

Contributions of non-spherical interactions to the second virial coefficient of ethane and hydrogen sulphide gases

PARAG SEAL AND P. K. BANDYOPADHYAY

Department of General Physics & X-rays, Indian Association for the Cultivation of Science, Calcutta 700032

(Received 13 September 1973)

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 C_2H_6 can be represented satisfactorily and the situation is worse for H_2S which has a sizeable dipole moment. The shape parameter and values of quadrupole moments have been also estimated for these substances.

1. INTRODUCTION

It is now generally believed that the transport properties of polyatomic gases are insensitive to the long-range anisotropic forces and the pressure and dielectric virial coefficients are quite sensitive to these (Spurling & Mason 1967, Singh & Datta 1970, Datta & Barua 1973). Therefore, attempts have recently been made to interpret the second virial coefficient data of a number of diatomic and polyatomic gases by including the non-spherical interactions. (Spurling & Mason 1967, Singh & Datta 1970, Datta & Barua 1973, Datta & Singh 1971) The spherical part of the interactions for these gases were determined from viscosity data. By using this method, the quadrupole moments and shape factors of a number of molecules have also been estimated. Calculations have been performed for the pressure and dielectric second virial coefficients of a number of polar gases. 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.

In this paper we have reported the results of our calculations for ethane and hydrogen sulphide gases the second pressure virial coefficients of which

have recently been measured (Khoury & Robinson 1971). 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.

2. FORMULATION AND RESULTS

(i) Ethane

The intermolecular potential used for representing the second pressure virial coefficient of ethane may be written as (Spurling & Mason 1967)

$$\phi(r) = \phi(sph) + \phi(q) + \phi(an) + \phi(q-id) + \phi(sh), \quad \dots (1)$$

where $\phi(sph)$, $\phi(q)$, $\phi(an)$, $\phi(q-id)$ and $\phi(sh)$ 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 was expressed by the Lennard-Jones (12 : 6) potential which may be written as

$$\phi(r) = 4\epsilon_0 \left[\left(\frac{\sigma_0}{r} \right)^{12} - \left(\frac{\sigma_0}{r} \right)^6 \right], \quad (2)$$

where $\bar{\alpha}_0$ is the depth of the potential and σ_0 is the value of the intermolecular distance for which $\phi(r) = 0$. The detailed expressions for the different terms on the r.h.s. of eq. (1) have been given elsewhere (Spurling & Mason 1967, Singh & Datta 1970).

Let us define the following reduced quantities,

$$\alpha^* = \bar{\alpha}/\sigma_0^3; \quad \Theta^* = \Theta/(\epsilon_0\sigma_0^5); \quad y = 2(\epsilon_0/kT)^{1/2}; \quad B^* = B(T)/b_0; \quad b_0 = (2/3)\pi N\sigma_0^3 \quad \dots (3)$$

where α is the mean polarisability and Θ is the quadrupole moment of the molecule. By using the formalism of Buckingham & Pople (1955), the reduced second virial coefficients may be written as,

$$B^*(T^*) = B^*(sph) + B^*(q) + B^*(an) + B^*(q-id) + B^*(sh) \\ + B^*(q \times an) + B^*(q \times sh) + B^*(an \times sh). \quad \dots (4)$$

The r.h.s. of eq. (4) indicates the different contributions to $B^*(T^*)$ which include the cross-terms. The expressions for these terms of the H_n functions defined by Buckingham & Pople (1955) have been given elsewhere (Spurling & Mason 1967, Singh & Datta 1970) and will not be repeated here.

The parameters σ_0 and ϵ_0/k for ethane were obtained from the available experimental viscosity data (Craven & Lambert 1951, Rankine & Smith 1921, Jung & Schimiek 1930) 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 cm² as recommended by Stogryn & Stogryn (1966). The shape factor was determined from the experimental $B(T)$ data of Khoury & Robinson (1971) 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 H₂S, the situation is slightly different from that of the nonpolar gases as viscosity is also known to significantly affected by the angle-dependent dipole-dipole interaction term (Monchick & Mason 1971). The other non-spherical terms which are of terms importance are not likely to affect the viscosity of polar gases. The interaction potentia. in this case may be written as (Rakshit 1971)

