H_6(y_{12}) + \frac{1}{5} y_{12}^2 \alpha_{\alpha,1}^2 H_{12}(y_{12}) \right] + \\
& + \left. \frac{\gamma_1 \mu_2^2}{2\sigma_{12}^3 \epsilon_{12}} H_6(y_{12}) + \frac{3\gamma_2 \Theta_1^2}{4\sigma_{12}^8 \epsilon_{12}} H_8(y_{12}) \right\}. \tag{54}
\end{aligned}$$

Similarly, we can derive the virial coefficients  $B_R^{(ij)}$  for other special cases.

From the discussion presented in this paper it follows that appropriate refraction measurements for compressed gaseous mixtures might provide some indirect information about the optical and electric properties of the isolated molecules, as well as about the force parameters for interacting unlike molecules.

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