

THE EQUATION OF STATE OF MULTIPOLAR GASES

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Synopsis

The equation of state in the approximation of the second virial coefficient B is discussed theoretically for gases consisting of unlike multipolar molecules. A molecule of species i is assumed to possess a permanent 2^n -pole moment $\mathbf{M}_i^{(n)}$, as well as a 2^n -pole moment $\mathbf{P}_i^{(n)}$ induced in it by the electric field $\mathbf{F}_j^{(n)}$ of order n of a neighbouring molecule of species j having the permanent 2^m -pole electric moment $\mathbf{M}_j^{(m)}$. Tensor formalism is used for deriving general expressions for the potential energy of electrostatic and inductational interaction of two multipolar molecules of species i and j . These energies then serve for computing two contributions to B : the one, of inductational type, is obtained in the first approximation and contains, in addition to terms with dipolar polarizability, terms accounting for the quadrupolar polarizability induced in the molecule by the molecular electric field gradient; the other, which is purely electrostatic, is obtained in the second approximation of the theory. Moreover, cross contributions to B between the electrostatic and inductational energies as well as contributions from dipolar anisotropy of dispersive-type interactions are computed. In computing the mean values of the respective powers of r_{ij} (the distance between the two molecules), a general Lennard-Jones (s - t)-type potential is applied. The theoretically derived non-central contributions to B are valid in general for molecules of arbitrary symmetry and arbitrary electrical structure; the expressions are applied to cases of axially symmetric, tetrahedral and octahedral molecules. For methane, the theoretical formulas allowed to determine numerically the octopole moment from experimental data on B to be $\Omega_{\text{CH}_4} = 5 \times 10^{-34}$ e.s.u. cm^3 .

§ 1. *Introduction.* Since the time of Van der Waals, Kamerlingh-Onnes and Keesom it has been known that deviations in the behaviour of real gases from that of a perfect gas are due essentially to molecular interactions. These interactions can, on the one hand, be computed theoretically by statistical mechanics applied to an appropriate molecular model and, on the other hand, determined experimentally from the equation of state of a gas, expressed in virial form:

$$pV = RT \left(1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \right), \quad (1)$$

where p , V and T are parameters of state and R is the gas constant.

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In the region of intermediate pressures the second virial coefficient B determines the most essential divergence from the equation of state of a perfect gas; the third C , fourth virial coefficient D and so forth are of little importance, their role increasing at high pressures. In a sufficiently rarefied gas, we are justified in expecting primarily pairwise molecular interactions the potential energy of which is accounted for by the second virial coefficient. Thus, the experimental value of B , measuring the deviation of the real gas under consideration from the perfect gas, provides information on the character and value of the intermolecular forces. The method, however, is of relatively simple application only if the gas consists of atoms or molecules that can be treated as spheres interacting centrally. The problem becomes highly involved if the gas consists of molecules having a complex electrical structure no longer admitting of the spherical approximation, since now their interaction potential energy depends not only on their distances but, moreover, largely on their mutual orientations. Nevertheless, a numerical solution can always be reached if, from the total potential energy of interaction of two molecules, we can separate the part dependent on the angular variables and consider it as a perturbation to the central-type energy. Now, since angular dependence of the potential energy arises primarily from electric multipoles in the molecule, investigation of B allows to determine not only the parameters of the central forces but, moreover, yields information concerning the electric (quadrupole, octopole, etc.) moments of the molecules.

In the case of a mixture of multipolar gases, the second virial coefficient of eq. (1) can be quite generally represented in the form

$$B_m = \sum_{ij} x_i x_j \{B_{ij}^{\text{centr}} + B_{ij}^{\text{noncentr}}\} \quad (2)$$

with x_i denoting the molar fraction of the i -th component of the mixture and

$$B_{ij}^{\text{centr}} = -2\pi N \int_0^{\infty} \{e^{-u_{ij}(r_{pq})/kT} - 1\} r_{pq}^2 dr_{pq} \quad (3)$$

being the contribution to B_m from the interaction energy of the central type $u_{ij}(r_{pq})$ between molecules p and q of species i and j having mutual distance r_{pq} .

The other contribution to B_m is related with the noncentral forces energy $v_{ij}(r_{pq}, \omega_p, \omega_q)$ considered as a perturbation to $u_{ij}(r_{pq})$ and is given as follows:

$$B_{ij}^{\text{noncentr}} = -\frac{N}{2\Omega^2} \sum_{n=1}^{\infty} \frac{1}{n!} \left(-\frac{1}{kT}\right)^n \iiint \{v_{ij}(r_{pq}, \omega_p, \omega_q)\}^n \times \\ \times e^{-u_{ij}(r_{pq})/kT} dr_{pq} d\omega_p d\omega_q \quad (4)$$

with ω_p and ω_q denoting angular variables determining the orientation of the p -th and q -th molecule, respectively, with $\Omega = \int d\omega_p = \int d\omega_q$.

Lennard-Jones¹⁾ performed the first full, numerical calculation of B

as given by eq. (3), for a central forces potential of general form

$$u_{ij}(r_{pq}) = -\frac{\lambda_{ij}^n}{r_{pq}^n} + \frac{\lambda_{ij}^m}{r_{pq}^m}, \quad (5)$$

wherein the first term accounts for the energy of attraction and the second for that of repulsion between the molecules. The Lennard-Jones model has since been applied in various modifications (cf. refs. 2-5).

The earliest calculations of the second virial coefficient for dipolar and quadrupolar molecules taking into account a noncentral forces potential are due to Keesom⁶), Debye⁷) and Falkenhagen⁸) and have been modified for higher accuracy by Stockmayer⁹), Rowlinson¹⁰), Pople¹¹) and others (see refs. 2 and 12-19).

Debye⁷) already pointed to the possibility of gaining information on the quadrupole moments of molecules from investigation of the equation of state of gases. To this aim, it is most convenient to proceed from data on the second virial coefficient (see refs. 11, 16, 20). Evaluations of molecular quadrupole moments are particularly satisfactory if we assume numerical values of central-forces parameters of the 6-12 Lennard-Jones potential from viscosity measurements in gases¹⁷). Recently, Orcutt²¹) generalized this method to the entire temperature range accessible in the experimental investigation of B and obtained fully realistic values of the quadrupole moments of various molecules. In a similar way, we obtained results for the octopole moment of tetrahedral molecules²²), and the possibility presents itself of determining the hexadecapole moment of octahedral molecules²³). This, although an indirect method of determining multipole moments, is of advantage owing to its conveniency in use and leads quickly to final results of sufficient accuracy, particularly if we are unable to perform the direct computations by wave functions.

Our present considerations are restricted to contributions to the second virial coefficient due to noncentral interactions of, in general, a tensorial nature. Thus, in computing (4), we assume that the potential energy v_{ij} of tensorial interaction consists of a term derived from electrostatic interaction between the permanent 2^n -pole moment of one molecule and the permanent 2^m -pole moment of another, and of a term derived from inductive interaction between the permanent 2^n -pole moment of a molecule and the 2^m -pole moment induced in another. Account is also taken of the anisotropy of dipolar polarizability of the molecules, as well as of the anisotropy of the London dispersional forces. The results for B obtained by tensor formalism hold in general for molecules of various kind and of arbitrary symmetry, and are applied to cases of molecules presenting the axial, tetrahedral or octahedral symmetry.

Since our considerations deal with weakly dipolar molecules or molecules presenting a small dipolar moment but at the same time having arbitrary

higher electric moments, as well as with nondipolar molecules having higher (quadrupole, octopole, hexadecapole, etc.) electric moments, the computations of noncentral contributions to B as given by eq. (4) are restricted to include the third approximation of classical perturbation calculus. Higher approximations containing moments of higher order are insignificant corrections to B and can be neglected. Clearly, this restriction cannot be made in the case of strongly dipolar molecules (but not possessing higher electric moments), for which exact calculations have been carried out by various authors (see, refs. 2, 6, 10, 12, 14, 18).

