Chapter 7

THEORETICAL

Contributions of non-spherical interaction on the pressure second virial coefficient, and the calculation of shape factor and quadrupole moment for C₂H₆ and H₂S gases
CONTRIBUTIONS OF NON-SPHERICAL INTERACTIONS TO THE SECOND VIRIAL COEFFICIENT OF ETHANE AND HYDROGEN SULPHIDE GASES

Abstract

Attempt has been made to represent the second pressure virial coefficient data for ethane and hydrogen sulphide gases by introducing different non-spherical terms in the interaction potential. The spherical part of the potential has been represented by Lennard-Jones (12 : 6) potential. The force parameters for spherical interactions have been obtained from the experimental viscosity data. The second virial coefficient data for C₂H₆ can be represented satisfactorily and the situation is worse for H₂S which has a sizeable dipole moment. The shape parameter and values of quadrupole moments have been also estimated for these substances.

Introduction

Our knowledge of the intermolecular forces for polyatomic gases is inadequate, though extensive work has been done during the last decade. This is primarily because of the presence of various long-range angle dependent terms in the intermolecular potential function for such gases. These non-spherical terms are likely to have an important effect on the thermodynamic properties.

The second virial coefficient analysis is one of the best probes for the investigation of the forces between interacting pair of molecules. It is generally believed that the virial coefficients
are much more sensitive to the non-spherical interactions than the transport properties. The method of analysis of the second virial coefficient \( B(T) \) is rather simple if we consider the gas consists of atoms or molecules as spheres interacting centrally. But situation becomes complicated when the molecules have complex electrical structures. Then the concept of spherical approximation fails, since now their interaction potential energy depends not only on their distance but also on their mutual orientations. But a numerical solution can be obtained if we can separate the part dependent on the angular variables from the total potential energy and consider it as perturbation to the spherical potential. The angular dependence of the potential energy arises primarily from permanent and induced electric multipoles in the molecule. Investigation of \( B(T) \) allows us to determine not only the parameters of the spherical potential but also yields information concerning electric multipole moments of the molecules.

The earliest calculations of \( B(T) \) for dipolar and quadrupolar molecules, taking into account a non-central potential energy, are due to Keesom\(^1\), Debye\(^2\) and Falkenhagen\(^3\). They have been modified for higher accuracy by Stockmayer\(^4\), Rowlinson\(^5\), Pople\(^6,7\), Castle et al\(^8\), Lawley and Smith\(^9\), Kielich\(^10\), McQuarrie and Levine\(^11\), Spurling and Mason\(^12\), Singh et al\(^13,14\), Kong\(^15,16\) and others\(^17-19\).

The discussions of the previous paragraphs allow us to calculate the spherical part of interactions for these gases from the viscosity data as it is not influenced by non-spherical
interactions. Moreover it also permits us to estimate the quadrupole moments and shape factors of a number of molecules. Calculations for the pressure and dielectric second virial coefficients of a number of polar gases have also been performed by this method. It was previously observed that by including only the spherically symmetric interactions the transport and equilibrium properties of the polyatomic gases could not be represented by a single set of parameters for the intermolecular potential. The inclusion of the non-spherical interactions for calculating the virial coefficients has solved this problem for a number of cases. In view of the success of the method it is useful to apply this to as many gases as possible for which the relevant data exist in the literature.

With this end in view we have calculated the quadrupole moments and shape parameter for ethane and hydrogen sulphide gases. The second pressure virial coefficients for these gases have recently been measured. The first molecule has a sizeable quadrupole moment and the latter a dipole and most probably a quadrupole moment which has not yet been measured experimentally.

