

Theory of Birefringence Induced in a Compressed Gas Mixture by an Electric Field Gradient

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Presented by W. RUBINOWICZ on July 6, 1960

Introduction

Quite recently, Buckingham [1] proposed a theory of optical birefringence induced in an isotropic medium by an electric field gradient. In the case of a gaseous medium, Buckingham derived the following expression for the difference

$$(1) \quad n_x - n_y = \frac{4\pi}{45} N_0 \left(B_{\alpha\beta:\gamma\delta} + \frac{1}{kT} \alpha_{\alpha\beta} H_{\alpha\beta} \right) F_{xx}$$

between the refractive indexes of a gas, for light propagation in the direction of the axis of a four-wire condenser and with electric vectors in the x and y directions. N_0 is the number of molecules in unit volume, k — Boltzman's constant, T — absolute temperature and $F_{xx} = -F_{yy}$ — electric field gradient ($F_{zz} = 0$). $H_{\alpha\beta}$ is the tensor of the quadrupole moment of the molecule, $\alpha_{\alpha\beta}$ — its polarizability tensor, whereas the tensor $B_{\alpha\beta:\gamma\delta}$ accounts for the quadrupole polarizability. The tensors $\alpha_{\alpha\beta}$ and $H_{\alpha\beta}$ are symmetrical in the indexes α, β , and $B_{\alpha\beta:\gamma\delta}$ — in the pairs of indexes α, β and γ, δ . The tensors relate to the isolated molecule.

Buckingham proposed that Eq. (1) be used for the direct determination of the quadrupole moment of the molecule, which is given as a rule by

$$(2) \quad H_{\alpha\beta} = \frac{1}{2} \sum_n e_n (3 r_{n\alpha} r_{n\beta} - r_n^2 \delta_{\alpha\beta}),$$

wherein e_n is the n -th electric charge of the molecule, and \vec{r}_n — its radius vector. Summation extends over all the charges of the molecule. $\delta_{\alpha\beta}$ is the unit tensor.

Moreover, Buckingham [1] derived an expression for $n_x - n_y$ in dense media (gases at high pressure, or liquids). It is the aim of the present paper to apply this theory to multi-component systems, and, in particular, to compressed gas mixtures.

Theory for a multi-component system

The generalization of Buckingham's theory [1] for a multi-component system yields

$$(3) \quad \frac{n_x - n_y}{nF_{xx}} V_m = \frac{(n^2 + 2)^2 (2\varepsilon + 3)}{15n^2} Q_m,$$

wherein V_m is the molar volume of the system under consideration, n — refractive index and ε — dielectric permittivity. Q_m denotes the molecular constant of the optical birefringence induced in the multi-component system by the electric field gradient, and is given by

$$(4) \quad Q_m = \frac{4\pi}{45} \left\{ \sum_{i=1}^{\nu} \left\langle \sum_{p=1}^{x_i N} B_{\alpha\beta:\alpha\beta}^{(p,i)} \right\rangle + \frac{1}{kT} \sum_{i=1}^{\nu} \sum_{j=1}^{\nu} \left\langle \sum_{p=1}^{x_i N} \sum_{q=1}^{x_j N} \alpha_{\alpha\beta}^{(p,i)} \mathbf{H}_{\alpha\beta}^{(q,j)} \right\rangle \right\},$$

x_i denotes the molar fraction of the i -th component of the system, ν — number of all components, and N — Avogadro's number, whilst the symbol $\langle \rangle$ is used to denote statistical averaging. The tensors $\alpha_{\alpha\beta}^{(p,i)}$, $\mathbf{H}_{\alpha\beta}^{(p,i)}$ and $B_{\alpha\beta:\gamma\delta}^{(p,i)}$ now refer to the p -th molecule of species i , immersed in the medium.

We shall now apply Eq. (4) to a gas mixture by the method used by Buckingham and Raab [2] in their theory of the dielectric permittivity of a compressed gas mixture. To this purpose, the molecular constant Q_m is expanded in powers of $1/V_m$:

$$(5) \quad Q_m = A_Q + \frac{B_Q}{V_m} + \frac{C_Q}{V_m^2} + \dots$$

The expansion coefficients A_Q , B_Q , C_Q , etc. are termed the first, second, third, etc. virial coefficients of the molecular constant Q_m .