§ 2. *The contribution to B_{ij} from electrostatic interaction.* We first calculate the electrostatic potential energy of interaction between two unlike molecules of species i and j . The molecules p and q of species i and j can be assumed to have arbitrary charge distributions with 2^n -pole and 2^m -pole electric moments, respectively. In the case of nonoverlapping charge distributions p and q separated by a distance \mathbf{r}_{pq} and having orientations specified by ω_p and ω_q the electrostatic potential energy is given by the following expansion^{24, 25)}

$$v_{ij}^{el}(\mathbf{r}_{pq}, \omega_p, \omega_q) = - \sum_{n=0}^{\infty} \frac{2^n n!}{(2n)!} \mathbf{M}_{pi}^{(n)}[n] \mathbf{F}_{qj}^{(n)}. \quad (6)$$

Here, $\mathbf{M}_{pi}^{(n)}$ is the n -th rank tensor of the electric multipole moment of the p -th molecule of species i defined as²⁵⁾

$$\mathbf{M}_{pi}^{(n)} = \sum_{\nu} e_{p\nu}^{(i)} r_{p\nu}^n \mathbf{S}^{(n)}(\mathbf{r}_{p\nu}), \quad (7)$$

where $e_{p\nu}^{(i)}$ is the ν -th electric charge of molecule p of species i and $\mathbf{r}_{p\nu}$ is its radius vector. The operator $\mathbf{S}^{(n)}$ of rank n is given by

$$\begin{aligned} \mathbf{S}^{(n)}(\mathbf{r}) &= \frac{(-1)^n}{n!} r^{n+1} \nabla^n \left(\frac{1}{r} \right) = \\ &= \frac{r^{-n}}{n!} \{ (2n-1)!! \mathbf{r}_1 \mathbf{r}_2 \dots \mathbf{r}_n - (2n-3)!! r^2 \sum U_{12} \mathbf{r}_3 \dots \mathbf{r}_n + \\ &+ (2n-5)!! r^4 \sum U_{12} U_{34} \mathbf{r}_5 \dots \mathbf{r}_n - (2n-7)!! r^6 \sum U_{12} U_{34} U_{56} \mathbf{r}_7 \dots \mathbf{r}_n + \\ &+ (-1)^k (2n-2k-1)!! r^{2k} \sum U_{12} \dots U_{2k-1, 2k} \mathbf{r}_{2k+1} \dots \mathbf{r}_n + \dots \}, \quad (8) \end{aligned}$$

where U_{12} is a unit tensor and $\sum U_{12} \mathbf{r}_3 \dots \mathbf{r}_n$ etc. are sums of terms obtained from the one written by interchanging the suffixes 1, 2, ... n . ∇ is the differential operator and the symbol $[n]$ in eq. (6) denotes n -fold contraction of the product of $\mathbf{M}^{(n)}$ and $\mathbf{F}^{(n)}$.

By (7) and (8), the consecutive (monopole, dipole, quadrupole, octopole

and hexadecapole) electric moments of the molecule are expressed as follows (for simplicity we have dropped p, i)

$$\begin{aligned}
 e &\equiv M^{(0)} = \sum_{\nu} e_{\nu}, \\
 \mu &\equiv M^{(1)} = \sum_{\nu} e_{\nu} \mathbf{r}_{\nu 1}, \\
 \Theta &\equiv M^{(2)} = \frac{1}{2} \sum_{\nu} e_{\nu} (3\mathbf{r}_{\nu 1} \mathbf{r}_{\nu 2} - r_{\nu}^2 \mathbf{U}_{12}), \\
 \Omega &\equiv M^{(3)} = \frac{1}{2} \sum_{\nu} e_{\nu} \{5\mathbf{r}_{\nu 1} \mathbf{r}_{\nu 2} \mathbf{r}_{\nu 3} - r_{\nu}^2 (\mathbf{U}_{12} \mathbf{r}_{\nu 3} + \mathbf{U}_{23} \mathbf{r}_{\nu 1} + \mathbf{U}_{31} \mathbf{r}_{\nu 2})\}, \\
 \Phi &\equiv M^{(4)} = \frac{1}{8} \sum_{\nu} e_{\nu} \{35\mathbf{r}_{\nu 1} \mathbf{r}_{\nu 2} \mathbf{r}_{\nu 3} \mathbf{r}_{\nu 4} - 5r_{\nu}^2 (\mathbf{U}_{12} \mathbf{r}_{\nu 3} \mathbf{r}_{\nu 4} + \mathbf{U}_{23} \mathbf{r}_{\nu 4} \mathbf{r}_{\nu 1} + \\
 &\quad + \mathbf{U}_{34} \mathbf{r}_{\nu 1} \mathbf{r}_{\nu 2} + \mathbf{U}_{14} \mathbf{r}_{\nu 2} \mathbf{r}_{\nu 3} + \mathbf{U}_{13} \mathbf{r}_{\nu 2} \mathbf{r}_{\nu 4} + \mathbf{U}_{24} \mathbf{r}_{\nu 1} \mathbf{r}_{\nu 3}) + \\
 &\quad + r_{\nu}^4 (\mathbf{U}_{12} \mathbf{U}_{34} + \mathbf{U}_{13} \mathbf{U}_{24} + \mathbf{U}_{14} \mathbf{U}_{23})\}. \tag{9}
 \end{aligned}$$

The electric field of order n of the 2^m -pole moments of molecule q of species j acting on molecule p of species i is of the form²⁵⁾

$$\mathbf{F}_{ij}^{(n)} = \sum_{m=0}^{\infty} \frac{(-1)^m 2^m m!}{(2m)!} {}^{(n)}\mathbf{T}_{pq}^{(m)}[m] \mathbf{M}_{ij}^{(m)}, \tag{10}$$

wherein

$${}^{(n)}\mathbf{T}_{pq}^{(m)} = -\nabla^{n+m} \left(\frac{1}{r_{pq}} \right), \quad p \neq q \tag{11}$$

is the tensor of rank $n + m$ describing the $(2^n$ -pole) – $(2^m$ -pole) interactions between the molecules p and q , and ∇ is directed from molecule q to p . In terms of the operators $\mathbf{S}^{(n)}$ defined by (8), the multipole interaction tensor of (11) is of the form

$${}^{(n)}\mathbf{T}_{pq}^{(m)} = (-1)^{n+m+1} (n + m)! r_{pq}^{-(n+m+1)} \mathbf{S}^{(n+m)}(\mathbf{r}_{pq}), \tag{12}$$

where $\mathbf{S}^{(n)}(\mathbf{r}_{pq}) = (-1)^n \mathbf{S}^{(n)}(\mathbf{r}_{qp})$ is given by eq. (8) if \mathbf{r} is replaced by \mathbf{r}_{pq} .