$$\phi(r) = \phi(12-6-3) + \phi(d-q) + \phi(d-id) + \phi(q) + \phi(q-id) + \phi(an) + \phi(id-ig), \quad \dots (5)$$

where $\phi(12-6-3)$ is the Stockmayer or (12-6-3) potential which may be written as (Hirschfelder, Curtiss & Bird 1954)

$$\phi(r) = -4\epsilon_0 \left(\left[\frac{\sigma_0}{r} \right]^{12} - \left(\frac{\sigma_0}{r} \right)^6 \right) - (\mu_1 \mu_2 / r^3) \rho, \quad (6)$$

where $\rho = 2 \cos \theta_1 \cos \theta_2 \sin \theta_1 \sin \theta_2 \cos \phi$.

The terms on the r.h.s. of eq. (5) which are due to the dipole moment of the polar molecule are given by

$$\begin{aligned} \phi(d-q) = \frac{3}{2} \frac{\mu^{\Theta}}{r^4} & \{ \cos \theta_1 (3 \cos^2 \theta_2 - 1) + 2 \sin \theta_1 \sin \theta_2 \cos \theta_2 \cos \phi \} \\ & + \{ \cos \theta_2 (3 \cos^2 \theta_1 - 1) + 2 \sin \theta_1 \sin \theta_2 \cos \theta_1 \cos \phi \}, \end{aligned} \quad (7)$$

$$\phi(d-id) = -\frac{1}{2} \frac{\mu^{\alpha}}{r^6} \{ (3 \cos^2 \theta_1 + 1) + (3 \cos^2 \theta_2 + 1) \}. \quad (8)$$

The other terms are the same as those used for ethane. Let us define the following reduced quantities in addition to those already defined in eq. (3) viz..

$$\mu^* = \mu / (\epsilon \sigma_0^3)^{\frac{1}{2}}. \quad \dots (9)$$

Then the reduced second virial coefficient may be expressed as,

$$\begin{aligned} B^*(T) = B^*(12-6-3) - B^*(d-q) - B^*(d-id) - B^*(q) - B^*(q-id) \\ - B^*(an) - B^*(sh) - B^*(id-ig). \end{aligned} \quad \dots (10)$$

The terms in eq. (6) which are due to the dipole moment may be expressed as,

$$B^*(12-6-3) = y^{-2} [H_{12}(y) - \frac{1}{2} H_6(y)] - \sum_{n=1}^{\infty} \frac{p^{2n}}{n!} \left\{ \frac{y^{4n-4}}{2^{4n+2} 3^{2n-1}} \right\} H_{6n}(y), \quad \dots (11a)$$

$$B^*(d-q) = -\frac{1}{64}(\mu^*\Theta^*)^2 \left[H_8(y) + \frac{1}{3}(p^2y^4)H_{14}(y) + \frac{1}{54}(p^4y^8)H_{20}(y) + \dots \right] \\ + \frac{1}{24}(25\mu^*\Theta^*y)^4 \left[H_{16}(y) + \frac{1}{3}(p^2y^4)H_{22}(y) + \dots \right], \quad \dots \text{ (11b)}$$

$$B^*(d-id) = \frac{1}{16}\alpha^*\mu^*y^{-2} \left[H_6(y) + \frac{1}{3}(p^2y^4)H_{12}(y) + \frac{1}{54}(p^4y^8)H_{18}(y) + \dots \right] \\ + \frac{11}{320}(\mu^*\alpha^*)^2 \left[H_{12}(y) + \frac{1}{3}(p^2y^4)H_{18}(y) + \dots \right]. \quad \dots \text{ (11c)}$$

The parameters σ_0 and ϵ_0/K for H_2S as given in eq. (6) were obtained from the experimental viscosity data (Rakshit 1971) and are shown in table 1. The dipole moment was taken to be 0.92 Debye as recommended by Stogryn & Stogryn (1966). 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 cm². The experimental and calculated values of $B^*(T^*)$ are shown in table 3.