Discussion will be restricted to the virial coefficients A_Q and B_Q only; for a gas mixture, these are given by

$$(6) \quad A_Q = \sum_{i=1}^{\nu} x_i A_Q^{(i)}; \quad B_Q = \sum_{i=1}^{\nu} \sum_{j=1}^{\nu} x_i x_j B_Q^{(ij)},$$

wherein, by the general expression of Eq. (4), we have

$$(7) \quad A_Q^{(i)} = \frac{4\pi}{45} N \left(B_{\alpha\beta:\alpha\beta}^{(i)} + \frac{1}{kT} \alpha_{\alpha\beta}^{(i)} \mathbf{H}_{\alpha\beta}^{(i)} \right),$$

$$(8) \quad B_Q^{(ij)} = \frac{2\pi N^2}{45\Omega^2} \iint \iint \left\{ B_{\alpha\beta:\alpha\beta}^{(ij)} - B_{\alpha\beta:\alpha\beta}^{(i)} - B_{\alpha\beta:\alpha\beta}^{(j)} + \right. \\ \left. + \frac{1}{kT} \left(\alpha_{\alpha\beta}^{(ij)} \mathbf{H}_{\alpha\beta}^{(ij)} - \alpha_{\alpha\beta}^{(i)} \mathbf{H}_{\alpha\beta}^{(i)} - \alpha_{\alpha\beta}^{(j)} \mathbf{H}_{\alpha\beta}^{(j)} \right) \right\} e^{-\frac{u_{ij}}{kT}} d\mathbf{r}_{ij}^{(12)} d\omega_i^{(1)} d\omega_j^{(2)}.$$

Herein, the tensors $\alpha_{\alpha\beta}^{(i)}$, $\mathbf{H}_{\alpha\beta}^{(i)}$ and $B_{\alpha\beta:\gamma\delta}^{(i)}$ are those of the isolated molecule of the i -th component of the gas, whilst $\alpha_{\alpha\beta}^{(ij)}$, $\mathbf{H}_{\alpha\beta}^{(ij)}$ and $B_{\alpha\beta:\gamma\delta}^{(ij)}$ refer to the inter-

acting pair of molecules "1" and "2" belonging to the i -th and j -th gas component, respectively. The quantity $u_{ij}^{(12)}$ is the total potential energy of interaction between a pair of molecules belonging to the i -th and j -th species; $\bar{r}_{ij}^{(12)}$ denotes the distance separating their centres, and $\omega_i^{(1)}$ and $\omega_j^{(2)}$ — their respective orientational variables; $\Omega = \int d\omega_i^{(1)} = \int d\omega_j^{(2)}$.

If, in particular, the tensors $\alpha_{\alpha\beta}^{(ij)}$, $H_{\alpha\beta}^{(ij)}$ and $B_{\alpha\beta;\gamma\delta}^{(ij)}$ are independent of the molecular fields, the second virial coefficient given by Eq. (8) reduces to the simpler form

$$(9) \quad B_Q^{(ij)} = \frac{2\pi N^2}{45kT\Omega^2} \iiint (\alpha_{\alpha\beta}^{(1,i)} H_{\alpha\beta}^{(2,j)} + H_{\alpha\beta}^{(1,i)} \alpha_{\alpha\beta}^{(2,j)}) e^{-\frac{u_{ij}^{(12)}}{kT}} d\bar{r}_{ij}^{(12)} d\omega_i^{(1)} d\omega_j^{(2)}.$$

The foregoing expression will now be discussed separately for the case of a mixture of non-dipolar gases and for that of polar ones.