By (10), the electrostatic potential energy (6) can be expressed in the following general form

$$v_{ij}^{\text{el}}(\mathbf{r}_{pq}, \omega_p, \omega_q) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{(-1)^{m+1} 2^{n+m} n! m!}{(2n)! (2m)!} \mathbf{M}_{pi}^{(n)}[n] {}^{(n)}\mathbf{T}_{pq}^{(m)}[m] \mathbf{M}_{qj}^{(m)}. \tag{13}$$

In the first approximation, electrostatic interactions of permanent multipoles do not contribute to B_{ij} , as the first power of v_{ij}^{el} vanishes on isotropic averaging i.e. on integration over all possible orientations of the molecules with equal probability. The first nonzero contribution to B_{ij} comes in the second approximation from the square of v_{ij}^{el} . By squaring v_{ij}^{el} given by (13) and then carrying out integration over all orientation coordi-

nates we obtain

$$\begin{aligned} \frac{1}{\Omega^2} \iint \{v_{ij}^{\text{el}}(r_{pq}, \omega_p, \omega_q)\}^2 d\omega_p d\omega_q &= \\ &= \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{2^{2(n+m)}(n! m!)^2}{(2n)! (2m)! (2n+1)! (2m+1)!} \times \\ &\times (\mathbf{M}_{pi}^{(n)}[n] \mathbf{M}_{pi}^{(n)})^{(n)} \mathbf{T}_{pq}^{(m)}[n+m]^{(n)} \mathbf{T}_{pq}^{(m)} (\mathbf{M}_{qj}^{(m)}[m] \mathbf{M}_{qj}^{(m)}). \end{aligned} \quad (14)$$

Considering that²⁴

$${}^{(n)} \mathbf{T}_{pq}^{(m)}[n+m] {}^{(n)} \mathbf{T}_{pq}^{(m)} = (2n+2m)! 2^{-(n+m)} r_{pq}^{-2(n+m+1)}, \quad (15)$$

we have by (14) from eq. (4) for the contribution to B from electrostatic interactions of multipolar molecules

$$\begin{aligned} B_{ij}^{\text{el}} &= -\frac{N}{4k^2 T^2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{2^{n+m} (2n+2m)! (n! m!)^2}{(2n)! (2m)! (2n+1)! (2m+1)!} \times \\ &\times (\mathbf{M}_i^{(n)}[n] \mathbf{M}_i^{(n)}) (\mathbf{M}_j^{(m)}[m] \mathbf{M}_j^{(m)}) \langle r_{ij}^{-2(n+m+1)} \rangle, \end{aligned} \quad (16)$$

with the radial average value

$$\langle r_{ij}^{-n} \rangle = \int r_{pq}^{-n} \exp \left\{ -\frac{u_{ij}(r_{pq})}{kT} \right\} d\mathbf{r}_{pq}. \quad (17)$$

From the general expression of eq. (16) we obtain up to the term with hexadecapole-hexadecapole interaction of two neutral molecules

$$\begin{aligned} B_{ij}^{\text{el}} &= -\frac{N}{6k^2 T^2} \{ (\mathbf{M}_i^{(1)} \cdot \mathbf{M}_i^{(1)}) (\mathbf{M}_j^{(1)} \cdot \mathbf{M}_j^{(1)}) \langle r_{ij}^{-6} \rangle + [(\mathbf{M}_i^{(1)} \cdot \mathbf{M}_i^{(1)}) (\mathbf{M}_j^{(2)} : \mathbf{M}_j^{(2)}) + \\ &+ (\mathbf{M}_i^{(2)} : \mathbf{M}_i^{(2)}) (\mathbf{M}_j^{(1)} \cdot \mathbf{M}_j^{(1)})] \langle r_{ij}^{-8} \rangle + \frac{4}{15} [3(\mathbf{M}_i^{(1)} \cdot \mathbf{M}_i^{(1)}) (\mathbf{M}_j^{(3)} : \mathbf{M}_j^{(3)}) + \\ &+ 7(\mathbf{M}_i^{(2)} : \mathbf{M}_i^{(2)}) (\mathbf{M}_j^{(2)} : \mathbf{M}_j^{(2)}) + 3(\mathbf{M}_i^{(3)} : \mathbf{M}_i^{(3)}) (\mathbf{M}_j^{(1)} \cdot \mathbf{M}_j^{(1)})] \langle r_{ij}^{-10} \rangle + \\ &+ \frac{4}{35} [5(\mathbf{M}_i^{(1)} \cdot \mathbf{M}_i^{(1)}) (\mathbf{M}_j^{(4)} :: \mathbf{M}_j^{(4)}) + 21(\mathbf{M}_i^{(2)} : \mathbf{M}_i^{(2)}) (\mathbf{M}_j^{(3)} : \mathbf{M}_j^{(3)}) + \\ &+ 21(\mathbf{M}_i^{(3)} : \mathbf{M}_i^{(3)}) (\mathbf{M}_j^{(2)} : \mathbf{M}_j^{(2)}) + 5(\mathbf{M}_i^{(4)} :: \mathbf{M}_i^{(4)}) (\mathbf{M}_j^{(1)} \cdot \mathbf{M}_j^{(1)})] \langle r_{ij}^{-12} \rangle + \\ &+ \frac{88}{175} [5(\mathbf{M}_i^{(2)} : \mathbf{M}_i^{(2)}) (\mathbf{M}_j^{(4)} :: \mathbf{M}_j^{(4)}) + 9(\mathbf{M}_i^{(3)} : \mathbf{M}_i^{(3)}) (\mathbf{M}_j^{(3)} : \mathbf{M}_j^{(3)}) + \\ &+ 5(\mathbf{M}_i^{(4)} :: \mathbf{M}_i^{(4)}) (\mathbf{M}_j^{(2)} : \mathbf{M}_j^{(2)})] \langle r_{ij}^{-14} \rangle + \\ &+ \frac{1144}{175} [(\mathbf{M}_i^{(3)} : \mathbf{M}_i^{(3)}) (\mathbf{M}_j^{(4)} :: \mathbf{M}_j^{(4)}) + (\mathbf{M}_i^{(4)} :: \mathbf{M}_i^{(4)}) (\mathbf{M}_j^{(3)} : \mathbf{M}_j^{(3)})] \langle r_{ij}^{-16} \rangle + \\ &+ \frac{9152}{735} (\mathbf{M}_i^{(4)} :: \mathbf{M}_i^{(4)}) (\mathbf{M}_j^{(4)} :: \mathbf{M}_j^{(4)}) \langle r_{ij}^{-18} \rangle \}. \end{aligned} \quad (18)$$

Further simplification of the general result of eq. (16) or (18) can be achieved by assuming a particular type of symmetry of the molecules. This will now be effected for the three cases most commonly occurring.

We shall first discuss the case of molecules exhibiting symmetry with respect to the z axis, for which we have

$$M_i^{(n)}[n] M_i^{(n)} = \frac{(2n)!}{2^n(n!)^2} \{M_i^{(n)}\}_2, \quad (19)$$

and eq. (16) assumes the simpler form of

$$B_{ij}^{\text{el}} = -\frac{N}{4k^2T^2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{(2n+2m)!}{(2n+1)!(2m+1)!} (M_i^{(n)})^2 (M_j^{(m)})^2 \langle r_{ij}^{-2(n+m+1)} \rangle, \quad (20)$$

where $M_i^{(n)}$ is the scalar multipole moment of order n for the axially-symmetric molecule of species i .

With the accuracy up to quadrupole-quadrupole interaction, eq. (20) yields the well-known result of Keesom⁶⁾

$$B_{ij}^{\text{el}} = -\frac{N}{6k^2T^2} \{ \mu_i^2 \mu_j^2 \langle r_{ij}^{-6} \rangle + \frac{3}{2} (\mu_i^2 \Theta_j^2 + \Theta_i^2 \mu_j^2) \langle r_{ij}^{-8} \rangle + \frac{21}{5} \Theta_i^2 \Theta_j^2 \langle r_{ij}^{-10} \rangle \}, \quad (21)$$

generalized to the case of unlike axially-symmetric molecules possessing a dipole as well as a quadrupole moment interacting with arbitrary central forces $u_{ij}(r_{pq})$ contained in the Boltzman factor in eq. (17).

