Theoretical Part.

Chapter 2.

Section 1: Introduction to the virial coefficients of Polyatomic gases.
In spite of the significant progress made in recent years, our knowledge of the intermolecular forces in polyatomic gases is still inadequate. This is primarily, due to various long-range, angle-dependent terms, present in the intermolecular potential function for such gases. These non-spherical terms are likely to have an important effect on the thermodynamic properties, both because of the additional cohesive energy and because of the loss of entropy associated with hindered rotation.

Analysis of the second virial coefficients in the equation of state, provides us one of the probes for investigation of the forces between interacting pair of molecules and it is widely believed that the virial coefficients are much more sensitive to the non-spherical interactions than the transport properties. The method of analysis of $B(T)$, 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 distance, 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 $B(T)$ allows to determine not only the parameters of the central forces, but moreover, yields information concerning the electric multipole moments of the molecules. These multipole moments have proved useful in the search for an understanding of the properties of imperfect gases, liquids and solids. Their measurements are also very important from the structural point of view as they provide us the knowledge about the shape, charge distribution and bond lengths of the molecule.

The earliest calculations of $B(T)$ for dipolar and quadrupolar molecules, taking into account a non-central potential energy, are due to Keesom, Debye and Falkenhagen. They have been modified for higher accuracy by Stockmayer, Rowlinson, Pople, Castle et al, Lawley and Smith, Kielich, McQuarrie and Levine, Spurling and Mason, Singh et al, König and others.

Buckingham and Pople dealt with in addition to the interaction of permanent dipoles, other directional intermolecular forces such as dipole-induced dipole interaction, quadrupole forces and the effect of molecular shape. They obtained detailed expressions for the corresponding $B(T)$ from statistical mechanics and applied them to experimental data of several polar gases. Castle et al modified Pople's formalism in such a way that the long-range forces are cut off
inside the molecular diameter. Such an expression can only be used for the determination of molecular parameters if it is supplemented by a term representing the short-range directional interactions. Lawley and Smith presented a new model for polar molecules, based on the concept of a point dipole, displaced from the origin of the dispersion and repulsion forces of the molecule. The second virial coefficients are evaluated numerically for the simplest form of the model, off-centre dipoles located in hard-sphere molecules. Dymond and Smith refined the model by the introduction of a Lennard-Jones central potential which reproduces B(T) with more realistic collision diameter than obtained from the Stockmayer potential model. Kielich developed a tensorial formalism of molecular multipole moments and calculated B(T) for dipolar, quadrupolar, octopolar and higher multipolar gases. McQuarrie and Levine followed a different approach and derived expression of virial coefficients for non-polar, axial molecules with permanent quadrupole moments and anisotropic polarizabilities in terms of several single and triple integrals, which depend only upon the central part of the potential. Spurling and Mason used a more sophisticated potential model for the quadrupolar molecules and evaluated the corresponding B(T) for a number of gases. Singh et al proposed a 'preaveraged' potential model, where the angle-dependent terms are statistically averaged. They calculated B(T) for polar gases including the effects of quadrupole, polarizability and anisotropy in the polarizability. This model is suitable in the temperature range where one molecule
is getting enough time to reorient itself in the local field of the other molecule. Kong\textsuperscript{15,16} modified Stockmayer potential function by assuming that the dispersion-repulsion part of the potential energy is the sum of all the pair interactions between constituent atomic groups on adjacent molecules and that the molecules are polarizable. With two adjustable potential parameters, this model closely reproduced the experimental $B(T)$ of a few polar gases.

Debye\textsuperscript{2} first pointed to the possibility of gaining information on the quadrupole moment from investigation of the equation of state of gases and the method is followed by Kielich\textsuperscript{10}. Orcutt\textsuperscript{21} generalized the method to the entire temperature range accessible in the experimental investigation of $B(T)$ and obtained fully realistic values of the quadrupole moments of various molecules. In a similar way, Kielich obtained results for the octopole moment of tetrahedral molecules\textsuperscript{22} and showed the possibility of determining the hexadecapole moment of octahedral molecules\textsuperscript{23}. Evaluation of molecular multipole moments from $B(T)$ are particularly satisfactory, if the central force parameters are obtained from the viscosity measurements over a range of temperature as the multipole moments have negligible effect on viscosity. Such procedure has been followed by Spurling and Mason\textsuperscript{12} and Singh and Das Gupta\textsuperscript{14} for the estimation of quadrupole moments and by Spurling et al\textsuperscript{24} in the evaluation of octopole moments of gases. This, although an indirect method of determining multipole moments, is of advantage owing to its convenience in use and leads quickly to final
results of sufficient accuracy, particularly if we are unable to perform the direct computations by wave functions.

The intermolecular potential for axially symmetric molecules can be expanded in such a way that the central force part is separated uniquely and the remaining directional parts classified in terms of various angular symmetries. In general, the intermolecular energy will depend on three Cartesian co-ordinates and three Eulerian angles of the molecules, but if the molecules are axially symmetric, the third Eulerian angle need not be considered. Strictly, this condition applies to diatomic and linear polyatomic molecules, but the general features of other more complex systems can often be represented by an axially symmetric model. Thus, in the treatment of $B(T)$ we shall write,

$$U = U_0(R) + U_1(R, \Theta_1, \Theta_2, \psi_1, \psi_2) \ldots \ldots (1)$$

where $U_0$ is the central and $U_1$, the remaining directional part of the intermolecular potential. According to classical statistical mechanics, $B(T)$ is given by,

$$B(T) = \frac{N}{8\pi} \int_{0}^{\infty} R^2 dR \int_{0}^{\pi} \sin \Theta_1 d\Theta_1 \int_{0}^{\pi} \sin \Theta_2 d\Theta_2 \int_{0}^{2\pi} d\psi_1 \int_{0}^{2\pi} d\psi_2 \left(1 - e^{-U/kt}\right) \ldots \ldots (2)$$

Treating the non-central forces $U_1$ as a perturbation on the central forces $U_0$ which is applicable only if the angular
dependence of the force-field is small, the $B(T)$ can be expanded in the form,

$$B(T) = B^{(0)}(T) + B^{(1)}(T) + B^{(2)}(T) + \ldots \ldots \ldots (3)$$

where,

$$B^{(0)}(T) = 2\pi N \int_0^\infty \left[ 1 - e^{-U_0/KT} \right] R^2 dR \ldots \ldots \ldots (3a)$$

and

$$B^{(m)}(T) = -\frac{N}{8\pi} \int d\omega_1 \int d\omega_2 \int_0^\infty R^2 dR \cdot \frac{1}{m!} \left( \frac{1}{KT} \right)^m \left[ U_1 \right]^m e^{-U_0/KT}, \ (m > 0) \ldots \ldots \ldots (3b)$$