Non-dipolar gas mixture

The total potential energy of the interaction between a pair of non-dipolar molecules of the i -th and j -th gas components, respectively, possessing a quadrupole moment and presenting anisotropic polarizability, is given by the expression [3]

$$(10) \quad u_{ij}^{(12)} = u(r_{ij}) - \frac{1}{9} H_{\alpha\beta}^{(1,i)} H_{\gamma\delta}^{(2,j)} T_{\alpha\beta\gamma\delta}^{(ij)} - \\ - \frac{1}{18} (\alpha_{\alpha\beta}^{(1,i)} H_{\gamma\delta}^{(2,j)} H_{\epsilon\eta}^{(2,j)} + \alpha_{\alpha\beta}^{(2,j)} H_{\gamma\delta}^{(1,i)} H_{\epsilon\eta}^{(1,i)}) T_{\alpha\gamma\delta}^{(ij)} T_{\beta\epsilon\eta}^{(ij)},$$

wherein $u(r_{ij})$ denotes the energy of central interaction of the molecules, the second term accounts for the quadrupole-quadrupole interaction energy, and the third — for that of quadrupole-induced dipole interaction. The tensors $T_{\alpha\beta\gamma}^{(ij)}$ and $T_{\alpha\beta\gamma\delta}^{(ij)}$ characterizing dipole-quadrupole (r_{ij}^{-4}) and quadrupole-quadrupole (r_{ij}^{-5}) interactions have been given here in the form in which they occur in Pop'e's paper [4].

Considering that the tensorial molecular interaction energy in Eq. (10) represents a perturbation in $u(r_{ij})$, Eq. (9) yields, by the method used in the theory of light scattering virial coefficients [3],

$$(11) \quad B_Q^{(ij)} = \text{quadr-quadr } B_Q^{(ij)} + \text{quadr-ind. dip } B_Q^{(ij)},$$

wherein

$$(12) \quad \text{quadr-quadr } B_Q^{(ij)} = \frac{64\pi N^2}{14175 k^3 T^3} \{ (3\alpha_{\alpha\beta}^{(i)} H_{\alpha\gamma}^{(i)} H_{\beta\gamma}^{(i)} - \alpha_{\alpha\alpha}^{(i)} H_{\beta\gamma}^{(i)} H_{\beta\gamma}^{(i)}) H_{\delta\epsilon}^{(j)} H_{\delta\eta}^{(j)} H_{\epsilon\eta}^{(j)} + \\ + (3\alpha_{\alpha\beta}^{(j)} H_{\alpha\gamma}^{(j)} H_{\beta\gamma}^{(j)} - \alpha_{\alpha\alpha}^{(j)} H_{\beta\gamma}^{(j)} H_{\beta\gamma}^{(j)}) H_{\delta\epsilon}^{(i)} H_{\delta\eta}^{(i)} H_{\epsilon\eta}^{(i)} \} \langle r_{ij}^{-10} \rangle + \dots,$$

is the second virial coefficient accounting for quadrupole-quadrupole interaction, whereas

$$(13) \quad \text{quadr-ind. dip } B_Q^{(ij)} = \frac{4\pi N^2}{4725 k^2 T^2} \{ (3\alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)} \alpha_{\beta\beta}^{(i)}) H_{\gamma\delta}^{(j)} H_{\gamma\epsilon}^{(j)} H_{\delta\epsilon}^{(j)} + \\ + (3\alpha_{\alpha\beta}^{(j)} \alpha_{\alpha\beta}^{(j)} - \alpha_{\alpha\alpha}^{(j)} \alpha_{\beta\beta}^{(j)}) H_{\gamma\delta}^{(i)} H_{\gamma\epsilon}^{(i)} H_{\delta\epsilon}^{(i)} + (3\alpha_{\alpha\beta}^{(i)} H_{\alpha\gamma}^{(i)} H_{\beta\gamma}^{(i)} - \\ - \alpha_{\alpha\alpha}^{(i)} H_{\beta\gamma}^{(i)} H_{\beta\gamma}^{(i)}) \alpha_{\delta\epsilon}^{(j)} H_{\delta\epsilon}^{(j)} + (3\alpha_{\alpha\beta}^{(j)} H_{\alpha\gamma}^{(j)} H_{\beta\gamma}^{(j)} - \alpha_{\alpha\alpha}^{(j)} H_{\beta\gamma}^{(j)} H_{\beta\gamma}^{(j)}) \alpha_{\delta\epsilon}^{(i)} H_{\delta\epsilon}^{(i)} \} \langle r_{ij}^{-8} \rangle + \dots$$

accounts for quadrupole-induced dipole interactions, and

$$(14) \quad \langle r_{ij}^{-n} \rangle = \int_0^{\infty} r_{ij}^{-n} e^{-\frac{u(r_{ij})}{kT}} d\bar{r}_{ij}$$

is a mean value depending solely on the model of central forces $u(r_{ij})$ adopted.

