

## Interaction second virial co-efficient of polar-quadrupolar gas mixtures

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**Abstract.** The interaction second virial coefficient of a binary polar-quadrupolar gas mixtures of non-spherical molecules of arbitrary symmetry has been calculated for a set of unlike force parameters which is obtained from the force parameters for like interactions by using empirical combination rules. In the calculation the influence of anisotropic interactions has been considered. The relative contribution of each branch of interactions has been evaluated as a function of temperature. The theoretical results have been compared with the experimental data of  $\text{CH}_3\text{F} + \text{N}_2$ ,  $\text{CH}_3\text{F} + \text{CO}_2$  and  $\text{CH}_3\text{Cl} + \text{CS}_2$ . The agreement between theory and experiment is satisfactory.

**Keywords.** Second virial coefficient; electric multipole moments; transport coefficients; perturbation method; polar-quadrupolar mixtures.

### 1. Introduction

The progress from spherical to non-spherical molecules involves difficulties in developing adequate models for the intermolecular interactions, especially to obtain a potential function capable of accounting for the transport as well as equilibrium properties of polyatomic fluids. A substantial improvement in the quantitative understanding of behaviour of polyatomic fluids can be made provided the angle-dependence of molecular interaction is properly accounted. Much attention has been focused, in the recent past, to study the effects of molecular anisotropy of the equilibrium properties of polyatomic fluids (Ananth *et al* 1974, Singh 1975, Shukla *et al* 1976; 1978). We have shown in our previous publications (Singh and Singh 1976, 1977; Singh 1977) that virial coefficients and dilute gas viscosity of single-component polyatomic gas mixtures can be satisfactorily explained with one set of force parameters and that almost all branches of anisotropic interactions are important. It has also been shown (Singh and Shukla 1978) that the mixture second virial coefficients of a binary nonpolar gas mixtures can be explained if the molecular anisotropy is accounted properly in the calculation. Here we report the calculation of interaction second virial coefficient of a binary polar—quadrupolar gas mixtures. A systematic study of this kind is of considerable importance, firstly because the calculation of mixture properties using the usual combination rules which relate the force parameters between unlike molecules to those between like molecules provides a severe test for the validity of a set of parameters of the pure components. Secondly, it gives valuable information about the anisotropic interactions between the molecules of different species. This information is often required for the proper correction of thermodynamic functions of mixtures.

## 2. Calculation and result

The potential energy of interaction between two polyatomic molecules is usually assumed to consist of a spherically symmetric component ( $\phi_{pq}(\bar{R}_{p_i}, \bar{R}_{q_j})$ ) plus a contribution  $V_{pq}(\bar{X}_{p_i}, \bar{X}_{q_j})$  due to the nonsphericity of the molecular charge distribution, i.e.

$$U_{pq}(\bar{X}_p, \bar{X}_q) = \phi_{pq}(\bar{R}_{p_i}, \bar{R}_{q_j}) + V_{pq}(\bar{X}_{p_i}, \bar{X}_{q_j}), \quad (1)$$

where  $\bar{X}_{p_i} = (\bar{R}_{p_i}, \omega_{p_i})$  is the vector describing both the location  $\bar{R}_{p_i}$  of the centre of  $i$ th molecule of species  $p$  and orientation  $\omega_{p_i}$  of the particle.

For the spherically symmetric part we use the Lennard-Jones (12-6) potential,

$$\phi_{pq}(\bar{R}_{p_i}, \bar{R}_{q_j}) = 4\epsilon_{pq} \left[ \left( \frac{\sigma_{pq}}{\gamma_{p_i q_j}} \right)^{12} - \left( \frac{\sigma_{pq}}{\gamma_{p_i q_j}} \right)^6 \right], \quad (2)$$

where

$$\gamma_{p_i q_j} = |\bar{R}_{p_i} - \bar{R}_{q_j}|.$$

The anisotropic contribution in (1) is conveniently divided into terms representing the classical electrostatic interaction, the anisotropy of the quantum mechanical dispersion forces, and the anisotropy of the repulsive part of the potential (i.e. shape of the molecular core);

$$V_{pq}(\bar{X}_{p_i}, \bar{X}_{q_j}) = V_{pq}^{\text{perm}} + V_{pq}^{\text{in}} + V_{pq}^{\text{dis}} + V_{pq}^{\text{sh}} \quad (3)$$

where (Stogryn 1969, 1970)