$B^{(0)}(T)$ being the value of $B(T)$ corresponding to a central force field $U_0(R)$. $\int d\omega_1$ and $\int d\omega_2$ have been written for integration over the angular co-ordinates. Lennard-Jones (12-6) potential has been widely used to represent central repulsive and attractive part of the potential. Then the angular integrations are straightforward and the radial integrations can be performed by the method of Lennard-Jones and leads to,

$$\int_0^\infty R e^{-U_0/KT} R^2 dR = \frac{1}{12} \int_0^\infty (2-k) y^{-4} H_k(y) \ldots \ldots \ldots (4a)$$

and

$$\int_0^\infty \left[ 1 - e^{-U_0/KT} \right] R^2 dR = \frac{1}{3} \int_0^\infty y^{-3} \left[ H_{12}(y) - \frac{1}{2} H_6(y) \right] \ldots \ldots \ldots (4b)$$

where $y = 2(\epsilon/KT)^{1/2}$, $\epsilon$, $k$, and $T$ being depth of the potential model, Boltzmann constant and absolute temperature.
respectively, \( \sigma \) is the collision diameter of the molecules and

\[
H_k (y) = y^{\frac{27-k}{6}} \sum \binom{6p+k-3}{12} y^p / p!
\]

... (4c)

But the spherically symmetric force-field of Lennard-Jones type are not as successful when the molecules become complex. Additional parameters related to the molecular geometry have been included to improve the representation of these systems. Kihara potential has been found to be more realistic and \( B(T) \) has been calculated for polar and quadrupolar gases with Kihara core model as the central potential.

Earlier work of Rowlinson on third virial coefficients for the angle-dependent potentials has been followed and refined by Levine et al., Storvick et al. and by the more recent works of Stogryn, Johnson et al. and Singh et al.

In case of lighter gases, as the temperature is lowered, the quantum effects become more and more significant and that can be taken into account by Wigner-Kirkwood expansion formalism. Extensive calculations of quantum \( B(T) \) by such formalism has been done only for spherical molecules. They should also be tried for the angle-dependent potentials for lighter polyatomic gases. Very few works in this line includes that of Wang Chang and Rakshit and Chowdhury for quadrupolar and of Pompe and Spurling for dipolar gases.
In the following sections, we have done the quantum corrections to the second virial coefficient of a quadrupolar gas $D_2$ and evaluated the multipole moments of the polyatomic gases $CO_2$ and $CH_4$ from viscosity and second virial coefficients.
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Chapter 2.

Section 2: Quantum corrections for the
Noncentral intermolecular forces
to the second virial coefficient
of Deuterium gas.
I. INTRODUCTION

The noncentral part of the intermolecular forces contributes materially to the second virial coefficient of a polyatomic gas. At low temperatures and for the lighter molecules it is necessary to consider quantum corrections to the second virial coefficient for both the central and noncentral parts of the interactions\(^1,2\). The quantum corrections for the central part of the intermolecular forces have been calculated extensively on Lennard - Jones (12-6) potential model by many workers\(^3\). But for the noncentral part, the quantum corrections have not yet been studied to sufficient extent by considering the various factors which arise owing to the presence of permanent and induced electric moments and the shape of molecule\(^4\). We have therefore thought it desirable to calculate the quantum corrections for the noncentral forces to the second virial coefficient of polyatomic molecules. For our present study we have chosen the \(D_2\) molecule, for which the convergence in the series expansion of the second virial coefficient in the ascending power of \(h^2\) can be easily achieved. This molecule also possesses significant quadrupole moment. From the contribution of the noncentral forces to the second virial coefficient, we have also estimated the quadrupole moment of \(D_2\) molecule.

II. THE PAIR POTENTIAL FUNCTION AND THE QUANTUM CORRECTIONS TO THE SECOND VIRIAL COEFFICIENT

The potential energy of interaction \(U(R)\) between two \(D_2\) molecules which possess significant quadrupole moments can be represented by the following function\(^4,5\),
\[ U(R) = U(\text{spher}) + U(\text{quad}) + U(\text{anis}) + U(\text{quad-ind dipole}) + U(\text{shape}) \] 

where,

\[ U(\text{spher}) = 4\epsilon \left( \frac{\sigma}{R} \right)^{12} \left[ (\frac{\sigma}{R})^{6} - 1 \right] \] 

which is the Lennard-Jones (12-6) potential,

\[ U(\text{quad}) = \frac{3}{4} \left( \frac{\Theta^2}{R^5} \right) \left[ 1 - 5 \cos^2 \Theta_1 - 5 \cos^2 \Theta_2 - 15 \cos \Theta_1 \cos \Theta_2 + 2(\sin \Theta_1 \sin \Theta_2 \cos \Psi + 4 \cos \Theta_1 \cos \Theta_2)^2 \right] \] 

\[ U(\text{anis}) = 4\epsilon \left( \frac{\sigma}{R} \right)^6 \left[ K - \frac{3}{2} K(1-K)(\cos^2 \Theta_1 + \cos^2 \Theta_2) - \frac{3}{2} K^2(\sin \Theta_1 \sin \Theta_2 \cos \Psi + 2 \cos \Theta_1 \cos \Theta_2)^2 \right] \] 

\[ U(\text{quad-ind dipole}) = -\frac{3}{8} \left( \frac{\Theta^2}{R^8} \right) (\sin^4 \Theta_1 + \sin^4 \Theta_2 + \cos^4 \Theta_1 + \cos^4 \Theta_2) \] 

\[ U(\text{shape}) = 4D\epsilon \left( \frac{\sigma}{R} \right)^{12} (3 \cos^2 \Theta_1 + 3 \cos^2 \Theta_2 - 2) \] 

\[ \Theta_1, \Theta_2 \text{ and } \Psi \text{ define the angles which determine the orientation of the molecule with respect to the line joining the centres of the molecules. It is assumed that the molecules have axially symmetric charge distributions. The quadrupole moment } \Theta \text{ is defined by,} \]

\[ \Theta = \frac{1}{2} \sum_i e_i (3z_i^2 - R_i^2) = \sum_i e_i (z_i^2 - x_i^2) \] 

where \( z_i \) and \( x_i \) are the components of \( R_i \) along axes parallel
and perpendicular to the molecular symmetry axes and $R_1$ is the distance from the centre of mass to the charge $e_1$. The average polarizability $\bar{\alpha}$ is given by $\bar{\alpha} = \frac{1}{3} (\alpha_{zz} + 2 \alpha_{xx})$, and the anisotropy in the polarizability $\kappa$ is defined by $\kappa = \frac{1}{3\bar{\alpha}} (\alpha_{zz} - \alpha_{xx})$, where $\alpha_{zz}$ and $\alpha_{xx}$ are the components of the polarizability tensor along the above defined principal axes. The quantity $D$ is the dimensionless shape and parameter of the molecule and must lie between -0.25 and 0.5. A negative $D$ corresponds to a platelike molecule and a positive $D$ to a rodlike one.