We now consider the case of molecules with octopole and hexadecapole moment, but not possessing permanent moments of lower order, i.e. presenting neither a dipole nor a quadrupole moment. This is the case of e.g. molecules having the tetrahedral symmetry, like methane, carbon tetrachloride, and so forth, when the octopole and hexadecapole moments are scalar quantities defined by (9) as

$$\Omega_i = \frac{5}{2} \sum_{\nu} e_{i\nu} x_{\nu} y_{\nu} z_{\nu}, \quad \Phi_i = \frac{7}{8} \sum_{\nu} e_{i\nu} (3z_{\nu}^2 x_{\nu}^2 - x_{\nu}^4), \quad (22)$$

and eq. (18) yields

$$B_{ij}^{\text{el}} = -\frac{528N}{175k^2T^2} \{ 9\Omega_i^2 \Omega_j^2 \langle r_{ij}^{-14} \rangle + 65(\Omega_i^2 \Phi_j^2 + \Phi_i^2 \Omega_j^2) \langle r_{ij}^{-16} \rangle + \frac{13900}{21} \Phi_i^2 \Phi_j^2 \langle r_{ij}^{-18} \rangle \}. \quad (23)$$

Here, the first term represents the contribution to B_{ij} from octopole-octopole interaction, the second – from octopole-hexadecapole interaction and the third term describes the hexadecapole-hexadecapole interaction of the molecules.

In the case of molecules having the octahedral symmetry (e.g. the molecule SF_6) the first nonzero moment is the hexadecapole moment and we obtain from (18)

$$B_{ij}^{\text{el}} = -\frac{91520N}{49k^2T^2} \Phi_i^2 \Phi_j^2 \langle r_{ij}^{-18} \rangle. \quad (24)$$

We see that in the case of octahedral molecules the first possible contribution to B_{ij} is that resulting from hexadecapole-hexadecapole interaction.

§ 3. *The contribution to B_{ij} from inductive interaction.* To within the induced-dipole approximation, the induction potential energy of two unlike molecules is given by

$$a v_{ij}^{\text{ind}}(r_{pq}, \omega_p, \omega_q) = -\frac{1}{2} \{ \mathbf{F}_{pi}^{(1)} \cdot \boldsymbol{\alpha}_{qj} \cdot \mathbf{F}_{pi}^{(1)} + \mathbf{F}_{qj}^{(1)} \cdot \boldsymbol{\alpha}_{pi} \cdot \mathbf{F}_{qj}^{(1)} \}, \quad (25)$$

or, by (10) for $n = 1$, in the following explicit form,

$$a v_{ij}^{\text{ind}}(r_{pq}, \omega_p, \omega_q) = -\frac{1}{2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{(-1)^{m+1} 2^{n+m} n! m!}{(2n)! (2m)!} \times \\ \times \{ \mathbf{M}_{pi}^{(n)} [n]^{(n)} \mathbf{T}_{pq}^{(1)} \cdot \boldsymbol{\alpha}_{qj} \cdot {}^{(1)} \mathbf{T}_{qp}^{(m)} [m] \mathbf{M}_{pi}^{(m)} + \\ + \mathbf{M}_{qj}^{(n)} [n]^{(n)} \mathbf{T}_{qp}^{(1)} \cdot \boldsymbol{\alpha}_{pi} \cdot {}^{(1)} \mathbf{T}_{pq}^{(m)} [m] \mathbf{M}_{qj}^{(m)} \}, \quad (26)$$

where $\boldsymbol{\alpha}_{pi}$ is the electric dipole polarizability tensor of molecule p of species i .

For the potential of eq. (26), eq. (4) becomes in the first approximation

$$a B_{ij}^{\text{ind}} = -\frac{N}{8kT} \sum_{n=0}^{\infty} \frac{2^n (2n+2)! (n!)^2}{(2n)! (2n+1)!} \{ \alpha_i (\mathbf{M}_j^{(n)} [n] \mathbf{M}_j^{(n)}) + \\ + (\mathbf{M}_i^{(n)} [n] \mathbf{M}_i^{(n)}) \alpha_j \} \langle r_{ij}^{-2(n+2)} \rangle, \quad (27)$$

where α_i is the scalar dipole polarizability of a molecule of species i .

We now generalize eq. (25) to the case of higher-order induced moments as already considered by Frenkel²⁶). The electric moment of order n induced in molecule p of species i by the electric field of the permanent 2^m -pole moments of molecule q of species j will be given as

$$\mathbf{P}_{pi}^{(n)} = \sum_{m=1}^{\infty} \frac{2^m m!}{(2m)!} {}^{(n)} \mathbf{A}_{pi}^{(m)} [m] \mathbf{F}_{qj}^{(m)}, \quad (28)$$

where ${}^{(n)} \mathbf{A}_{pi}^{(m)}$ is the tensor of rank $n + m$ characterizing the polarization of the permanent 2^m -pole moment of molecule p of species i due to the molecular electric field of order m defined by eq. (10).

In particular, we obtain from (28) for a first-order induced moment ($n = 1$), or induced dipole moment,

$$\mathbf{P}_{pi}^{(1)} = {}^{(1)} \mathbf{A}_{pi}^{(1)} \cdot \mathbf{F}_{qj}^{(1)} + \frac{1}{3} {}^{(1)} \mathbf{A}_{pi}^{(2)} : \mathbf{F}_{qj}^{(2)} + \frac{1}{15} {}^{(1)} \mathbf{A}_{pi}^{(3)} : \mathbf{F}_{qj}^{(3)} + \dots, \quad (29)$$

where ${}^{(1)} \mathbf{A}_{pi}^{(1)}$, ${}^{(1)} \mathbf{A}_{pi}^{(2)}$, and ${}^{(1)} \mathbf{A}_{pi}^{(3)}$ are tensors of the dipole electric polarization induced in molecule p of species i by the first-order molecular electric field $\mathbf{F}_{qj}^{(1)}$ (or, in brief, electric field), by the second-order field $\mathbf{F}_{qj}^{(2)}$ (or field gradient) and by the third-order field $\mathbf{F}_{qj}^{(3)}$ (or gradient of field gradient), respectively.

Similarly, for $n = 2$ we obtain from (28) the second-order induced

moment, or induced quadrupole moment

$$\mathbf{P}_{pi}^{(2)} = {}^{(2)}\mathbf{A}_{pi}^{(1)} \cdot \mathbf{F}_{qi}^{(1)} + \frac{1}{3} {}^{(2)}\mathbf{A}_{pi}^{(2)} : \mathbf{F}_{qi}^{(2)} + \frac{1}{15} {}^{(2)}\mathbf{A}_{pi}^{(3)} : \mathbf{F}_{qi}^{(3)} + \dots, \quad (30)$$

where ${}^{(2)}\mathbf{A}_{pi}^{(1)}$, ${}^{(2)}\mathbf{A}_{pi}^{(2)}$, ... are the tensors of the quadrupole electric polarization of molecule p of species i due, respectively, to the electric field, field gradient, etc.

In terms of the induced moments $\mathbf{P}_{pi}^{(n)}$, the total induction potential energy is given as

$$v_{ij}^{\text{ind}}(\mathbf{r}_{pq}, \omega_p, \omega_q) = -\frac{1}{2} \sum_{n'=1}^{\infty} \frac{2^{n'} n'!}{(2n')!} \{ \mathbf{F}_{pi}^{(n')} [n'] \mathbf{P}_{qi}^{(n')} + \mathbf{F}_{qi}^{(n')} [n'] \mathbf{P}_{pi}^{(n')} \}, \quad (31)$$

or, by eq. (28), in terms of multipole polarizability tensors ${}^{(n)}\mathbf{A}^{(m)}$,

$$v_{ij}^{\text{ind}}(\mathbf{r}_{pq}, \omega_p, \omega_q) = -\frac{1}{2} \sum_{n'=1}^{\infty} \sum_{m'=1}^{\infty} \frac{2^{n'+m'} n'! m'!}{(2n')! (2m')!} \{ \mathbf{F}_{pi}^{(n')} [n'] {}^{(n')} \mathbf{A}_{qi}^{(m')} [m'] \mathbf{F}_{pi}^{(m')} + \mathbf{F}_{qi}^{(n')} [n'] {}^{(n')} \mathbf{A}_{pi}^{(m')} [m'] \mathbf{F}_{qi}^{(m')} \}. \quad (32)$$