$$V_{pq}^{\text{perm}} = \sum_{s=1}^{\infty} \sum_{t=1}^{\infty} a_{st} M_{p_i}^{(s)} [s] T_{p_i q_j}^{(s+t)} [t] M_{q_j}^{(t)}, \quad (4)$$

$$V_{pq}^{\text{in}} = -\frac{1}{2} \sum_{s=1}^{\infty} \sum_{t=1}^{\infty} a_{st} [M_{p_i}^{(s)} [s] T_{p_i q_j}^{(s+1)} [1] \hat{\alpha}_{q_j} [1] T_{q_j p_i}^{(t+1)} [t] M_{p_i}^{(t)} + M_{q_j}^{(s)} [s] T_{q_j p_i}^{(s+1)} [1] \hat{\alpha}_{p_i} [1] T_{p_i q_j}^{(t+1)} [t] M_{q_j}^{(t)}] \quad (5)$$

$$V_{pq}^{\text{dis}} = \frac{2}{3} \left( \frac{\epsilon_{pq} \sigma_{pq}^6}{\alpha_p \alpha_q} \right) [(\hat{\alpha}_{p_i} \cdot T_{p_i q_j}^{(2)}): (\hat{\alpha}_{q_j} \cdot T_{p_i q_j}^{(2)} - \bar{\alpha}_p \bar{\alpha}_q T_{p_i q_j}^{(2)}): T_{p_i q_j}^{(2)}] \quad (6)$$

$$V_{pq}^{\text{sh}} = 4D_{pq} \epsilon_{pq} (\sigma_{pq}/\gamma_{p_i q_j})^{12} [3 \cos^2 \theta_{p_i} + 3 \cos^2 \theta_{q_j} - 2] \quad (7)$$

with

$$a_{st} = \frac{(-1)^{(s+1)} s^{s+t} s! t!}{(2s)! (2t)!}$$

$M_{p_i}^{(s)}$  is the  $s$ -rank molecular electric multipole tensor of molecule  $i$  of species  $p$  and  $T_{p_i q_j}^{(s+t)}$  is the  $(s+t)$  rank interaction tensor

$$T_{p_i q_j}^{(s+t)} = \nabla^{(s+t)} \left( \frac{1}{r_{p_i q_j}} \right). \quad (8)$$

$\Delta^{(s+t)}$  means the gradient operator applied  $(s+t)$  times performed with respect to the co-ordinates of the molecules indicated by the second subscript i.e.  $q_j$ . The notation  $[i]$  indicates  $i$ -fold contraction of the tensors,  $\hat{\alpha}$  is the electric dipole polarisability tensor and  $\bar{\alpha} = (1/3) \text{tr} \cdot \hat{\alpha}$ .

The statistical mechanical expression for the interaction second virial coefficient is written as

$$B_{pq}(T) = B_{pq}^{(0)} - \frac{N}{2\Omega^2} \sum_{n=1}^{\infty} \frac{1}{n!} \left( -\frac{1}{kT} \right)^n \int_0^{\infty} \int_{\omega p_i} \int_{\omega q_j} V_{pq}^n \exp(-\phi_{pq}/kT) r_{p_i q_j}^2 dr_{p_i q_j} d\omega_{p_i} d\omega_{q_j} \quad (9)$$

$$\text{where } B_{pq}^{(0)} = -2\pi N \int_0^{\infty} [\exp(-\phi_{pq}/kT) - 1] r_{p_i q_j}^2 dr_{p_i q_j} \quad (10)$$

is the interaction second virial coefficient for a central force field.

The contribution of different branches of interaction to the interaction second virial coefficient has been evaluated by using a perturbation method in which tensor forces  $V_{pq}$  are taken as perturbation of pair central forces  $\phi_{pq}$ . The series expansion has been carried out to a sufficient length so that the proper convergence is achieved to a sufficient degree of accuracy.

The unlike force parameters  $\sigma_{pq}$ ,  $\epsilon_{pq}$ , and  $D_{pq}$  have been estimated from the force parameters for like interactions by using the usual combination rules. These mixing rules are semiempirical and have little theoretical justification. For energy  $\epsilon_{pq}$  and size  $\sigma_{pq}$  the most commonly used combination rules are

$$\begin{aligned} \epsilon_{pq} &= (\epsilon_{pp} \epsilon_{qq})^{1/2} \xi^2 \\ \sigma_{pq} &= \frac{1}{2} (\sigma_{pp} + \sigma_{qq}) \xi^{-1/6} \end{aligned} \quad (11)$$

where the subscripts  $p$  and  $q$  refer, respectively, to the polar and quadrupolar molecules and

$$\xi = 1 + \frac{1}{4} \left( \frac{\bar{\alpha}_q \mu_p^{*2}}{\sigma_{qq}^3} \right) \left( \frac{\epsilon_{pp}}{\epsilon_{qq}} \right)^{1/2}$$