**Formula and Results**

(i) **Ethane**:

The intermolecular potential used for representing the second pressure virial coefficient of ethane may be written as,

\[
\Phi^{(2)} = \Phi^{(\text{Sph})} + \Phi^{(\text{quad})} + \Phi^{(\text{anis})} + \Phi^{(\text{quad - ind dipole})} + \Phi^{(\text{shape})} \tag{1}
\]
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where Φ(sphe), Φ(quad), Φ(anis), Φ(quad-ind. dipole) and Φ(Shape) are respectively the contributions of the spherical part, the quadrupole moment, anisotropy in polarizability, quadrupole-induced dipole interaction and shape factor, to the total intermolecular potential. The spherical part of the interaction is expressed by the Lennard - Jones (12:6) potential which may be written as

\[ \Phi(\text{sphe}) = 4\epsilon_0 \left( \frac{\sigma_0}{\rho} \right)^{12} - \left( \frac{\sigma_0}{\rho} \right)^6 \]  

The other non-spherical terms can be written as

\[ \Phi(\text{quad}) = \frac{3}{4} \left( \frac{\sigma_0}{\rho} \right)^4 \left[ 1 - 5 \cos^2 \theta_1 - 5 \cos^2 \theta_2 - 15 \cos^2 \theta_1 \cos^2 \theta_2 \right. 
+ 2 \left( \sin \theta_1 \sin \theta_2 \cos \phi - 4 \cos \theta_1 \cos \theta_2 \right)^2 \]  

\[ \Phi(\text{anis}) = \frac{4}{5} \epsilon_0 \left( \frac{\sigma_0}{\rho} \right)^6 \left[ \kappa - \frac{3}{2} \kappa^2 \left( \cos^2 \theta_1 + \cos^2 \theta_2 \right) \right. 
\left. - \frac{3}{2} \kappa^2 \left( \sin \theta_1 \sin \theta_2 \cos \phi - 2 \cos \theta_1 \cos \theta_2 \right)^2 \right] \]  

\[ \Phi(\text{quad-ind. dipole}) = \frac{9}{8} \left( \frac{\sigma_0}{\rho} \right)^2 \left( \sin^4 \theta_1 + \sin^4 \theta_2 + 4 \cos^4 \theta_1 + 4 \cos^4 \theta_2 \right) \]  

\[ \Phi(\text{shape}) = 4D\epsilon_0 \left( \frac{\sigma_0}{\rho} \right)^{10} \left( 3 \cos^2 \theta_1 + 3 \cos^2 \theta_2 - 2 \right) \]  

where \( \epsilon_0 \) is the depth of the potential and \( \sigma_0 \) is the value of intermolecular distance for which \( \Phi(\rho) = 0 \). \( \theta_1, \theta_2, \phi \) 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 $\Theta$ is defined by\textsuperscript{12},

$$\Theta = \sum \varepsilon_i (Z_i^2 - \chi_i^2)$$

and $\bar{\alpha} = \frac{1}{3} (\alpha_{||} + 2\alpha_{\perp})$ and $\kappa = (\alpha_{||} + \alpha_{\perp})/3\bar{\alpha}$ are the mean polarizability and the anisotropy of the polarizability respectively. $\alpha_{||}$ being the polarizability along the axis of symmetry and $\alpha_{\perp}$ that perpendicular to it.

Let us define the following reduced quantities\textsuperscript{12}

$$\alpha^* = \bar{\alpha}/\sigma_0^3 \quad ; \quad \Theta^* = \Theta/(\varepsilon_0\sigma_0^5)^{1/2} \quad ; \quad \gamma = 2 (\varepsilon_0/kT)^{1/2}$$

$$B^* = B(T)/b_o \quad ; \quad b_o = \left( \frac{2}{3} \right) \Pi_N \sigma_0^3 \quad \ldots \quad (3)$$

By using the formalism of Buckingham and Pople\textsuperscript{7}, the reduced second virial coefficients may be written as\textsuperscript{12},

$$B^*(T) = B^*(12-6) + B^*(\text{quad}) + B^*(\text{anis}) + B^*(\text{quad-anis}) + B^*(\text{shape}) + B^*(\text{quad-shape}) + B^*(\text{anis-shape}) + \ldots \quad \ldots (4)$$