From eqs. (10) and (32) it follows that the total potential energy of induction is of the form

$$v_{ij}^{\text{ind}}(\mathbf{r}_{pq}, \omega_p, \omega_q) = -\frac{1}{2} \sum_{n'=1}^{\infty} \sum_{m'=1}^{\infty} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{(-1)^{n'+m} 2^{n+m+n'+m'} n! m! n'! m'!}{(2n)! (2m)! (2n')! (2m')!} \times \\ \times \{ \mathbf{M}_{pi}^{(n)} [n] {}^{(n)} \mathbf{T}_{pq}^{(n')} [n'] {}^{(n')} \mathbf{A}_{qi}^{(m')} [m'] {}^{(m')} \mathbf{T}_{qp}^{(m)} [m] \mathbf{M}_{pi}^{(m)} + \\ + \mathbf{M}_{qi}^{(n)} [n] {}^{(n)} \mathbf{T}_{qp}^{(n')} [n'] {}^{(n')} \mathbf{A}_{pi}^{(m')} [m'] {}^{(m')} \mathbf{T}_{pq}^{(m)} [m] \mathbf{M}_{qi}^{(m)} \}. \quad (33)$$

By (33), we obtain from (4) in the first approximation up to the term with the field gradient quadrupole polarizability

$$B_{ij}^{\text{ind}} = {}_a B_{ij}^{\text{ind}} + {}_q B_{ij}^{\text{ind}}, \quad (34)$$

where ${}_a B_{ij}^{\text{ind}}$ is the contribution to B_{ij} arising from the dipole polarizability approximation of the induction energy and is given by (27), whereas ${}_q B_{ij}^{\text{ind}}$ is that from the quadrupole polarizability approximation and is given by

$${}_q B_{ij}^{\text{ind}} = -\frac{N}{48kT} \sum_{n=0}^{\infty} \frac{2^n (2n+4)! (n!)^2}{(2n)! (2n+1)!} \{ q_i (\mathbf{M}_j^{(n)} [n] \mathbf{M}_j^{(n)}) + \\ + (\mathbf{M}_i^{(n)} [n] \mathbf{M}_i^{(n)}) q_j \} \langle r_{ij}^{-2(n+3)} \rangle, \quad (35)$$

with $q = \mathbf{U}_{13} : {}^{(2)}\mathbf{A}_{12,34}^{(2)} : \mathbf{U}_{24}/15$ denoting the scalar quadrupole polarizability.

For axially symmetrical molecules we have (19) and the expressions (27) and (35) assume the simpler form of

$${}_a B_{ij}^{\text{ind}} = -\frac{N}{4kT} \sum_{n=0}^{\infty} (n+1) \{ \alpha_i (\mathbf{M}_j^{(n)})^2 + (\mathbf{M}_i^{(n)})^2 \alpha_j \} \langle r_{ij}^{-2(n+2)} \rangle, \quad (36)$$

$${}_q B_{ij}^{\text{ind}} = -\frac{N}{12kT} \sum_{n=0}^{\infty} (n+1)(n+2)(2n+3) \{ q_i (\mathbf{M}_j^{(n)})^2 + (\mathbf{M}_i^{(n)})^2 q_j \} \langle r_{ij}^{-2(n+3)} \rangle, \quad (37)$$

or up to the term with quadrupole moment

$${}_a B_{ij}^{\text{ind}} = -\frac{N}{2kT} \{(\alpha_i \mu_j^2 + \mu_i^2 \alpha_j) \langle r_{ij}^{-6} \rangle + \frac{3}{2}(\alpha_i \Theta_j^2 + \Theta_i^2 \alpha_j) \langle r_{pq}^{-8} \rangle\}, \quad (38)$$

$${}_q B_{ij}^{\text{ind}} = -\frac{N}{2kT} \{5(q_i \mu_j^2 + \mu_i^2 q_j) \langle r_{ij}^{-8} \rangle + 14(q_i \Theta_j^2 + \Theta_i^2 q_j) \langle r_{ij}^{-10} \rangle\}. \quad (39)$$

Similarly, eqs. (27) and (35) yield, for molecules possessing the tetrahedral symmetry,

$${}_a B_{ij}^{\text{ind}} = -\frac{12N}{5kT} \{(\alpha_i \Omega_j^2 + \Omega_i^2 \alpha_j) \langle r_{ij}^{-10} \rangle + \frac{2^5}{7}(\alpha_i \Phi_j^2 + \Phi_i^2 \alpha_j) \langle r_{ij}^{-12} \rangle\}, \quad (40)$$

$${}_q B_{ij}^{\text{ind}} = -\frac{12N}{kT} \{3(q_i \Omega_j^2 + \Omega_i^2 q_j) \langle r_{ij}^{-12} \rangle + \frac{11 \cdot 0}{7}(q_i \Phi_j^2 + \Phi_i^2 q_j) \langle r_{ij}^{-14} \rangle\}. \quad (41)$$

For $\Omega = 0$, eqs. (40) and (41) conform to the case of octahedral molecules with hexadecapole moment.

§ 4. *Further contributions to B_{ij} .* A further contribution to B_{ij} within the framework of the second approximation results from the cross term $v_{ij}^{\text{el}} v_{ij}^{\text{ind}}$. In the case when the dipole polarizability tensor α is isotropic the term $v_{ij}^{\text{el}} \times v_{ij}^{\text{ind}}$ vanishes by averaging over all orientations, but it is nonzero if the tensor α is anisotropic and if, moreover, the molecule possesses a dipole or quadrupole moment. Indeed, by (13) and (26), on integration over the angular coordinates and on neglecting the moments higher than quadrupole, we have from (4)

$$\begin{aligned} B_{ij}^{\text{cross}} = & \frac{2N}{5k^2 T^2} \{(\alpha_i : \Theta_i)(\mu_j \cdot \Theta_j \cdot \mu_j) + (\mu_i \cdot \Theta_i \cdot \mu_i)(\alpha_j : \Theta_j)\} \langle r_{ij}^{-11} \rangle + \\ & + \frac{8N}{35k^2 T^2} \{(\alpha_i : \Theta_i)[\Theta_j : (\Theta_j \cdot \Theta_j)] + \\ & + [\Theta_i : (\Theta_i \cdot \Theta_i)](\alpha_j : \Theta_j)\} \langle r_{ij}^{-13} \rangle. \end{aligned} \quad (42)$$

In the case of molecules exhibiting the axial symmetry, we have

$$\alpha_i : \Theta_i = 3\alpha_i \kappa_i \Theta_i, \quad \Theta_i : (\Theta_i \cdot \Theta_i) = \frac{3}{4} \Theta_i^3, \quad \mu_i \cdot \Theta_i \cdot \mu_i = \mu_i^2 \Theta_i,$$

and eq. (42) reduces to

$$\begin{aligned} B_{ij}^{\text{cross}} = & \frac{6N}{5k^2 T^2} \Theta_i \Theta_j \{(\alpha_i \kappa_i \mu_j^2 + \mu_i^2 \alpha_j \kappa_j) \langle r_{ij}^{-11} \rangle + \\ & + \frac{3}{7}(\alpha_i \kappa_i \Theta_j^2 + \Theta_i^2 \alpha_j \kappa_j) \langle r_{ij}^{-13} \rangle\}, \end{aligned} \quad (43)$$

wherein $\kappa_i = (\alpha_{zz}^{(i)} - \alpha_{xx}^{(i)})/3\alpha_i$ is the anisotropy of dipole polarizability of the axially symmetric molecule of species i . It is immediately obvious that in

the case of isotropic dipole polarizability, i.e. when $\kappa_i = 0$, the contribution (43) vanishes.