At low temperatures the two quantum effects, diffraction and symmetry, become important for the case of light molecules and must be considered in calculating the second virial and the transport properties of the gas. In the temperature range where the quantum effects are of the nature of correction to classical laws, the second virial coefficient $B(T)$ can be expanded as a series in the form

$$B(T) = B_{cl}(T) + \left[ \frac{h^2}{m} B_I^{(tr)}(T) + \frac{h^2}{m} B_{II}^{(tr)}(T) + \ldots \right]$$

$$+ \left[ \frac{h^2}{I} B_I^{(rot)}(T) + \frac{h^2}{I} B_{II}^{(rot)}(T) + \ldots \right] + \frac{h^2}{m} \frac{3}{2} B_0$$

where $B_{cl}(T)$ is the classical value of $B(T)$ and $B_I$ and $B_{II}$ are, respectively, the first and second quantum corrections. In deriving the above expression, Wang Chang has assumed that the diatomic molecules may be represented by rigid three-
dimensional rotators of mass m and moment of inertia I. In Eqn. (3) the terms proportional to successive power of \((h^2 / m)\) are the quantum deviations due to the translational contributions and those proportional to the successive power of \((h^2 / I)\) are due to the rotational contributions. The last term \(B_0\) is due to the symmetry effect; the upper sign is for the molecules obeying Bose - Einstein statistics and the lower one for the Fermi - Dirac.

Let us define the following reduced quantities,
\[
\alpha^* = \alpha / \sigma^3, \quad \beta^* = \beta / (\epsilon \sigma^5)^{1/2}, \quad \gamma = \gamma (\epsilon / kT)^{1/2}
\]
\[
\Delta^* = \h / (m \epsilon)^{1/2}, \quad \Delta^* = \h / (\epsilon \sigma^5)^{1/2}, \quad \beta = \beta / 2 \pi N_0 \sigma^3 \quad \ldots \quad (4)
\]

In term of these reduced quantities, \(B_{cl}(T)\) for the potential model of Eqn. (1) can be written as:
\[
B_{cl*} = B_{cl*} (12-6) + B_{cl*} (\text{quad}) + B_{cl*} (\text{anis}) + B_{cl*} (\text{quad-ind. dipole})
+ B_{cl*} (\text{shape}) + B_{cl*} (\text{quad X anis}) + B_{cl*} (\text{quad X shape})
+ B_{cl*} (\text{anis X shape}) + \ldots \quad \ldots \quad (5)
\]
where, the contributions of the non-spherical terms have been derived by considering them as a perturbation to the central potential and taking only one of them at a time.
The different terms of the expression (5) are given by,

\[ B_{cl}^* (12-6) = y^{-2} \left[ H_{12}(y) - \frac{1}{2} H_6(y) \right] , \quad \ldots \quad (5.1) \]

\[ B_{cl}^* \text{ (quad)} = -\frac{7}{320} \kappa^2 \left[ H_{10}(y) - \frac{18}{343} y^2 \kappa^2 H_{16}(y) + \ldots \right] , \quad \ldots \quad (5.2) \]

\[ B_{cl}^* \text{ (anis)} = -\frac{1}{20} \kappa^2 \left[ 1 + \frac{16}{10} \kappa^2 \right] H_{12}(y) + \ldots , \quad \ldots \quad (5.3) \]

\[ B_{cl}^* \text{ (quad. ind. dipole)} = -\frac{3}{16} \kappa^2 y^{-2} \left[ H_8(y) - \frac{6}{35} \kappa y^2 \kappa^2 \right] H_{12}(y) + \ldots , \quad \ldots \quad (5.4) \]

\[ B_{cl}^* \text{ (shape)} = -\frac{1}{5} D^2 H_{24}(y) + \ldots , \quad \ldots \quad (5.5) \]

\[ B_{cl}^* \text{ (quad. X anis)} = \frac{9}{100} \kappa^2 \kappa^2 H_{11}(y) + \ldots , \quad \ldots \quad (5.6) \]

\[ B_{cl}^* \text{ (quad. X shape)} = D y^2 \kappa^2 \left[ \frac{3}{50} D H_{22}(y) + \frac{1}{56} \kappa^2 \right] H_{12}(y) + \ldots , \quad \ldots \quad (5.7) \]

\[ B_{cl}^* \text{ (anis X shape)} = \frac{1}{5} D H_{18}(y) + \ldots , \quad \ldots \quad (5.8) \]

The function \( H_n(y) \) is defined by,

\[ H_n(y) = 12 y^4 \kappa^{n-3} \int_0^\infty R^{-n} \exp\left(-U^0/\kappa T\right) R^2 dR \quad \ldots \quad (6) \]
where $U^0$ is the Lennard-Jones (12-6) potential given in Eqn. (1.1). This function has been tabulated by Buckingham and Pople. 7

The statistical mechanical expression for $B_T^{(tr)}$ is written as,

$$B_T^{(tr)}(T) = \frac{1}{4} N (48 \pi \frac{2}{k} \frac{3}{T^3} - 1) \int \int \exp \left( -\frac{U}{kT} \right) \left( \frac{\partial U^0}{\partial R} \right)^2 R^2 dR d\Omega,$$

$$\ldots \ (7)$$

where, $d\Omega = \int \int \int d(\cos \theta_1) d(\cos \theta_2) d\psi$

When the potential function of Eqn. (1) is written in the form,

$$U = U^0 + U^1$$

(where $U^0$ is the Lennard-Jones (12-6) potential representing the central forces and $U^1$ is the sum of all the orientation-dependent terms), and it is substituted in Eqn. (7), we get,

$$B_T^{(tr)} = B_T^{o(tr)} + B_T^{1(tr)}, \ldots \ (8)$$

where

$$B_T^{o(tr)} = \frac{2U N}{48 \pi \frac{2}{k} \frac{3}{T^3}} \int_0^\infty \exp \left( -\frac{U^0}{kT} \right) \left( \frac{\partial U^0}{\partial R} \right)^2 R^2 dR,$$

$$\ldots \ (9)$$

and

$$B_T^{1(tr)} = \frac{1}{4} N (48 \pi \frac{2}{k} \frac{3}{T^3} - 1) \int \int \exp \left( -\frac{U^0}{kT} \right) \left[ \left( \frac{\partial U^1}{\partial R} \right)^2 + 2 \frac{\partial U^0}{\partial R} \cdot \frac{\partial U^0}{\partial R} \right] + \sum_{n=1}^\infty (-\frac{U^1}{kT})^n (n!)^{-1} \frac{\partial}{\partial R} (\frac{\partial}{\partial R} (U^0 + U^1))^2 \int R^2 dR d\Omega,$$

$$\ldots \ (10)$$
Since $U^1$ is the sum of several terms, we solve the Eqn. (10) by the method of Pople\(^4\) and others\(^5\). Writing each term as reduced quantity, we find that $B^*_I (tr)$ can be written as,

$$B^*_I (tr) = B^*_I (tr) (12-6) + B^*_I (tr) (quad) + B^*_I (tr) (anis)$$

$$+ B^*_I (tr) (quad - ind. dipole) + B^*_I (tr) (shape)$$

$$+ B^*_I (tr) (quad \times anis) + B^*_I (tr) (quad \times shape)$$

$$+ B^*_I (tr) (anis \times shape) + higher - order cross terms,$$

... (11)

where,

$$B^*_I (tr) (12-6) = \left( \frac{3}{64} \right) \pi^2 y^2 \left[ 4 H_{26}(y) + H_{14}(y) - 4 H_{20}(y) \right],$$