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 expression (4) are given by,

$$B^*(12-6) = \gamma^{-2} \left[ H_{12}(y) - \frac{1}{2} H_6(y) \right] \quad \ldots \quad \ldots (5a)$$

$$B^*(\text{quad}) = -\frac{7}{320} \Theta^* \left[ \frac{H_{10}(y)}{3} - \frac{18}{343} (y\Theta^*)^2 H_{15}(y) + \ldots \right] \quad \ldots (5b)$$

$$B^*(\text{anis}) = -\frac{1}{20} \kappa^2 \left( 1 + \frac{19}{10} \kappa^2 \right) H_{12}(y) + \ldots \quad \ldots (5c)$$
The function \( H_n(y) \) is defined by,

\[
H_n(y) = 12 y \int_0^\infty R^{-n} \exp \left( -\frac{U_0}{RT} \right) R^2 dR
\]

where \( U_0 \) is the Lennard-Jones (12:6) potential given by eqn. (2a). This function has been tabulated by Buckingham and Pople.\(^7\)

The parameters \( \sigma_0 \) and \( \epsilon_0/\kappa \) for ethane were obtained from the available experimental viscosity data\(^{21-23}\) and are shown in Table 1 together with the other relevant data used for the calculation of different \( B^* \) values. The quadrupole moment was taken to be \( \Theta = -0.65 \times 10^{-26} \) esu cm\(^2\) as recommended by Stogryn and Stogryn.\(^{24}\)

The shape factor was determined from the experimental \( B(T) \) data of Khoury and Robinson\(^{20}\) at different temperatures and the average value thus obtained was 0.14. The individual contributions of the different \( B^* \) terms are shown in Table 2, together with the experimental values of \( B^*(T) \).
(ii) Hydrogen Sulphide:

For polar molecule like H$_2$S the situation is slightly different from that of the non-polar gases as viscosity is also known to be significantly affected by the angle-dependent dipole-dipole interaction term$^{25}$. The other non-spherical terms which are of importance are not likely to affect the viscosity of polar gases. The interaction potential in this case may be written as$^{18}$,

\[ \Phi(r) = \Phi(12-6-3) + \Phi(\text{di.-quad}) + \Phi(\text{di.-ind.dip}) + \Phi(\text{quad}) \]
\[ + \Phi(\text{quad.-ind.dip}) + \Phi(\text{anis}) + \Phi(\text{ind.dip.-ind.quad}) \]
\[ + \Phi(\text{shape}) \ldots \ldots \ldots \ldots \ldots \ldots (7) \]

where $\Phi(12-6-3)$ is the Stockmayer or (12-6-3) potential which may be written as$^{26}$

\[ \Phi(r) = 4\varepsilon \left[ \left( \frac{\sigma_1}{r} \right)^{12} - \left( \frac{\sigma_1}{r} \right)^6 \right] - \left( \frac{\mu_1 \mu_2}{r^3} \right) \rho \ldots \ldots \ldots \ldots \ldots \ldots (8) \]

where, $\rho = 2 \cos \theta_1 \cos \theta_2 \sin \theta_1 \sin \theta_2 \cos \phi \ldots \ldots \ldots \ldots \ldots \ldots \ldots (8a)$

The terms on the right hand side of eqn. (7) which are due to the dipole moment of the polar molecule are given by

\[ \Phi(\text{di.-quad}) = \frac{3}{2} \frac{\mu \Theta}{\gamma^4} \left[ \left\{ \cos \theta_1 \left( 3 \cos^2 \theta_2 - 1 \right) + 2 \sin \theta_1 \sin \theta_2 \cos \theta_1 \cos \phi \right\} \right. \]
\[ \left. + \left\{ \cos \theta_2 \left( 3 \cos^2 \theta_1 - 1 \right) + 2 \sin \theta_1 \sin \theta_2 \cos \theta_1 \cos \phi \right\} \right] \ldots \ldots (8a) \]

\[ \Phi(\text{di.-ind.dipole}) = -\frac{1}{2} \frac{\mu \alpha}{\gamma^6} \left[ (3 \cos^2 \theta_1 + 1) + (3 \cos^2 \theta_2 + 1) \right], \ldots \ldots (9b) \]

\[ \Phi(\text{ind.dip.-ind.quad}) = -\frac{12 \mu \Theta \alpha}{\gamma^7} \left( \cos^3 \theta_1 \right) \ldots \ldots \ldots \ldots \ldots \ldots (9c) \]
The other terms of eqn.(7) are represented by eqns. (2b-2e). Let us define another reduced quantity in addition to those already defined in eqn.(3),
\[ \mu^* = \mu / \left( \epsilon_0 \sigma_0^3 \right)^{1/2} \quad \ldots \quad \ldots \quad \ldots \quad (10) \]