Similarly, we can calculate higher approximations to B_{ij} taking into account the terms $(v_{ij}^{el})^3$, $(v_{ij}^{el})^4$, etc. To avoid complicating the final results, we restrict our calculations to the contribution from electrostatic interactions in the third approximation, and obtain by (4) and (13) for molecules possessing a dipole as well as a quadrupole moment

$$B_{ij}^{(3)el} = \frac{2N}{5k^3T^3} \{(\boldsymbol{\mu}_i \cdot \boldsymbol{\Theta}_i \cdot \boldsymbol{\mu}_i)(\boldsymbol{\mu}_j \cdot \boldsymbol{\Theta}_j \cdot \boldsymbol{\mu}_j) \langle r_{ij}^{-11} \rangle + \\ + \frac{4}{7}[(\boldsymbol{\mu}_i \cdot \boldsymbol{\Theta}_i \cdot \boldsymbol{\mu}_i)(\boldsymbol{\Theta}_j \cdot \boldsymbol{\Theta}_j : \boldsymbol{\Theta}_j) + (\boldsymbol{\Theta}_i \cdot \boldsymbol{\Theta}_i : \boldsymbol{\Theta}_i)(\boldsymbol{\mu}_j \cdot \boldsymbol{\Theta}_j \cdot \boldsymbol{\mu}_j)] \langle r_{ij}^{-13} \rangle + \\ + \frac{3^2}{4^3}(\boldsymbol{\Theta}_i \cdot \boldsymbol{\Theta}_i : \boldsymbol{\Theta}_i)(\boldsymbol{\Theta}_j \cdot \boldsymbol{\Theta}_j : \boldsymbol{\Theta}_j) \langle r_{ij}^{-15} \rangle\}. \quad (44)$$

In the case of axially symmetrical molecules eq. (44) assumes the simpler form

$$B_{ij}^{(3)el} = \frac{2N}{5k^3T^3} \Theta_i \Theta_j \{ \mu_i^2 \mu_j^2 \langle r_{ij}^{-11} \rangle + \frac{3}{7}(\mu_i^2 \Theta_j^2 + \Theta_i^2 \mu_j^2) \langle r_{ij}^{-13} \rangle + \\ + \frac{18}{4^3} \Theta_i^2 \Theta_j^2 \langle r_{ij}^{-15} \rangle \}. \quad (45)$$

Let us now, moreover, take into consideration in the above calculations the additional potential energy resulting from the anisotropic dispersive forces discussed for axially-symmetric molecules by De Boer and Heller²⁷), and by London²⁸) and De Boer²⁹). For molecules of arbitrary symmetry we have in the dipole-dipole approximation¹⁷)

$$v_{ij}^{anis-disp} = -\frac{1}{4} \left(\frac{h\nu_i h\nu_j}{h\nu_i + h\nu_j} \right) \times \\ \times \{ (\boldsymbol{\alpha}_{pi} \cdot {}^{(1)}\mathbf{T}_{pq}^{(1)}) : (\boldsymbol{\alpha}_{qj} \cdot {}^{(1)}\mathbf{T}_{pq}^{(1)}) - \alpha_i \alpha_j ({}^{(1)}\mathbf{T}_{pq}^{(1)} : {}^{(1)}\mathbf{T}_{pq}^{(1)}) \}, \quad (46)$$

where $h\nu_i$ and $h\nu_j$ are characteristic energies of the two interacting molecules of species i and j .

Obviously, in the first approximation, the anisotropic dispersive interactions of molecules do not contribute to B_{ij} ; however, in the second approximation, we have by (4) and (46)

$$B_{ij}^{anis-disp} = -\frac{N}{1600k^2T^2} \left(\frac{h\nu_i h\nu_j}{h\nu_i + h\nu_j} \right)^2 \{ 19(\boldsymbol{\alpha}_i : \boldsymbol{\alpha}_i)(\boldsymbol{\alpha}_j : \boldsymbol{\alpha}_j) - \\ - 27\alpha_i^2(\boldsymbol{\alpha}_j : \boldsymbol{\alpha}_j) - 27(\boldsymbol{\alpha}_i : \boldsymbol{\alpha}_i)\alpha_j^2 - 9\alpha_i^2\alpha_j^2 \} \langle r_{ij}^{-12} \rangle, \quad (47)$$

or, for axially-symmetric molecules,

$$B_{ij}^{anis-disp} = -\frac{9N}{400k^2T^2} \left(\frac{h\nu_i h\nu_j}{h\nu_i + h\nu_j} \right)^2 \alpha_i^2 \alpha_j^2 (5\kappa_i^2 + 5\kappa_j^2 + 19\kappa_i^2 \kappa_j^2) \langle r_{ij}^{-12} \rangle, \quad (48)$$

since we have in this special case $\boldsymbol{\alpha}_i : \boldsymbol{\alpha}_i = 3\alpha_i^2(1 + 2\kappa_i^2)$.

A further contribution to B_{ij} should come from the cross term $v_{ij}^{\text{el}} v_{ij}^{\text{anis-disp}}$; we obtain for quadrupole molecules from (4) by (13) and (46)

$$B_{ij}^{\text{el-disp}} = \frac{3N}{25k^2T^2} \left(\frac{h\nu_i h\nu_j}{h\nu_i + h\nu_j} \right) (\alpha_i : \Theta_i)(\alpha_j : \Theta_j) \langle r_{ij}^{-11} \rangle. \quad (49)$$

In the case of axially-symmetric molecules, the above expression transforms to

$$B_{ij}^{\text{el-disp}} = \frac{27N}{25k^2T^2} \left(\frac{h\nu_i h\nu_j}{h\nu_i + h\nu_j} \right) \alpha_i \kappa_i \Theta_i \alpha_j \kappa_j \Theta_j \langle r_{ij}^{-11} \rangle. \quad (50)$$

From eqs. (47) and (49), or (48) and (50), we see that when the anisotropic dispersive force is taken into consideration, there are two opposing contributions to B_{ij} , namely, a positive contribution (49) or (50) from the cross term between the anisotropic dispersive forces and the quadrupole-quadrupole interaction, and a negative contribution from the square of the pure anisotropic dispersive energy.

In the same way, one can calculate other contributions to B_{ij} due to the second and higher approximations; the latter however, are of the second order in the dipole polarizability or higher-order polarizabilities, and in general play a smaller role as compared with the contributions calculated above.

§ 5. *Applications to special cases and discussion.* In order to compute effectively the average value $\langle r_{ij}^{-n} \rangle$ defined by (17), we have to know the law according to which the forces of attraction and repulsion between the molecules vary with the distance r_{pq} . Assuming, in general, that the energy of central interaction of the molecules is given by

$$u_{ij}(r_{pq}) = \frac{F_{ij}}{s^t} \varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{pq}} \right)^s - \left(\frac{\sigma_{ij}}{r_{pq}} \right)^t \right\}, \quad (51)$$

we obtain from (17) by the Lennard-Jones method

$$\langle r_{ij}^{-n} \rangle^{(s-t)} = \frac{4\pi\sigma_{ij}^{3-n}}{s y_{ij}^4 s^t} H_n^{s-t}(y_{ij}) = \frac{6b_{ij} H_n^{s-t}(y_{ij})}{s N y_{ij}^4 \sigma_{ij}^n}, \quad (52)$$

wherein ε_{ij} and σ_{ij} are the central force parameters having the dimensions of an energy and length, respectively, and

$$H_n^{s-t}(y_{ij}) = y_{ij}^{(4s+6-2n)/s} \sum_{m=0}^{\infty} \frac{1}{m!} y_{ij}^{2m(s-t)/s} \Gamma \left(\frac{tm + n - 3}{s} \right) \quad (53)$$

with $y_{ij} = 2(\varepsilon_{ij}/kT)^{\frac{1}{2}}$ and $b_{ij} = \frac{2}{3}\pi N \sigma_{ij}^3$.