... (11.1)

$$B^*_I (tr) (quad) = \left( \frac{7}{1024} \right) \pi^4 y^2 \left[ \frac{5}{6} H_{12}(y) + 2y^2 \left\{ H_{18}(y) - 2H_{24}(y) \right\} + \frac{3}{5} y^4 \left\{ 4 H_{36}(y) + H_{24}(y) - 4H_{30}(y) \right\} + \right],$$

... (11.2)

$$B^*_I (tr) (anis) = -\left( \frac{3}{128} \right) \pi^2 \kappa^2 (1-2\kappa) y^2 \left[ 2 H_{14}(y) + 4y^2 \right.$$

$$\left\{ H_{20}(y) - 2 H_{26}(y) \right\} + y^4 \left\{ 4 H_{38}(y) + H_{26}(y) - 4 H_{20}(y) \right\} + \right],$$

... (11.3)

$$B^*_I (tr) (quad \times ind. dipole) = \left( \frac{3}{256} \right) \pi^2 \kappa^2 y^2.$$

$$\left[ 8 \left\{ H_{16}(y) - 2 H_{22}(y) \right\} + 3y^2 \left\{ 4 H_{34}(y) + H_{22}(y) - 4 H_{28}(y) \right\} + \right],$$

... (11.4)
\[ B_I^{*(\text{tr}) \ (\text{shape})} = \left( \frac{3}{80 \pi^2} \right) (D^2 y^2) \left[ 8 H_{26}(y) + 8 y^2 \left\{ H_{32}(y) - 2 H_{38}(y) \right\} \right] \\
+ y^4 \left\{ H_{38}(y) + 4 H_{50}(y) - 4 H_{44}(y) \right\} - \frac{16}{7} D y^2 \left\{ 2 H_{38}(y) + \\
y^2 \left\{ H_{44}(y) - 2 H_{50}(y) \right\} \right\} + \ldots \right] , \quad \ldots \ (11.5) \]

\[ B_I^{*(\text{tr}) \ (\text{quad x anis})} = -\left( \frac{27}{80 \pi^2} \right) \left( \frac{2}{5} \right) y^2 H_{13}(y) + \ldots \right] , \quad \ldots \ (11.6) \]

\[ B_I^{*(\text{tr}) \ (\text{quad x shape})} = -\left( \frac{1}{128 \pi^2} \right) \left( \frac{48}{5} \right) D y^4 \left[ \frac{48}{5} \Phi^* D H_{31}(y) - 7 \Phi^* 3 H_{24}(y) + \ldots \right] , \quad \ldots \ (11.7) \]

\[ B_I^{*(\text{tr}) \ (\text{anis x shape})} = -\left( \frac{3}{80 \pi^2} \right) \left( \frac{2}{7} \right) y^2 \left[ 4 H_{20}(y) + \frac{8}{7} y^2 H_{26}(y) - 8 D y^2 \left\{ \frac{2}{7} + \frac{3}{5} \right\} H_{32}(y) + \ldots \right] , \quad \ldots \ (11.8) \]

A method similar to that adopted for \( B_I^{*(\text{tr})} \) leads to the following expression for \( B_I^{*(\text{rot})} \),

\[ B_I^{*(\text{rot})} = B_I^{*(\text{rot}) \ (\text{quad})} + B_I^{*(\text{rot}) \ (\text{anis})} + B_I^{*(\text{rot}) \ (\text{quad-ind. dipole})} + B_I^{*(\text{rot}) \ (\text{shape})} + B_I^{*(\text{rot}) \ (\text{quad x anis})} + B_I^{*(\text{rot}) \ (\text{quad x shape})} + B_I^{*(\text{rot}) \ (\text{anis x shape})} + \text{higher-order terms}, \ldots \ (12) \]

where,

\[ B_I^{*(\text{rot}) \ (\text{quad})} = \left( \frac{7}{5120 \pi^2} \right) \left( \frac{4}{5} \right) y^2 H_{10}(y) + \ldots \right] , \quad \ldots \ (12.1) \]
\[ B_1^{\text{*(rot) (anis)}} = (1/640 \pi^2) \left[ \kappa^2 (1 - \kappa)^2 y^2 H_{12}(y) + \cdots \right], \quad (12.2) \]

\[ B_1^{\text{*(rot) (quad-ind. dipole)}} = (3/5120 \pi^2) \left[ \Theta^2 \kappa^2 y^2 H_{18}(y) + \cdots \right], \quad (12.3) \]

\[ B_1^{\text{*(rot) (shape)}} = (1/160 \pi^2) \left[ \Theta^2 \kappa^2 y^2 H_{24}(y) - \frac{2}{7} \kappa D y^2 H_{36}(y) + \cdots \right], \quad (12.4) \]

\[ B_1^{\text{*(rot) (quad X anis)}} = -(19/3840 \pi^2) \left[ \Theta^2 \kappa^2 y^2 H_{11}(y) + \cdots \right], \quad (12.5) \]

\[ B_1^{\text{*(rot) (quad X shape)}} = - (1/1600 \pi^2) \left[ \Theta^2 y^4 \left[ 6D H_{29}(y) + \frac{19}{7} \Theta^2 H_{22}(y) + \cdots \right] \right], \quad (12.6) \]

\[ B_1^{\text{*(rot) (anis X shape)}} = (1/160 \pi^2) \kappa D y^2 \left[ H_{18}(y) - \frac{2}{7} (1 - \kappa) D y^2 H_{30}(y) - \frac{52}{35} \kappa D y^2 H_{30}(y) + \cdots \right], \quad (12.7) \]

For \( D_2 \) molecules, the second quantum correction is important only at very low temperatures. Thus for the temperature range of our interest, we can neglect safely the contribution due to the rotations of the molecules to the second quantum correction term. In \( B_1^{\text{*(tr)}} \), however, those terms of nonspherical forces whose contributions are supposed to be of any importance
have been included. Thus, for $B_{II}^{*(tr)}$ we get,

$$B_{II}^{*(tr)} = B_{II}^{*(tr)} (12-6) + B_{II}^{*(tr)} \text{ (quad)} + B_{II}^{*(tr)} \text{ (shape)}$$

$$+ \cdots , \quad \cdots \quad (13)$$

where,

$$B_{II}^{*(tr)} (12-6) = (1/10240 \pi^4) y^4 \left( \begin{array}{c}
2052 H_{28}(y) + 153 H_{16}(y) \\
-1116 H_{22}(y) \\
+ 20 y^2 \left[ H_{22}(y) - 6 H_{28}(y) + 12 H_{34}(y) - 8 H_{40}(y) \right] \end{array} \right)$$

$$-15 y^4 \left[ H_{28}(y) - 8 H_{34}(y) + 24 H_{40}(y) - 32 H_{46}(y) \right] + \cdots \quad (13.1)$$

$$B_{II}^{*(tr)} \text{ (quad)} = -(7/245760 \pi^4) y^4 \left[ \frac{95}{2} H_{14}(y) \right]$$

$$- y^2 \left[ 506 H_{26}(y) - 145 H_{20}(y) \right] + \cdots \quad (13.2)$$

$$B_{II}^{*(tr)} \text{ (shape)} = -(3/1600 \pi^4) y^4 \left[ 171 H_{28}(y) \right]$$

$$+ y^2 \left[ 113 H_{34}(y) - 382 H_{40}(y) + \cdots \right] \quad \cdots \quad (13.3)$$