Assuming the Lennard-Jones potential [5] for $u(r_{ij})$, in the form [6]

$$(15) \quad u(r_{ij}) = 4\varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\},$$

the expression of Eq. (14) yields [7]

$$(16) \quad \langle r_{ij}^{-n} \rangle = \frac{\pi \sigma_{ij}^{3-n}}{3y_{ij}^4} H_n(y_{ij}); \quad y_{ij} = 2 \left(\frac{\varepsilon_{ij}}{kT} \right)^{1/2}.$$

Herein, ε_{ij} and σ_{ij} are the well-known central forces parameters having the dimensions of energy and length, and

$$(17) \quad H_n(y_{ij}) = y_{ij}^{\frac{27-n}{6}} \sum_{s=0}^{\infty} \Gamma\left(\frac{6s+n-3}{12}\right) \frac{y_{ij}^s}{s!}$$

— the functions introduced by Pople [8]; these have been tabulated by Buckingham and Pople [7] for n ranging from 6 to 17 and for values $0.6 \leq y \leq 3.2$.

For molecules possessing axial symmetry, Eqs. (12) and (13), with respect to (16), reduce to

$$(18) \quad \text{quadr-quadr } B_Q^{(ij)} = \frac{\pi^2 N^2}{3150 kT \sigma_{ij}^7 \varepsilon_{ij}^2} (\alpha_{(i)} \delta_{(i)} \mathbf{H}_{(j)} + \\ + \mathbf{H}_{(i)} \alpha_{(j)} \delta_{(j)}) \mathbf{H}_{(i)}^2 \mathbf{H}_{(j)}^2 H_{10}(y_{ij}) + \dots,$$

$$(19) \quad \text{quadr-ind. dip } B_Q^{(ij)} = \frac{\pi^2 N^2}{1050 kT \sigma_{ij}^5 \varepsilon_{ij} y_{ij}^2} (\alpha_{(i)} \delta_{(i)} \mathbf{H}_{(j)} + \\ + \mathbf{H}_{(i)} \alpha_{(j)} \delta_{(j)}) (\alpha_{(i)} \delta_{(i)} \mathbf{H}_{(j)}^2 + \mathbf{H}_{(i)}^2 \alpha_{(j)} \delta_{(j)}) H_8(y_{ij}) + \dots,$$

wherein

$$(20) \quad \mathbf{H} = \mathbf{H}_{33} = \frac{1}{2} \sum_n e_n (3Z_n^2 - r_n^2) = -2\mathbf{H}_{11} = -2\mathbf{H}_{22}$$

is the quadrupole moment of an axially symmetric molecule, and the quantities

$$(21) \quad \delta = \frac{\alpha_{\parallel} - \alpha_{\perp}}{3\alpha} \quad \text{and} \quad \alpha = \frac{1}{3} (\alpha_{\parallel} + 2\alpha_{\perp})$$

denote the optical anisotropy of the molecule and its mean polarizability, respectively, α_{\parallel} being the polarizability in the direction of the axis of symmetry of the molecule, and α_{\perp} — that in the direction perpendicular to this axis.

Polar gas mixture

For polar molecules possessing a permanent dipole moment μ_α and quadrupole moment $H_{\alpha\beta}$, the total potential interaction energy is given by (see [3], [4])

$$(22) \quad u_{ij}^{(12)} = u(r_{ij}) + \mu_\alpha^{(1,i)} \mu_\beta^{(2,j)} T_{\alpha\beta}^{(ij)} + \frac{1}{3} (\mu_\alpha^{(1,i)} H_{\beta\gamma}^{(2,j)} - H_{\alpha\beta}^{(1,i)} \mu_\gamma^{(2,j)}) T_{\alpha\beta\gamma}^{(ij)} - \\ - \frac{1}{9} H_{\alpha\beta}^{(1,i)} H_{\gamma\delta}^{(2,j)} T_{\alpha\beta\gamma\delta}^{(ij)} - \frac{1}{2} (\alpha_{\alpha\beta}^{(1,i)} \mu_\gamma^{(2,j)} \mu_\delta^{(2,j)} + \alpha_{\alpha\beta}^{(2,j)} \mu_\gamma^{(1,i)} \mu_\delta^{(1,i)}) T_{\alpha\gamma}^{(ij)} T_{\beta\delta}^{(ij)} + \dots;$$

here, in addition to the energy $u(r_{ij})$ due to central forces, terms accounting for the energy of electrostatic dipole-dipole (r_{ij}^{-3}), dipole-quadrupole (r_{ij}^{-4}), quadrupole-quadrupole (r_{ij}^{-5}), dipole-induced dipole (r_{ij}^{-6}) etc. interactions occur.