For $s = 12$ and $t = 6$, i.e. for a 12-6 Lennard-Jones potential, the functions (53) are reduced to the functions $H_n^{12-6}(y)$ introduced by Pople⁽¹¹⁾

and tabulated by Buckingham and Pople¹²), whereas for $s = 18$ and $t = 6$ we have functions which have been discussed and tabulated by Saxena and Joshi¹⁸) as well as the functions for $s = 28$ and $t = 7$.

Recurring to eq. (52), we can represent the contributions to B_{ij} from various noncentral interactions, as computed in sections 2, 3 and 4, in a form suitable for direct numerical estimations, provided the parameters ε_{ij} and σ_{ij} , and other molecular parameters are known.

In the case of a one-component gas consisting of axially-symmetric molecules with a small dipole moment μ and arbitrary quadrupole moment Θ , the expressions (21), (38), (39), (43), (45), (48), (50) and (52), transform to the following formulas:

$$B^{\text{el}}(s-t) = -\frac{b}{16s} \left\{ \left(\frac{\mu^2}{\varepsilon\sigma^3} \right)^2 H_6^{s-t}(y) + 3 \left(\frac{\mu^2}{\varepsilon\sigma^3} \right) \left(\frac{\Theta^2}{\varepsilon\sigma^5} \right) H_8^{s-t}(y) + \right. \\ \left. + \frac{21}{5} \left(\frac{\Theta^2}{\varepsilon\sigma^5} \right)^2 H_{10}^{s-t}(y) - \frac{3}{5} y^2 \left(\frac{\Theta^2}{\varepsilon\sigma^5} \right) \left[\left(\frac{\mu^2}{\varepsilon\sigma^3} \right)^2 H_{11}^{s-t}(y) + \frac{6}{7} \left(\frac{\mu^2}{\varepsilon\sigma^3} \right) \left(\frac{\Theta^2}{\varepsilon\sigma^5} \right) \times \right. \right. \\ \left. \left. \times H_{13}^{s-t}(y) + \frac{18}{49} \left(\frac{\Theta^2}{\varepsilon\sigma^5} \right)^2 H_{15}^{s-t}(y) \right] \right\}, \quad (54)$$

$$B^{\text{ind}}(s-t) = -\frac{3b}{2sy^2} \left\{ \left(\frac{\alpha}{\sigma^3} \right) \left[\left(\frac{\mu^2}{\varepsilon\sigma^3} \right) H_6^{s-t}(y) + \frac{3}{2} \left(\frac{\Theta^2}{\varepsilon\sigma^5} \right) H_8^{s-t}(y) \right] + \right. \\ \left. + \left(\frac{q}{\sigma^5} \right) \left[5 \left(\frac{\mu^2}{\varepsilon\sigma^3} \right) H_8^{s-t}(y) + 14 \left(\frac{\Theta^2}{\varepsilon\sigma^5} \right) H_{10}^{s-t}(y) \right] \right\}, \quad (55)$$

$$B^{\text{anis-disp}}(s-t) = -\frac{27b}{64s} \left(\frac{h\nu}{\varepsilon} \right)^2 \left(\frac{\alpha}{\sigma^3} \right)^4 \kappa^2 (0.05 + 0.095\kappa^2) H_{12}^{s-t}(y), \quad (56)$$

$$B^{\text{cross}}(s-t) = \frac{9b\kappa}{10s} \left(\frac{\alpha}{\sigma^3} \right) \left(\frac{\Theta^2}{\varepsilon\sigma^5} \right) \times \\ \times \left\{ \left[\left(\frac{\mu^2}{\varepsilon\sigma^3} \right) + \frac{9}{40} \left(\frac{h\nu}{\varepsilon} \right) \left(\frac{\alpha}{\sigma^3} \right) \kappa \right] H_{11}^{s-t}(y) + \frac{3}{7} \left(\frac{\Theta^2}{\varepsilon\sigma^5} \right) H_{13}^{s-t}(y) \right\}. \quad (57)$$

On putting in the above expressions $\mu = 0$, we obtain formulas for a quadrupole gas discussed numerically in a preceding paper¹⁷) (see also ref. 21).

For a gas of tetrahedral molecules with an octopole and hexadecapole moment, the expressions (23), (40) and (41) become by (52)

$$B^{\text{el}}(s-t) = -\frac{198b}{175s} \left\{ 9 \left(\frac{\Omega^2}{\varepsilon\sigma^7} \right)^2 H_{14}^{s-t}(y) + 130 \left(\frac{\Omega^2}{\varepsilon\sigma^7} \right) \left(\frac{\Phi^2}{\varepsilon\sigma^9} \right) H_{16}^{s-t}(y) + \right. \\ \left. + \frac{13000}{21} \left(\frac{\Phi^2}{\varepsilon\sigma^9} \right)^2 H_{18}^{s-t}(y) \right\}, \quad (58)$$

$$B^{\text{ind}}(s-t) = -\frac{36b}{5sy^2} \left\{ \left(\frac{\alpha}{\sigma^3} \right) \left[\left(\frac{\Omega^2}{\varepsilon\sigma^7} \right) H_{10}^{s-t}(y) + \frac{25}{7} \left(\frac{\Phi^2}{\varepsilon\sigma^9} \right) H_{12}^{s-t}(y) \right] + \right. \\ \left. + 15 \left(\frac{q}{\sigma^5} \right) \left[\left(\frac{\Omega^2}{\varepsilon\sigma^7} \right) H_{12}^{s-t}(y) + \frac{110}{21} \left(\frac{\Phi^2}{\varepsilon\sigma^9} \right) H_{14}^{s-t}(y) \right] \right\}. \quad (59)$$

In the case when the terms with hexadecapole moment can be neglected in the above result, we have in a good approximation

$$B^{\text{ind}}(s-t) = -\frac{36b}{5sy^2} \left(\frac{\alpha}{\sigma^3} \right) \left(\frac{\Omega^2}{\varepsilon\sigma^7} \right) H_{10}^{s-t}(y), \quad (60)$$

$$B^{\text{el}}(s-t) = -\frac{1782b}{175s} \left(\frac{\Omega^2}{\varepsilon\sigma^7} \right)^2 H_{14}^{s-t}(y). \quad (61)$$

If the parameters ε and σ are known, we can determine from (60) and (61) the value of the octopole moment of the tetrahedral molecule of the gas investigated. For example, using the 12-6 potential parameters of methane: $\varepsilon/k = 137^\circ\text{K}$ and $\sigma = 3.882 \text{ \AA}$ from viscosity data²⁾, we obtain by (60) and (61) the values of B assembled in table I, where it is seen that good agreement between the calculated ($B^{\text{calc}} = B^{\text{ind}} + B^{\text{el}}$) and experimental values of Thomaes *et al.*³⁰⁾ result if the octopole moment of the CH_4 molecule is $\Omega = 5 \times 10^{-34}$ e.s.u. cm^3 . It is also seen that the contributions to B^{calc} from the existence of non-central interactions of the methane molecules of the octopole-induced dipole and octopole-octopole types (the figures in the third and fourth columns of table I) average 15 per cent of the contribution from the central forces alone (column 2 of table I).

We also note that the value of the octopole moment of the CH_4 molecule determined from the second dielectric virial coefficient (B_D) data obtained by Johnston *et al.*³¹⁾ amounts to²²⁾ $\Omega_{\text{CH}_4} = 6 \times 10^{-34}$ e.s.u. cm^3 . Direct calculation by Paar (as cited from ref. 31), who used a one-centre wave function with Slater orbitals, gave the value $\Omega_{\text{CH}_4} = 6.5 \times 10^{-34}$ e.s.u. cm^3 in good agreement with our result from the data for B and B_D . As the complete, exact calculation of molecular octopole or higher moments from known wave functions is beset with great difficulties, the indirect, simple ways of determining Ω in tetrahedral molecules as discussed here gain considerable importance and in many cases can yield fully reliable results, especially if satisfactory agreement is achieved for the entire range of temperatures accessible in the experimental investigation of the second virial coefficients (other methods are discussed in refs. 20, 22 and 32).