The contribution to the second virial coefficient due to symmetry effect $f_{s1}$,

$$B_{0}^{*} (T^*) = -(3/256) \left[ y^3 / (\pi^5) \right] \quad (14)$$
III. RESULTS AND DISCUSSION

For the analysis of the second virial coefficient data of $D_2$, we have used the following equation,

$$B^*(T^*) = B_{c1}^*(T^*) + \left( \Lambda^2 B^*_I(\text{tr})(T^*) + \delta^2 B^*_I(\text{rot})(T^*) \right)$$

$$+ \left( \Lambda_4^4 B^*_I(\text{tr})(T^*) - \Lambda^2 B^*_O(\text{T}) \right) ... \ (15)$$

The evaluation of the right-hand side of Eqn. (15) requires the knowledge of the parameters $\epsilon, \sigma, \Lambda^\pi, \delta^\pi, \bar{\epsilon}, \kappa, \varphi$ and $D$. Instead of calculating $B(T)$ from Eqn. (15) with the known values of all the parameters, we have used the experimental data of second virial coefficient to determine the molecular quadrupole moment and shape factor of $D_2$ molecule. The method adopted for this is to attribute to the noncentral forces the entire difference between the measured values of the second virial coefficient and the values calculated from the central force parameters reproducing viscosity data.\(^5,6\)

For central force parameters $\epsilon, \sigma$ and $\Lambda^\pi$, we have used the values recently determined by Diller and Mason\(^8\) from the viscosity data of Coreman et al\(^9\). The values are,

$$\frac{\epsilon}{k} = 35.0 \quad \sigma = 2.976 \quad \Lambda^\pi = 1.238. \ ... \ (16)$$

The values of the other parameters which have been used in the present calculation are\(^10\),

$$\bar{\epsilon} = 0.7954 \quad \varphi = 0.1153 \quad \text{and} \delta^\pi = 9.9358 \ ... \ (17)$$
The parameters $D$ and $\Theta$, which give the best fit with the experimental $B(T)$ data, are,

$$D = 0.22 \quad \text{and} \quad \Theta = 0.84 \times 10^{-26} \text{ esu.}$$

In Table I the values of the different terms of Eqn. (15) are given for several values of $\gamma$, and in Table II the calculated values of the second virial coefficients are compared with the values (interpolated) obtained from the experimental data of Michels, de Graaf, and Ten Seldam\textsuperscript{11}. The agreement between calculated and experimental values is satisfactory.

The values of the shape factor $D$ obtained from different methods are compared in Table III. The theoretical values quoted in the table are for $H_2$. We, however, believe that the values of the parameters $D$ and $\Theta$ are almost same for $H_2$ and $D_2$. The agreement between the values of $D$ obtained in this section and calculated by de Boer\textsuperscript{12} and Roberts\textsuperscript{13} for $H_2$ is excellent.

The value of the quadrupole moment obtained in this section is about 30% higher than the value obtained by Kolos and Wolniewicz\textsuperscript{14} from theoretical calculation. It has in general been found that the magnitude of the quadrupole moments determined from viscosity and second virial coefficient data tend to be high\textsuperscript{15}. This may be due to the inadequacy of Lennard–Jones (12-6) potential to describe the spherically symmetric part of the potential. The assumption that the contribution of the noncentral part of the potential to the transport coefficients is negligible and that the contribution to the second virial...
coefficient is significant may not also be strictly valid. Recently, Smith, Munn, and Mason\textsuperscript{16} have calculated the effect of quadrupole-quadrupole interaction on the transport coefficients and found that the effect is small but not negligible. Since the transport coefficients are more sensitive to the repulsive part of the potential, the effect of the nonsphericity due to the shape of the molecule on transport coefficient should be evaluated. In conclusion, it appears fair to say that a reasonable estimate of the molecular quadrupole moment can be obtained from viscosity and second virial coefficient data and by representing the central forces with a more realistic potential function such as Kihara potential\textsuperscript{17} and by calculating the effect of nonsphericity due to the shape of the molecule on viscosity, the accuracy of this method may be further improved.
Table I. Values of the first and second quantum correction terms to the second virial coefficient of \( D_2 \)

<table>
<thead>
<tr>
<th>( y )</th>
<th>( B_{cl}^* )</th>
<th>( \Lambda^<em>2B_I^</em>(\text{tr}) )</th>
<th>( \delta^<em>2B_I^</em>(\text{rot}) )</th>
<th>( \Lambda^<em>4B_{II}^</em>(\text{tr}) )</th>
<th>( \Lambda^<em>8B_0^</em> )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.44927</td>
<td>0.01307</td>
<td>0.00159</td>
<td>-0.00012</td>
<td>-0.00027</td>
</tr>
<tr>
<td>0.7</td>
<td>0.39401</td>
<td>0.01996</td>
<td>0.00318</td>
<td>-0.00035</td>
<td>-0.00044</td>
</tr>
<tr>
<td>0.8</td>
<td>0.31134</td>
<td>0.02884</td>
<td>0.00531</td>
<td>-0.00070</td>
<td>-0.00065</td>
</tr>
<tr>
<td>0.9</td>
<td>0.19939</td>
<td>0.04045</td>
<td>0.00861</td>
<td>-0.00133</td>
<td>-0.00093</td>
</tr>
<tr>
<td>1.0</td>
<td>0.07020</td>
<td>0.05495</td>
<td>0.01340</td>
<td>-0.00235</td>
<td>-0.00127</td>
</tr>
<tr>
<td>1.1</td>
<td>-0.08839</td>
<td>0.07520</td>
<td>0.01999</td>
<td>-0.00445</td>
<td>-0.00169</td>
</tr>
<tr>
<td>1.2</td>
<td>-0.26572</td>
<td>0.10084</td>
<td>0.02867</td>
<td>-0.00833</td>
<td>-0.00220</td>
</tr>
</tbody>
</table>
Table II. Comparison of calculated and experimental second virial coefficient of D₂.

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>B (T) (cm³/mol)</th>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>388.9</td>
<td>15.41</td>
<td>15.26</td>
<td></td>
</tr>
<tr>
<td>386.7</td>
<td>13.80</td>
<td>13.60</td>
<td></td>
</tr>
<tr>
<td>218.8</td>
<td>11.44</td>
<td>11.32</td>
<td></td>
</tr>
<tr>
<td>172.8</td>
<td>8.21</td>
<td>8.34</td>
<td></td>
</tr>
<tr>
<td>140.0</td>
<td>4.49</td>
<td>4.64</td>
<td></td>
</tr>
<tr>
<td>97.2</td>
<td>-4.88</td>
<td>-4.90</td>
<td></td>
</tr>
</tbody>
</table>

Table III. Values of shape factor D obtained from different methods.