Table 1. Values of the molecular parameters used for ethane and hydrogen sulphide gases

Gas	Potential parameter		K	μ in e.s.u. cm.	Θ in e.s.u. cm ²	D
	$\sigma \text{ \AA}$	c/k^0K				
Ethane	4.428	223	0.1125	-	-0.65×10^{-26}	0.14
Hydrogen sulphide	3.578	310	0.0536	0.92×10^{-18}	2.24×10^{-26}	-0.08

3. DISCUSSION OF RESULTS

For ethane as shown in table 2, 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_2H_6 obtained as 0.14 is reasonable (Spurling & Mason 1967) and the sign is positive which is expected 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.

Table 2. Experimental and calculated second virial coefficient for ethane

T °K	$B^*(12-6)$	$B^*(\text{quad.}) \times 10^{-4}$	$B^*(\text{anis})$	$B^*(g.\text{ind.}) \times 10^{-4}$	$B^*(g \times \text{anis}) \times 10^{-4}$	$B^*(\text{shape})$	$B^*(\text{anis.}) \times \text{shape}$	$B^*(g. \times \text{shape})$	$B^*(\text{cal})$	$B^*(\text{exp.})$
298	-1.5211	-0.4380	0.0164	-10.4531	2.5507	-0.05947	-0.0556	0.00043	-1.6201	-1.66
323	-1.3009	-0.3623	0.0136	-9.3539	2.1147	-0.0518	-0.0472	0.00035	-1.3867	-1.39
348	-1.1082	-0.3033	0.0115	-8.6102	1.7752	-0.0456	-0.0405	0.00029	-1.1832	-1.18
373	-0.9703	-0.2622	0.0099	-7.7640	1.5378	-0.04202	-0.0359	0.00025	-1.0386	-1.02
398	-0.8293	-0.2257	0.0086	-7.1105	1.3266	-0.0372	-0.0316	0.00022	-0.8899	-0.88
423	-0.7295	-0.1996	0.0076	-6.6181	1.1757	-0.0343	-0.0286	0.00019	-0.7851	-0.76
448	-0.6253	-0.1758	0.0068	-6.1873	1.0376	-0.0315	-0.0257	0.00017	-0.6761	-0.66
473	-0.5444	-0.1574	0.0061	-5.8243	0.9311	-0.0293	-0.0235	0.00015	-0.5915	-0.57

Table 3. Experimental and calculated second virial coefficients for hydrogen sulphide

T °K	$B^*(12-6-3)$	$B^*(d-q)$	$B^*(d-ind)$	$B^*(\text{quad.})$	$B^*(g.\text{ind.})$	$B^*(\text{ans})$	$B^*(\text{shape})$	$B^*(\text{ind-ind})$	$B^*(\text{cal})$	$B^*(\text{expt})$
298	-2.7453	0.1293	0.1444	0.0652	0.0685	0.0085	0.0429	0.0004	-3.1960	-3.51
323	-2.3670	0.1041	0.1266	0.0525	0.0597	0.0068	0.0362	0.00028	-2.7531	-2.87
348	-2.0827	0.0853	0.1120	0.0431	0.0528	0.0056	0.0312	0.0002	-2.4119	-2.41
373	-1.8437	0.0717	0.1012	0.0362	0.0476	0.0048	0.0274	0.00017	-2.1319	-2.05
398	-1.6394	0.0611	0.0922	0.0310	0.0433	0.0041	0.0244	0.00012	-1.8952	-1.76
423	-1.4556	0.0524	0.0842	0.0266	0.0395	0.0035	0.0219	0.00008	-1.6832	-1.54
448	-1.3095	0.0458	0.0778	0.0233	0.0366	0.0031	0.0199	0.00007	-1.5157	-1.34
473	-1.1718	0.0403	0.0724	0.0205	0.0339	0.0027	0.0182	0.00006	-1.3694	-1.16

For H_2S , 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 (Spurling & Mason 1967). 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 (Rakshit 1971) may be a better representation than the (12-6-3) potential used by us. The force parameters obtained by Khoury & Robinson (1971) from $B(T)$ data completely fail to represent the experimental viscosity data. This shows the relative success obtained by including different non-spherical terms in the interaction potential for calculating second virial coefficient.

ACKNOWLEDGMENT

Authors are grateful to Prof. A. K. Barua for suggesting the problem and his kind help and guidance throughout the progress of the work.

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