Substitution of the foregoing expansion in Eq. (9) yields the second virial coefficient in the form

$$(23) \quad B_Q^{(ij)} = \text{dip-dip } B_Q^{(ij)} + \text{dip-quadr } B_Q^{(ij)} + \text{quadr-quadr } B_Q^{(ij)} + \text{dip-ind. dip } B_Q^{(ij)} + \dots$$

The first term herein accounts for dipole-dipole interaction and is given by

$$(24) \quad \text{dip-dip } B_Q^{(ij)} = \frac{\pi N^2}{3375 k^3 T^3} \{ (3\alpha_{\alpha\beta}^{(i)} \mu_\alpha^{(i)} \mu_\beta^{(i)} - \alpha_{\alpha\alpha}^{(i)} \mu_\beta^{(i)} \mu_\beta^{(i)}) H_{\gamma\delta}^{(j)} \mu_\gamma^{(j)} \mu_\delta^{(j)} + \\ + (3\alpha_{\alpha\beta}^{(j)} \mu_\alpha^{(j)} \mu_\beta^{(j)} - \alpha_{\alpha\alpha}^{(j)} \mu_\beta^{(j)} \mu_\beta^{(j)}) H_{\gamma\delta}^{(i)} \mu_\gamma^{(i)} \mu_\delta^{(i)} \} \left\{ \langle r_{ij}^{-6} \rangle + \frac{12\mu_{(i)}^2 \mu_{(j)}^2}{49k^2 T^2} \langle r_{ij}^{-12} \rangle + \dots \right\},$$

whilst the second term, which relates to dipole-quadrupole interaction, has the form