<table>
<thead>
<tr>
<th>Method of calculation</th>
<th>Shape factor D</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>From viscosity and { second virial data }</td>
<td>0.22</td>
<td>This work</td>
</tr>
<tr>
<td>Theoretical</td>
<td>0.19</td>
<td>Roberts¹³</td>
</tr>
</tbody>
</table>
REFERENCES


Chapter 2.

Section 3: Molecular multipole moments determined from Viscosity and second virial coefficients.
I. INTRODUCTION

The long-range orientation-dependent forces between two polyatomic molecules are explained in terms of permanent and induced electric moments of the isolated molecules\(^1\). The transport coefficients of dilute gases are much less sensitive to these forces than the second virial coefficients\(^2\)\(^3\). This provides a convenient basis for the determination of the multipole moments of molecules from the measurements of viscosity and second virial coefficients\(^4\)\(^5\). The procedure is to attribute to the higher multipoles the entire difference between the measured values of the second virial coefficients and values calculated from central force parameters reproducing the viscosity data.

The method of determining the molecular multipole moments from the viscosity and second virial data is an indirect one as it requires assumptions to be made about the intermolecular forces before multipole moments can be computed. The magnitude of the moments determined from this method is in general higher\(^6\) than those determined from the direct methods such as induced birefringence\(^7\) and molecular beam resonance\(^8\). This may be due to the inadequacy of the Lennard - Jones (12-6) potential model, which has been used in almost all work to date, to describe the central force of the interaction potential.
The Kihara potential model which is written as\textsuperscript{9},

\[ U(R) = 4\epsilon \left\{ \left[ (\sigma - 2a)/(R - 2a) \right]^{12} - \left[ (\sigma - 2a)/(R - 2a) \right]^6 \right\}, \]  \hspace{1cm} \cdots \hspace{1cm} (1)

where \( a \) is the core radius, \( \sigma \) is the value of \( R \) for which \( U(R) = 0 \), and \( \epsilon \) is the maximum energy of attraction, has been found more realistic\textsuperscript{9-11} in representing the central forces than the Lennard–Jones and other commonly used models. We have, therefore, thought it desirable to calculate the molecular multipole moments from the viscosity and second virial coefficients data using the Kihara model to represent the central forces. In this section we have calculated the quadrupole moment of \( \text{CO}_2 \) and octopole moment of \( \text{CH}_4 \) which are, respectively, the first nonvanishing electric poles of the molecules.

II. THE PAIR POTENTIAL FUNCTION AND THE SECOND VIRIAL COEFFICIENT

The total potential energy of interaction between two polyatomic molecules can be written as\textsuperscript{4,12},

\[ U = U^0 + U^1 \] \hspace{1cm} \cdots \hspace{1cm} (2)

where \( U^0 \) is the Kihara potential representing the central forces and \( U^1 \) is the sum of all orientation-dependent terms.
For CO₂, \( U^1 \) is given as,

\[
U^1 = U^1(\text{quadrupole}) + U^1(\text{quadrupole-induced dipole})
\]

\[
+ U^1(\text{anisotropy}) + U^1(\text{shape}) \ldots \ldots (3)
\]

where the different terms of the expression (3) have been given in section 2 of this chapter.

It is convenient to write the expressions for the second virial coefficient in terms of the reduced quantities which are defined as,

\[
a^* = \frac{2a}{(\sigma - 2a)} , \quad \alpha^* = \frac{\alpha}{(\sigma - 2a)^3},
\]

\[
\beta^* = \frac{\beta}{(\sigma - 2a)^5} , \quad y = 2(\varepsilon / kT)^{1/2},
\]

\[
B^* = \frac{B}{b_0} , \quad b_0 = \frac{2}{3} \pi N(\sigma - 2a)^3. \ldots (4)
\]

In terms of these reduced quantities the second virial coefficient \( B(T) \) for the potential model of Eqn. (2) can be written as,

\[
B^* = B^*(\text{Kihara}) + B^*(\text{quad}) + B^*(\text{anis}) + B^*(\text{quad-ind. dipole})
\]

\[
+ B^*(\text{shape}) + B^*(\text{quad X anis}) + B^*(\text{quad X shape})
\]

\[
+ B^*(\text{anis X shape}) \ldots \ldots (5)
\]

where the non-spherical contributions are derived by considering them as a perturbation to the central Kihara potential and taking only one of them at a time. Such derivation has been
shown in the Appendix, for \( B^{*}(\text{quad}) \) as an example.

\[
B^{*}(\text{Kihara}) = y^{-2} \left[ H_{12}(y) - \frac{1}{2} H_{6}(y) \right] + 3a^{*} y^{-2} \left[ H_{18}(y) - \frac{1}{2} H_{7}(y) \right] + 3a^{*2} y^{-2} \left[ H_{14}(y) - \frac{1}{2} H_{8}(y) \right] + a^{*3},
\]

(5.1)

\[
B^{*}(\text{quad}) = -\frac{7}{220} \sum_{\lambda=0}^{\infty} \frac{(-1)^{\lambda}}{(7+\lambda)!} \frac{(7+\lambda)!}{7! \lambda!} a^{*\lambda} H_{\lambda+10}(y) + \cdots, \quad \cdots
\]

(5.2)

\[
B^{*}(\text{anis}) = -\frac{1}{20} \kappa^{2} \left[ 1 + \frac{19}{20} \kappa^{2} \right] \left[ H_{12}(y) + a^{*2} H_{14}(y) + 2a^{*} H_{13}(y) \right] + \cdots, \quad \cdots
\]

(5.3)

\[
B^{*}(\text{quad - ind. dipole}) = -\frac{3}{16} \sum_{\lambda=0}^{\infty} \frac{(-1)^{\lambda}}{5! \lambda!} a^{*\lambda} H_{\lambda+8}(y) + \cdots, \quad \cdots
\]

(5.4)

\[
B^{*}(\text{shape}) = -\frac{1}{5} \kappa^{2} \left[ H_{24}(y) + a^{*2} H_{26}(y) + 2a^{*} H_{25}(y) \right] + \cdots, \quad \cdots
\]

(5.5)

\[
B^{*}(\text{anis \times shape}) = \frac{1}{5} \kappa D \left[ H_{18}(y) + a^{*2} H_{20}(y) + 2a^{*} H_{19}(y) \right] + \cdots, \quad \cdots
\]

(5.6)

\[
B^{*}(\text{quad \times anis}) = \frac{9}{100} \kappa^{2} \sum_{\lambda=0}^{\infty} \frac{(-1)^{\lambda}}{2! \lambda!} a^{*\lambda} H_{\lambda+11}(y) + \cdots, \quad \cdots
\]

(5.7)
\begin{align*}
B^\ast (\text{quad X shape}) &= \frac{1}{56} y^2 \delta_4^4 D \sum_{\lambda=0}^{\infty} (-1)^\lambda \frac{(7+\lambda)!}{7! \lambda!} a^\lambda H_{\lambda+22}(y) \\
&+ \frac{3}{50} y^2 \delta_2 \delta_2 D^2 \sum_{\lambda=0}^{\infty} (-1)^\lambda \frac{(2+\lambda)!}{2! \lambda!} a^\lambda H_{\lambda+23}(y) + \ldots, \quad (5.8)
\end{align*}

The $H_n(y)$ functions have been defined and tabulated by Buckingham and Pople\textsuperscript{13}.