It is also worth mentioning that supplementary and at the same time verifying information on the molecular quadrupoles or octopoles can be obtained from investigations of the second virial coefficients of appropriately chosen gas mixtures.

In the case of a two-component gas wherein the one component consists

TABLE I

| Calculated and experimental values of the second virial coefficient of methane (in cm ³ /mole), for $\alpha = 2.6 \times 10^{-24}$ cm ³ and $\Omega = 5 \times 10^{-34}$ e.s.u.cm ³ | | | | | |
|---|--------------------------|------------------------|-----------------------|-------------------------|------------------------|
| T°K | $B^{\text{centr}}(12-6)$ | $B^{\text{ind}}(12-6)$ | $B^{\text{el}}(12-6)$ | $B^{\text{calc}}(12-6)$ | $B^{\text{exper}}(80)$ |
| 142.6 | -174.8 | -3.0 | -24.3 | -202.1 | -205.6 |
| 176.7 | -119.2 | -2.1 | -14.7 | -136.0 | -135.0 |
| 239.8 | -63.9 | -1.5 | -7.7 | -73.1 | -73.0 |
| 295.0 | -37.9 | -1.1 | -5.1 | -44.1 | -44.5 |

of molecules with the small dipole moment μ_1 and the other consists of molecules with the quadrupole moment Θ_2 , we obtain by results derived in sections 2, 3 and 4 for the interaction between the dipole molecule 1 and quadrupole molecule 2

$$\begin{aligned}
 B_{12}^{\text{noncentr}}(s-t) = & - \\
 & - \frac{27b_{12}}{3200s} \left(\frac{h\nu_1 h\nu_2}{\varepsilon_{12}h\nu_1 + \varepsilon_{12}h\nu_2} \right)^2 \left(\frac{\alpha_1}{\sigma_{12}^3} \right)^2 \left(\frac{\alpha_2}{\sigma_{12}^3} \right)^2 (5\kappa_1^2 + 5\kappa_2^2 + 19\kappa_1^2\kappa_2^2) H_{12}^{s-t}(\gamma_{12}) - \\
 & - \frac{3b_{12}}{4sy_{12}^2} \left\{ \left(\frac{\mu_1^2}{\varepsilon_{12}\sigma_{12}^3} \right) \left[\left(\frac{\alpha_2}{\sigma_{12}^3} \right) H_6^{s-t}(\gamma_{12}) + 5 \left(\frac{q_2}{\sigma_{12}^5} \right) H_8^{s-t}(\gamma_{12}) \right] + \right. \\
 & + \frac{3}{2} \left(\frac{\Theta_2^2}{\varepsilon_{12}\sigma_{12}^5} \right) \left[\left(\frac{\alpha_1}{\sigma_{12}^3} \right) H_8^{s-t}(\gamma_{12}) + \frac{28}{3} \left(\frac{q_1}{\sigma_{12}^5} \right) H_{10}^{s-t}(\gamma_{12}) \right] + \\
 & \left. + \frac{y_{12}^2}{8} \left(\frac{\mu_1^2}{\varepsilon_{12}\sigma_{12}^3} \right) \left(\frac{\Theta_2^2}{\varepsilon_{12}\sigma_{12}^5} \right) H_8^{s-t}(\gamma_{12}) \right\}. \quad (62)
 \end{aligned}$$

On putting herein $\mu_1 = 0$ and $\kappa_1 = 0$, we obtain immediately the result for interaction between an atom possessing the dipole and quadrupole polarizabilities α_1 and q_1 and a quadrupolar molecule, namely

$$\begin{aligned}
 B_{12}^{\text{noncentr}}(s-t) = & - \\
 & - \frac{27b_{12}}{640s} \left(\frac{h\nu_1 h\nu_2}{\varepsilon_{12}h\nu_1 + \varepsilon_{12}h\nu_2} \right)^2 \left(\frac{\alpha_1}{\sigma_{12}^3} \right)^2 \left(\frac{\alpha_2}{\sigma_{12}^3} \right)^2 \kappa_2^2 H_{12}^{s-t}(\gamma_{12}) - \\
 & - \frac{9b_{12}}{8sy_{12}^2} \left\{ \left(\frac{\alpha_1}{\sigma_{12}^3} \right) H_8^{s-t}(\gamma_{12}) + \frac{28}{3} \left(\frac{q_1}{\sigma_{12}^5} \right) H_{10}^{s-t}(\gamma_{12}) \right\} \left(\frac{\Theta_2^2}{\varepsilon_{12}\sigma_{12}^5} \right). \quad (63)
 \end{aligned}$$

Analogously, for $\Theta_2 = 0$ and $\kappa_2 = 0$, eq. (62) yields a formula describing the interaction of an atom with a dipolar molecule.

The contribution to B_{12} arising from interaction between a dipolar molecule of species 1 with moment μ_1 and a tetrahedral molecule of species

2 with octopole moment Ω_2 is of the form

$$B_{12}^{\text{noncentr}}(s-t) = -\frac{3b_{12}}{10s} \left(\frac{\mu_1^2}{\varepsilon_{12}\sigma_{12}^3} \right) \left(\frac{\Omega_2^2}{\varepsilon_{12}\sigma_{12}^7} \right) H_{10}^{s-t}(y_{12}). \quad (64)$$

For the interaction between a quadrupolar molecule 1 and a tetrahedral molecule 2 we have

$$B_{12}^{\text{noncentr}}(s-t) = -\frac{27b_{12}}{20s} \left(\frac{\Theta_1^2}{\varepsilon_{12}\sigma_{12}^5} \right) \left(\frac{\Omega_2^2}{\varepsilon_{12}\sigma_{12}^7} \right) H_{12}^{s-t}(y_{12}). \quad (65)$$

Similarly, we obtain from (18) for the contributions to B_{12} from interaction of an octahedral molecule 2 possessing the hexadecapole moment Φ_2 with, respectively, a dipolar molecule

$$B_{12}^{\text{noncentr}}(s-t) = -\frac{15b_{12}}{14s} \left(\frac{\mu_1^2}{\varepsilon_{12}\sigma_{12}^3} \right) \left(\frac{\Phi_2^2}{\varepsilon_{12}\sigma_{12}^9} \right) H_{12}^{s-t}(y_{12}), \quad (66)$$

with a quadrupolar molecule

$$B_{12}^{\text{noncentr}}(s-t) = -\frac{99b_{12}}{14s} \left(\frac{\Theta_1^2}{\varepsilon_{12}\sigma_{12}^5} \right) \left(\frac{\Phi_2^2}{\varepsilon_{12}\sigma_{12}^9} \right) H_{14}^{s-t}(y_{12}), \quad (67)$$

and with a tetrahedral molecule possessing the octopole moment Ω_1

$$B_{12}^{\text{noncentr}}(s-t) = -\frac{2574b_{12}}{35s} \left(\frac{\Omega_1^2}{\varepsilon_{12}\sigma_{12}^7} \right) \left(\frac{\Phi_2^2}{\varepsilon_{12}\sigma_{12}^9} \right) H_{16}^{s-t}(y_{12}). \quad (68)$$

In concluding it can be said that, in the situation when the method of direct calculation of the higher-multipole (quadrupole, octopole and hexadecapole) moments of molecules with more than two atoms from known wave functions generally presents considerable difficulties, the indirect method of determining molecular multipoles discussed in the present paper is of great convenience in its applications and leads in a simple way to results the accuracy of which is in many cases reliable and satisfactory.

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