Then the reduced second virial coefficient may be expressed as,
\[ B^*(T) = B^*(12-6-3) - B^*(\text{dipole-quad}) - B^*(\text{dipole-ind.dipole}) \]
\[ - B^*(\text{quad.}) - B^*(\text{quad-ind.dipole}) - B^*(\text{anis}) - B^*(\text{shape}) \]
\[ - B^*(\text{ind.dip-ind.quad}) \quad \ldots \quad \ldots \quad \ldots \quad (11) \]

The terms in eqn.(8) may be expressed as,
\[ B^*(12-6-3) = \sqrt{3} \left[ H_{12}(\gamma) - \frac{1}{2} H_6(\gamma) \right] - \sum_{n=1}^{\infty} \frac{p^{2n}}{n!} \left\{ \frac{\sqrt{3}^{n-1}}{2^{n+2} 3^{n-1}} \right\} H_{6n}(\gamma) \]
\[ B^*(\text{dipole-quad}) = \frac{1}{8} \left( \mu^* \alpha^* \right)^2 \left[ H_8(\gamma) + \frac{1}{3} (p_{yd}^2) H_{14}(\gamma) + \frac{1}{54} (p_{yd}^4) H_{20}(\gamma) + \ldots \right] \]
\[ + \frac{1}{24} \left( \mu^* \alpha \right)^4 \left[ H_{16}(\gamma) + \frac{1}{3} (p_{yd}^2) H_{22}(\gamma) + \ldots \right] \quad (12a) \]
\[ B^*(\text{dipole-ind.dipole}) = \frac{1}{16} \alpha^* \mu^* \gamma^2 \left[ H_6(\gamma) + \frac{1}{3} (p_{yd}^2) H_{12}(\gamma) + \frac{1}{54} (p_{yd}^4) H_{18}(\gamma) + \ldots \right] \]
\[ + \frac{11}{320} \left( \mu^* \alpha \right)^2 \left[ H_{12}(\gamma) + \frac{1}{3} (p_{yd}^2) H_{18}(\gamma) + \ldots \right] \quad \ldots \quad (12b) \]
\[ B^*(\text{quad}) = \frac{7}{320} \alpha^* \gamma \left[ H_{10}(\gamma) + \frac{1}{3} (p_{yd}^2) H_{16}(\gamma) + \frac{1}{54} (p_{yd}^4) H_{22}(\gamma) + \ldots \right] \]
\[ + \frac{9}{160} \left( \alpha^* \gamma \right)^2 \left[ H_{15}(\gamma) + \frac{1}{3} (p_{yd}^2) H_{21}(\gamma) + \ldots \right] \quad \ldots \quad (12c) \]
\[ B^*(\text{quad-ind.dipole}) = \frac{3}{16} \alpha^* \gamma^2 \left[ H_8(\gamma) + \frac{1}{3} (p_{yd}^2) H_{14}(\gamma) + \frac{1}{54} (p_{yd}^4) H_{20}(\gamma) + \ldots \right] \]
\[ + \frac{9}{256} \left( \alpha^* \gamma \right)^2 \left[ H_{16}(\gamma) + \frac{1}{3} (p_{yd}^2) H_{22}(\gamma) + \ldots \right] \quad \ldots \quad (12d) \]
The parameters $\sigma_o$ and $\varepsilon_o/k$ for H$_2$S as given in eqn.(8) were obtained from the experimental viscosity data$^{18}$ and are shown in Table 1. The dipole moment was taken to be 0.92 Debye as recommended by Stogryn and Stogryn$^{24}$. The values of the shape factor and quadrupole moment were estimated by fitting to the experimental B(T) data. These values were obtained as $D = -0.08; \theta = 2.24 \times 10^{-26}$ esu cm$^2$. The experimental and calculated values of $B^*(T)$ are shown in Table 3.