The noncentral part of the potential energy of interaction between two CH\textsubscript{4} molecules is mainly due to:

(i) octopole-octopole interaction and

(ii) octopole-induced-dipole interaction\textsuperscript{14},

the other terms of Eqn. (3) being negligible. The contributions of these forces to the second virial coefficient have been derived by Kielich\textsuperscript{14} and the expressions appropriate to the Kihara model can be written as,

\begin{align*}
B^\ast &= B^\ast (\text{Kihara}) + B^\ast (\text{oct}) + B^\ast (\text{oct-ind. dipole}), \quad \ldots (6)
\end{align*}

where,

\begin{align*}
B^\ast (\text{oct}) &= -\frac{297}{360} \Omega_4^4 \sum_{\lambda=0}^{\infty} (-1)^\lambda \frac{(11+\lambda)!}{11! \lambda!} a^\lambda H_{\lambda+41}(y) + \ldots, \quad \ldots (6.1)
\end{align*}

\begin{align*}
B^\ast (\text{oct-ind. dipole}) &= -\frac{3}{5} y^{-2} \alpha \Omega^2 \sum_{\lambda=0}^{\infty} (-1)^\lambda \frac{(7+\lambda)!}{7! \lambda!} a^\lambda H_{\lambda+10}(y) + \ldots, \quad \ldots (6.2)
\end{align*}
Here,

\[ \Omega \times^2 = \Omega^2 / \varepsilon (\sigma - 2a)^7 \]

For molecules having tetrahedral symmetry the octopole moment is defined as,

\[ \Omega = \frac{5}{2} \sum \frac{e_1 x_1 y_1 z_1}{i} \quad \ldots \quad (7) \]

III. CALCULATION OF THE MOLECULAR MULTIPOLE MOMENTS

By taking known values of the parameters \( \varepsilon, \sigma, 2a, \alpha \) and \( \kappa \) the equations (5) and (6) can be solved for \( \Theta \) and \( \Omega \). The magnitude of the moments determined from Eqns. (5) and (6) is sensitive to the values of the central force parameters \( \varepsilon, \sigma \) and \( 2a \). Therefore, we have redetermined these from the temperature dependence of dilute gas viscosity data using the more reliable method described by Hanley. The best set of the force parameters thus found have been given in Table I.

Table I. Force parameters from viscosity data.

<table>
<thead>
<tr>
<th>Gas</th>
<th>( \sigma ) (Å)</th>
<th>( \varepsilon / K ) (°K)</th>
<th>a*</th>
<th>Ref. for data</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>3.640</td>
<td>321.2</td>
<td>0.43</td>
<td>15-19</td>
</tr>
<tr>
<td>CH₄</td>
<td>3.622</td>
<td>184.5</td>
<td>0.14</td>
<td>20-23</td>
</tr>
</tbody>
</table>
Equation (5) has been solved for two unknown parameters and \( D \) using the second virial data at several temperatures. Eqn. (6) involves only one unknown parameter \( \Omega \) and its value can be obtained for each temperature corresponding to the observed value of the second virial coefficient. The mean value of the moments thus obtained has been given in Table II along with the values of the other parameters used in the calculation. The second virial coefficients calculated with these mean values of moments have been given in Table III for \( \text{CO}_2 \) and \( \text{CH}_4 \) together with the experimental values\(^{24-29} \). It can be seen that good agreement was obtained over the entire temperature range of our interest.

Table II. Molecular multipole moment and other parameters for virial coefficient calculation.

<table>
<thead>
<tr>
<th>Gas</th>
<th>( \hat{\beta} X \times 10^{26} ) esu. cm(^2)</th>
<th>( \Lambda X \times 10^{24} ) esu. cm(^3)</th>
<th>( \alpha ) (( 10^3 ))</th>
<th>( \kappa )</th>
<th>( D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 )</td>
<td>4.33</td>
<td>...</td>
<td>2.65</td>
<td>0.2642</td>
<td>0.20</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>0.0</td>
<td>3.52</td>
<td>2.60</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>
Table III. Comparison of calculated and experimental second virial coefficient of CO$_2$ and CH$_4$.

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>Exptl$^{24-27}$</th>
<th>Calc</th>
<th>T(°K)</th>
<th>Exptl$^{28,29}$</th>
<th>Calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>570.9</td>
<td>13.8</td>
<td>15.8</td>
<td>609.9</td>
<td>-8.74</td>
<td>-8.05</td>
</tr>
<tr>
<td>449.5</td>
<td>38.5</td>
<td>41.9</td>
<td>376.5</td>
<td>20.30</td>
<td>20.69</td>
</tr>
<tr>
<td>396.5</td>
<td>59.3</td>
<td>59.6</td>
<td>328.0</td>
<td>32.86</td>
<td>33.02</td>
</tr>
<tr>
<td>321.1</td>
<td>102.2</td>
<td>101.6</td>
<td>255.4</td>
<td>62.70</td>
<td>62.67</td>
</tr>
<tr>
<td>265.4</td>
<td>156.6</td>
<td>154.9</td>
<td>184.5</td>
<td>124.70</td>
<td>122.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>139.5</td>
<td>210.25</td>
<td>210.81</td>
</tr>
</tbody>
</table>

IV. DISCUSSION

A summary of values for the quadrupole moment of CO$_2$ has been reported previously by Stogryn and Stogryn$^6$. The most reliable experimental value of $\overline{\text{C}} \text{O}_2$ reported earlier is that obtained from the studies on induced birefringence$^{30}$. The value $\overline{\text{C}} \text{O}_2$ = $-4.1 \times 10^{-26}$ esu. cm$^2$ of Buckingham and Disch$^{30}$ has recently been revised by Stogryn and Stogryn using the recent value of $\alpha_{zz} - \alpha_{xx}$$^{31}$. The value of $\overline{\text{C}} \text{O}_2$ = $-4.3 \times 10^{-26}$ esu. cm$^2$ thus obtained, is in excellent agreement with that obtained by us.
The value of $\theta_{CO_2}$ determined in this work appears only slightly different from the values obtained by Orcutt and Spurling and Mason, using the Lennard-Jones (12-6) potential to represent the central forces. Orcutt in his analysis of the second virial coefficient has used only a few of the terms of Eqn. (5), while Spurling and Mason have taken into account the effect of quadrupole-quadrupole interaction on viscosity.