$$(25) \quad \text{dip-quadr } B_Q^{(ij)} = \frac{4\pi N^2}{4725 k^3 T^3} \{ [(3\alpha_{\alpha\beta}^{(i)} \mu_\alpha^{(i)} \mu_\beta^{(i)} - \alpha_{\alpha\alpha}^{(i)} \mu_\beta^{(i)} \mu_\beta^{(i)}) H_{\gamma\delta}^{(j)} H_{\gamma\epsilon}^{(j)} H_{\delta\epsilon}^{(j)} + \\ + (3\alpha_{\alpha\beta}^{(j)} \mu_\alpha^{(j)} \mu_\beta^{(j)} - \alpha_{\alpha\alpha}^{(j)} \mu_\beta^{(j)} \mu_\beta^{(j)}) H_{\gamma\delta}^{(i)} H_{\gamma\epsilon}^{(i)} H_{\delta\epsilon}^{(i)} + (3\alpha_{\alpha\beta}^{(i)} H_{\alpha\gamma}^{(i)} H_{\beta\gamma}^{(i)} - \\ - \alpha_{\alpha\alpha}^{(i)} H_{\beta\gamma}^{(i)} H_{\beta\gamma}^{(i)}) H_{\delta\epsilon}^{(j)} \mu_\delta^{(j)} \mu_\epsilon^{(j)} + (3\alpha_{\alpha\beta}^{(j)} H_{\alpha\gamma}^{(j)} H_{\beta\gamma}^{(j)} - \alpha_{\alpha\alpha}^{(j)} H_{\beta\gamma}^{(j)} H_{\beta\gamma}^{(j)}) H_{\delta\epsilon}^{(i)} \mu_\delta^{(i)} \mu_\epsilon^{(i)}] \langle r_{ij}^{-8} \rangle - \\ - \frac{16}{15kT} [(3\alpha_{\alpha\beta}^{(i)} H_{\alpha\gamma}^{(i)} \mu_\beta^{(i)} \mu_\gamma^{(i)} - \alpha_{\alpha\alpha}^{(i)} H_{\beta\gamma}^{(i)} \mu_\beta^{(i)} \mu_\gamma^{(i)} - \alpha_{\alpha\beta}^{(i)} H_{\alpha\beta}^{(i)} \mu_\gamma^{(i)} \mu_\gamma^{(i)}) (3H_{\delta\epsilon}^{(j)} H_{\eta\delta}^{(j)} \mu_\epsilon^{(j)} \mu_\eta^{(j)} - \\ - H_{\delta\epsilon}^{(j)} H_{\delta\epsilon}^{(j)} \mu_\eta^{(j)} \mu_\eta^{(j)}) + (3\alpha_{\alpha\beta}^{(j)} H_{\alpha\gamma}^{(j)} \mu_\beta^{(j)} \mu_\gamma^{(j)} - \alpha_{\alpha\alpha}^{(j)} H_{\beta\gamma}^{(j)} \mu_\beta^{(j)} \mu_\gamma^{(j)} - \\ - \alpha_{\alpha\beta}^{(j)} H_{\alpha\beta}^{(j)} \mu_\gamma^{(j)} \mu_\gamma^{(j)}) (3H_{\delta\epsilon}^{(i)} H_{\delta\eta}^{(i)} \mu_\epsilon^{(i)} \mu_\eta^{(i)} - H_{\delta\epsilon}^{(i)} H_{\delta\epsilon}^{(i)} \mu_\eta^{(i)} \mu_\eta^{(i)})] \langle r_{ij}^{-11} \rangle + \\ - \frac{4}{15kT} [5 (\alpha_{\alpha\beta}^{(i)} H_{\alpha\beta}^{(i)} H_{\gamma\delta}^{(j)} H_{\gamma\delta}^{(j)} + \alpha_{\alpha\beta}^{(j)} H_{\alpha\beta}^{(j)} H_{\gamma\delta}^{(i)} H_{\gamma\delta}^{(i)}) \mu_{(i)}^2 \mu_{(j)}^2 + 2 (3H_{\alpha\beta}^{(i)} H_{\alpha\gamma}^{(i)} \mu_\beta^{(i)} \mu_\gamma^{(i)} - \\ - H_{\alpha\beta}^{(i)} H_{\alpha\beta}^{(i)} \mu_{(i)}^2) \alpha_{\delta\epsilon}^{(j)} H_{\delta\epsilon}^{(j)} \mu_{(j)}^2 + 2 (3H_{\alpha\beta}^{(j)} H_{\alpha\gamma}^{(j)} \mu_\beta^{(j)} \mu_\gamma^{(j)} - H_{\alpha\beta}^{(j)} H_{\alpha\beta}^{(j)} \mu_{(j)}^2) \alpha_{\delta\epsilon}^{(i)} H_{\delta\epsilon}^{(i)} \mu_{(i)}^2 + \\ + 2 (3\alpha_{\alpha\beta}^{(i)} H_{\alpha\gamma}^{(i)} \mu_\beta^{(i)} \mu_\gamma^{(i)} - \alpha_{\alpha\alpha}^{(i)} H_{\beta\gamma}^{(i)} \mu_\beta^{(i)} \mu_\gamma^{(i)}) H_{\delta\epsilon}^{(j)} H_{\delta\epsilon}^{(j)} \mu_{(j)}^2 + 2 (3\alpha_{\alpha\beta}^{(j)} H_{\alpha\gamma}^{(j)} \mu_\beta^{(j)} \mu_\gamma^{(j)} - \\ - \alpha_{\alpha\alpha}^{(j)} H_{\beta\gamma}^{(j)} \mu_\beta^{(j)} \mu_\gamma^{(j)}) H_{\delta\epsilon}^{(i)} H_{\delta\epsilon}^{(i)} \mu_{(i)}^2] \langle r_{ij}^{-11} \rangle + \dots \}.$$