Discussion of Results

For ethane as shown in Table 1, the contributions of the non-spherical interaction terms is about 10% of the total second virial coefficient. The significant non-spherical contributions...
are from the shape factor and the cross-term involving anisotropy and shape factor. With one set of force parameters both the viscosity and second virial coefficient data can be represented by considering non-spherical interaction. The value of the shape parameter for \( C_6 \) obtained as 0.14 is reasonable\(^{12}\) and the sign is positive due to its rod-like shape. On the other hand from the force parameters obtained from the virial data by neglecting the non-spherical interactions one can represent the experimental viscosity data within 5-6% which is outside the experimental error.

For \( HgS \), the contributions of the non-spherical interactions apart from the dipole-dipole term to the second virial coefficient is about 20-25\%. The dipole-quadrupole and the dipole-induced dipole terms have the maximum contributions. The sign and magnitude of the shape factor obtained are reasonable\(^{12}\). The value of the quadrupole moment thus obtained cannot be compared with the data from any other source. The experimental second virial data cannot be represented very satisfactorily even by including the non-spherical interaction terms. This may very well be due to the approximation made in representing the dipole-dipole term in the calculation of the second virial coefficient. For example, a pre-averaged potential\(^{18}\) may be a better representation than the (12-6-3) potential used by us. The force parameters obtained by Khoury and Robinson\(^{20}\) from \( B(T) \) data completely fail to represent the experimental viscosity data. This shows the relative success obtained by using different non-spherical terms in the interaction potential for calculating second virial coefficient.
### Table 1

Values of the Molecular Parameters used for Ethane and Hydrogen Sulphide Gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>Potential Parameter</th>
<th>( \sigma ) in Å</th>
<th>( E/k ) in ( \text{eV} )</th>
<th>( \Gamma ) in ( \text{e.s.u.cm} )</th>
<th>( \Theta ) in ( \text{e.s.u.cm}^2 )</th>
<th>( D )</th>
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<tr>
<td>Ethane</td>
<td></td>
<td>4.428</td>
<td>223</td>
<td>0.1125</td>
<td>-0.65x10^26</td>
<td>.14</td>
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<tr>
<td>Hydrogen sulphide</td>
<td></td>
<td>3.578</td>
<td>310</td>
<td>0.0536</td>
<td>2.24x10^-26</td>
<td>.08</td>
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</table>
Table 2
Experimental and calculated second virial coefficient for ethane

<table>
<thead>
<tr>
<th>T°K (12-6)</th>
<th>B* (quad) x 10^-4</th>
<th>B* (anis) x 10^-4</th>
<th>B* (q-ind.d) x 10^-4</th>
<th>B* (qxanis) x 10^-4</th>
<th>B* (Shape)</th>
<th>B* (Cal)</th>
<th>B* (exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-1.5211</td>
<td>-0.4380</td>
<td>0.0154</td>
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<td>-0.0556</td>
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<tr>
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<td>0.0115</td>
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<td>-0.0456</td>
<td>-0.0405</td>
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### Table 3

**Experimental and calculated Second Virial Coefficients for Hydrogen Sulphide**

<table>
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<tr>
<th>$T_0$K</th>
<th>$B^*$</th>
<th>$B^*$</th>
<th>$B^*$</th>
<th>$B^*$</th>
<th>$B^*$</th>
<th>$B^*$</th>
<th>$B^*$</th>
<th>$B^*$</th>
<th>$B^*$</th>
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<tbody>
<tr>
<td></td>
<td>(12-6-3) (d-q)</td>
<td>(d-ind) (quad)</td>
<td>(q-ind) (ans)</td>
<td>(shape) (ind-ind)(Cal)</td>
<td>(expt)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>0.0000</td>
<td>-1.3604</td>
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REFERENCES

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