Regarding the shape parameter $D$ which also has been calculated, little is known theoretically except that in order to keep the $\epsilon \left[ (\sigma - 2a)/(R - 2a) \right]^{12}$ term in the overall potential positive, the value of $D$ must lie within -0.25 to +0.5. A negative $D$ corresponds to a plate-like molecule and a positive $D$ to a rod-like one. CO$_2$ can be treated as a rod-like molecule. If we compare the ratio of the length $l$ to width $d$ as calculated from the known molecular geometries and the Van der Waals radii of the peripheral atoms, we find that $l/d$ for H$_2$ and CO$_2$ is almost the same $^{32}$ ($l/d = 2.6$). In the section 2, by similar analysis as presented here, we have obtained $D$ for deuterium molecule as 0.22 which is in very good agreement with the theoretically calculated values of de Boer $^{33}$ and Roberts $^{34}$. On the basis of the above argument, we expect that $D$ of CO$_2$ should be near 0.22. Our value $D_{CO_2} = 0.2$ is in good agreement with this expectation. Spurling and Mason have obtained $D_{CO_2} = -0.1$ which seems to be unrealistic.
Spurling et al. have summarized the previously reported values of the octopole moment of methane. Our value is very near to that obtained by themselves from the second virial data using the spherical shell central potential and is considerably smaller than those obtained by using the Lennard-Jones (12-6) potential. The higher value of the molecular multipole moments obtained by using the Lennard-Jones (12-6) potential to represent the central forces is probably due to the fact that in selecting the parameters of the Lennard-Jones (12-6) potential, the dispersion forces are underestimated leading to a corresponding overestimation of the molecular multipole moments.

The quantum mechanical estimate of $\Omega_{\text{CH}_4}$ is still more difficult. The spread in the various calculated values obtained so far is unfortunately rather large. In view of these uncertainties, we recommend the following value,

$$\Omega_{\text{CH}_4} = \pm (3.5 \pm 0.2) \times 10^{-34} \text{ esu. cm}^3$$

as obtained by us and Spurling et al.

In course of the present calculations we have found that a large number of sets of central force parameters can be obtained which can reproduce the viscosity data with almost equal consistency. These different sets of force parameters yield quite different values of the multipole moments when they are used in conjunction with the second virial data of narrow temperature range. Only one or very few sets of central force parameters give consistent
values of the multipole moments when second virial data extending over a wide temperature range are used. Therefore, extreme care should be taken in selecting the central force parameters.

In conclusion it may be said that reasonable values of the molecular multipole moments can be obtained from the analysis of the second virial and viscosity data. This method, owing to its simplicity, is specially useful for molecules for which accurate wave mechanical calculations are extremely difficult.
To derive the contribution of quadrupole - quadrupole interaction to $B(T)$, we shall write,

$$U(R, \theta, \psi) = 4 \left[ \left( \frac{\Omega - 2a}{R - 2a} \right)^{12} - \left( \frac{\Omega - 2a}{R - 2a} \right)^6 \right] + \frac{3}{4} \frac{\Theta^2}{R^5} F(\Theta_1, \Theta_2, \psi)$$

where $F(\Theta_1, \Theta_2, \psi)$ represents the angle dependent part.

In the reduced form,

$$U^* = 4 \left[ (R^*-a^*)^{-12} - (R^*-a^*)^{-6} + \frac{3}{16} \frac{\Theta^*^2}{R^*5} \right] F(\Theta_1, \Theta_2, \psi)$$

Putting $R^*-a^* = x$,

$$U^* = 4 \left[ x^{-12} - x^{-6} + \frac{3}{16} \frac{\Theta^*^2}{(x + a^*)^{-5}} \right] F(\Theta_1, \Theta_2, \psi)$$

Now,

$$B(T) = \frac{N}{4} \int_0^\infty \int_\Omega \left( 1 - e^{-U/KT} \right) R^2 dR d\Omega$$

or

$$B^*(T^*) = \frac{3}{8} \int_0^\infty \int_\Omega \left( 1 - e^{-U^*/T^*} \right) R^* dR^* d\Omega$$

$$= \frac{3}{8} \int_0^\infty \int_\Omega 1 - e^{-U^*_{\text{Kihara}}/T^*} \cdot \sum_{n=0}^\infty \frac{1}{n!} (-U^*_{\text{quad}}/T^*)^n R^* dR^* d\Omega$$

$$= B^* \left( \text{Kihara} \right) + B^* \left( \text{quad} \right)$$
where, $B^\ast (\text{quad}) = - \frac{3}{8} e^{-y^2(x^{12}_{-}x^{-6})}$.

$$
\sum_{n=1}^{\infty} \int \int_{\Omega} \left[ \frac{3}{16} \cdot y^2 \cdot \mathbf{F}(\theta_1, \theta_2, \psi) \right]^n (x+a^*)^{-5n+2} \, dx \, d\Omega.
$$

In this integration, limit of $x$ is from $-a^*$ to $\infty$. But since for the potential model used, $U^*$ is infinity for $B^* \leq a^*$, i.e. the integrand vanishes in the region $x = -a^* \rightarrow 0$, we can put the limit for $x$ to be from $0$ to $\infty$. Then using the binomial expansion,

$$(x+a^*)^{-5n+2} = \sum_{\lambda=0}^{\infty} \left[ \frac{(-1)^{\lambda}}{(-5n+2-\lambda)!} \right] (a^*)^\lambda$$

$B^\ast (\text{quad}) = - \frac{3}{8} \sum_{n=1}^{\infty} \frac{1}{n!} (\frac{3}{16} \cdot y^2) n \int \int_{\Omega} (-1)^{\lambda} \left[ \frac{(5n+\lambda-3)!}{(5n-3)!} \right] (x+a^*)^{-5n+2} \, dx \, d\Omega$

According to Buckingham and Pople,$^{13}$

$$
\int \ldots \ldots \, dx = \frac{1}{12} y^{-4} H_{5n+\lambda}(\gamma).
$$

$$
\int \ldots \ldots \, d\Omega \text{ vanishes for } \ n = 1
$$

$$
= \frac{224}{45} \pi \text{ for } \ n = 2.
$$
Hence, the first nonvanishing term of $B^\ast(\text{quad})$ appears for $n = 2$ and is given by,

\[
\frac{3}{8\pi^2} \cdot \frac{1}{2} \cdot \frac{9}{256} \cdot 4^4 \int y^4 \sum_{\lambda=0}^{\infty} (-1)^\lambda \frac{(7+\lambda)!}{7!\lambda!} a^\lambda
\]

\[
= \frac{1}{12} \cdot \frac{y^4}{H_{\lambda+10}(y)} \cdot \frac{224}{45} \cdot \frac{8\pi}{320} \cdot 4^4 \sum_{\lambda=0}^{\infty} (-1)^\lambda \frac{(7+\lambda)!}{7!\lambda!} a^\lambda H_{\lambda+10}(y)
\]
REFERENCES

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