The quantity $\text{quadr-quadr. } B_Q^{(ij)}$ is given by Eq. (12), whereas the contribution from $\text{quadr-quadr. dipole interaction}$ has the form

$$(26) \quad \text{dip-ind. dip } B_Q^{(ij)} = \frac{\pi N^2}{3375 k^2 T^2} \left\{ (3 \alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(j)} - \alpha_{\alpha\alpha}^{(i)} \alpha_{\beta\beta}^{(j)}) \mathbf{H}_{\gamma\delta}^{(j)} \mu_\gamma^{(j)} \mu_\delta^{(j)} + \right. \\ \left. + (3 \alpha_{\alpha\beta}^{(j)} \alpha_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(j)} \alpha_{\beta\beta}^{(i)}) \mathbf{H}_{\gamma\delta}^{(i)} \mu_\gamma^{(i)} \mu_\delta^{(i)} + (3 \alpha_{\alpha\beta}^{(i)} \mu_\alpha^{(i)} \mu_\beta^{(i)} - \alpha_{\alpha\alpha}^{(i)} \mu_\beta^{(i)} \mu_\beta^{(i)}) \mathbf{H}_{\gamma\delta}^{(j)} \alpha_{\gamma\delta}^{(j)} + \right. \\ \left. + (3 \alpha_{\alpha\beta}^{(j)} \mu_\alpha^{(j)} \mu_\beta^{(j)} - \alpha_{\alpha\alpha}^{(j)} \mu_\beta^{(j)} \mu_\beta^{(j)}) \mathbf{H}_{\gamma\delta}^{(i)} \alpha_{\gamma\delta}^{(i)} \right\} \langle r_{ij}^{-6} \rangle + \dots$$

For axially symmetric molecules, with respect to Eq. (16), the foregoing expressions reduce to

$$(27) \quad \text{dip-dip } B_Q^{(ij)} = \frac{\pi^2 N^2}{27000 k T \sigma_{ij}^3 \varepsilon_{ij}^2} \left\{ \alpha_{(i)} \delta_{(i)} \mu_{(i)}^2 \mathbf{H}_{(j)} \mu_{(j)}^2 + \mathbf{H}_{(i)} \mu_{(i)}^2 \alpha_{(j)} \delta_{(j)} \mu_{(j)}^2 \right\} \times \\ \times \left\{ H_6(y_{ij}) + \frac{3 \mu_{(i)}^2 \mu_{(j)}^2 y_{ij}^4}{196 \sigma_{ij}^6 \varepsilon_{ij}^2} H_{12}(y_{ij}) + \dots \right\},$$

$$(28) \quad \text{dip-quadr } B_Q^{(ij)} = \frac{\pi^2 N^2}{12600 k T \sigma_{ij}^5 \varepsilon_{ij}^2} \left\{ \alpha_{(i)} \delta_{(i)} \mathbf{H}_{(j)} + \mathbf{H}_{(i)} \alpha_{(j)} \delta_{(j)} \right\} \times \\ \times \left\{ (\mu_{(i)}^2 \mathbf{H}_{(j)}^2 + \mathbf{H}_{(i)}^2 \mu_{(j)}^2) H_8(y_{ij}) - \frac{y_{ij}^2}{\sigma_{ij}^3 \varepsilon_{ij}} \mu_{(i)}^2 \mathbf{H}_{(i)} \mathbf{H}_{(j)} \mu_{(j)}^2 H_{11}(y_{ij}) + \dots \right\},$$

$$(29) \quad \text{dip-ind. dip } B_Q^{(ij)} = \frac{\pi^2 N^2}{2250 k T \sigma_{ij}^3 \varepsilon_{ij} y_{ij}^2} \left\{ \alpha_{(i)} \delta_{(i)} \mathbf{H}_{(j)} + \mathbf{H}_{(i)} \alpha_{(j)} \delta_{(j)} \right\} \times \\ \times \left\{ \alpha_{(i)} \delta_{(i)} \mu_{(j)}^2 + \mu_{(i)}^2 \alpha_{(j)} \delta_{(j)} \right\} H_6(y_{ij}) + \dots$$

Binary gas mixture

For a binary gas mixture, the expansion of Eq. (5) can be put in the following form:

$$(30) \quad Q_m = x_1 A_Q^{(1)} + x_2 A_Q^{(2)} + \frac{1}{V_m} \left(x_1^2 B_Q^{(11)} + 2x_1 x_2 B_Q^{(12)} + x_2^2 B_Q^{(22)} \right) + \dots,$$

with

$$(31) \quad x_1 + x_2 = 1, \quad V_m = \frac{1}{\rho} (x_1 M_1 + x_2 M_2),$$

M_1 and M_2 being the molecular weight of the "1" and "2" component, respectively, and ρ — the density of the mixture.

If, in particular, the "1" component is a non-dipolar gas whose molecules possess the quadrupole moment $\mathbf{H}_{(1)}$, the "2" component being a dipolar gas of molecules of dipolar moment $\mu_{(2)}$, the foregoing expressions yield (neglecting the tensor $B_{\alpha\beta:\gamma\delta}$)

$$(32) \quad A_Q^{(1)} = \frac{4\pi N}{15 k T} \alpha_{(1)} \delta_{(1)} \mathbf{H}_{(1)}, \quad A_Q^{(2)} = B_Q^{(22)} = 0,$$

$$(33) \quad B_Q^{(11)} = \frac{2\pi^2 \alpha_{(1)} \delta_{(1)} H_{(1)}^3 N^2}{525 kT \sigma_{11}^5 \varepsilon_{11} y_{11}^2} \left\{ \alpha_{(1)} \delta_{(1)} H_8(y_{11}) + \frac{H_{(1)}^2 y_{11}^2}{6 \sigma_{11}^2 \varepsilon_{11}} H_{10}(y_{11}) \right\},$$

$$(34) \quad B_Q^{(12)} = \frac{\pi^2 H_{(1)} \alpha_{(2)} \delta_{(2)} N^2}{75 kT \sigma_{12}^3 \varepsilon_{12} y_{12}^2} \left\{ \frac{H_{(1)}^2 \alpha_{(2)} \delta_{(2)}}{14 \sigma_{12}^2} H_8(y_{12}) + \right. \\ \left. + \frac{1}{30} \alpha_{(1)} \delta_{(1)} \mu_{(2)}^2 H_6(y_{12}) + \frac{H_{(1)}^2 \mu_{(2)}^2 y_{12}^2}{168 \sigma_{12}^2 \varepsilon_{12}} H_8(y_{12}) \right\},$$

with the usual combination rules [6]

$$\sigma_{12} = \frac{1}{2} (\sigma_1 + \sigma_2), \quad \varepsilon_{12} = (\varepsilon_1 \varepsilon_2)^{1/2}.$$

The case of a carbon dioxide — methyl fluoride mixture will now be considered as an example. With the following data (see [1], [4], [6], [7]) for CO₂:

$$\alpha_{(1)} = 2.92 \times 10^{-24} \text{ cm}^3, \quad \delta_{(1)} = 0.27, \quad H_{(1)} = -5 \times 10^{-26} \text{ e.s.u.}, \\ \sigma_{11} = 4 \times 10^{-8} \text{ cm}, \quad \varepsilon_{11/k} = 190^\circ \text{ K},$$

and for CH₃F:

$$\alpha_{(2)} = 2.6 \times 10^{-24} \text{ cm}^3, \quad \delta_{(2)} = 0.11, \quad \mu_{(2)} = 1.82 \times 10^{-18} \text{ e.s.u.}, \\ \sigma_{22} = 3.33 \times 10^{-8} \text{ cm}, \quad \varepsilon_{22/k} = 205^\circ \text{ K},$$

Eqs. (33) and (34) yield, for $T = 300^\circ \text{K}$,

$$B_Q^{(11)} = -(1.04 + 25.61) \times 10^{-12} = -26.65 \times 10^{-12} \text{ e.s.u. mole}^{-2}, \\ B_Q^{(12)} = -(0.05 + 0.20 + 4.68) \times 10^{-13} = -0.49 \times 10^{-12} \text{ e.s.u. mole}^{-2}.$$

By the foregoing evaluation, the contributions of the dipole-induced dipole and quadrupole-induced dipole interaction to the second virial coefficient B_Q are quite negligible when compared to those deriving from quadrupole-quadrupole or dipole-quadrupole interaction.

Finally, it should be noted that, similarly to Buckingham's equation (1) or to A_Q , investigation of the second virial coefficient B_Q can yield i.a. decisive information on the sign of the molecular quadrupole moment.

The author wishes to express his sincere thanks to Professor A. Piekara for his interest in the present paper and for his helpful discussions.

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