Table 1. Potential parameters, molecular dipole and quadrupole moments, shape and other parameters used in virial coefficients calculation

Molecule	$\sigma(A)$	$\epsilon/k(K)$	$D$	$\bar{z}(A^2)$	$K$	$\mu \times 10^{18}(\text{esu cm})$	$\Theta \times 10^{16}(\text{esu cm}^2)$		Reference
							Value	Method of determination	
$\text{N}_2$	3.650	92.5	0.02	1.730	0.176	0.00	-1.40	Induced birefringence	a
$\text{CO}_2$	3.932	197.5	0.16	2.925	0.257	0.00	-4.30	Induced birefringence	a
$\text{CS}_2$	4.509	495.8	0.17	8.740	0.366	0.00	1.80	Microwave line Broadening ( $\text{NH}_3$ )	b
$\text{CH}_3\text{F}^*$	4.199	155.0	-0.23	3.550	0.256	1.81	-0.40	Induced birefringence	c
$\text{CH}_3\text{Cl}^*$	4.050	225.0	0.16	4.560	0.094	1.89	1.20	Magnetic susceptibility	d

\*Preaveraged potential parameters values are given

a. Buckingham *et al* (1968); b. Smith (1956); c. Morris (1974); d. Vanderhart and Flygare (1970);

$\mu_p^*$  is the reduced dipole moment of the polar molecule. For the shape parameter  $D_{pq}$  we use

$$D_{pq} = (D_{pp} D_{qq})^{1/2}$$

in general,  $\epsilon_{pq}$ ,  $\sigma_{pq}$  and  $D_{pq}$  have intermediate values between  $\epsilon_{pp}$  and  $\epsilon_{qq}$ ,  $\sigma_{pp}$  and  $\sigma_{qq}$  and  $D_{pp}$  and  $D_{qq}$ . The like potential parameters for the pure gases ( $N_2$ ,  $CO_2$ ,  $CS_2$ ,  $CH_3F$  and  $CH_3Cl$ ) are given in table 1. These parameters are those determined by us (Singh and Singh 1976, 1977) from the dilute gas viscosity data and found suitable to explain the second and third virial coefficients of pure components. Table 1 also lists the values of electric multipole moments used in the calculation. These values were taken from the independent measurements and are supposed to be the best available values, to date.

The contribution of different branches of pair interaction to the interaction second virial coefficient is given in table 2 at one temperature for the mixtures  $CH_3F + N_2$  and  $CH_3F + CO_2$  and at three temperatures for  $CH_3Cl + CS_2$ . Calculations have been performed for two sets of potential parameters for polar molecules which were determined by us (Singh and Singh 1977) using the Monchick and Mason (1961) method (unaveraged model) and the preaveraged model. It has, however, been found that the calculated values are more close to the experimental values when preaveraged potential parameters are used. We, therefore, report here only the results obtained from the preaveraged potential model. It can be seen from table 2 that the contribution of all branches of anisotropic interaction is substantial.

Table 3 compares the calculated values of the interaction second virial coefficient with the values obtained from the experimental data. In the temperature range considered here these mixtures remain inert and a probable chemical reaction is not expected. The experimental values of the mixture virial coefficients are derived from gas compressibility measurements by fitting an isotherm with a polynomial in density. These values are then combined with the virial coefficients for pure components to

**Table 2.** Contribution of different branches of pair interaction to the interaction second virial coefficient  $B_{12}$  (in  $cm^3/mole$ )

Mixture	T (K)	$B_{12}$ (12-6)	$B_{12}$ (dip quad)	$B_{12}$ (quad)	$B_{12}$ (dip-in dip)	$B_{12}$ (quad-in dip)
$CH_3F + N_2$	298.0	- 27.87	- 2.75	-0.02	- 4.11	-0.38
$CH_3F + CO_2$	298.0	- 86.77	-21.24	-0.14	- 6.85	-2.90
$CH_3Cl + CS_2$	323.0	-283.87	- 3.52	-0.16	-22.71	-1.11
	349.4	-261.87	- 2.78	-0.14	-19.93	-0.96
	429.8	-160.34	- 1.68	-0.08	-14.59	-0.71

  

$B_{12}$ (dis)	$B_{12}$ (sh)	$B_{12}$ (perm $\times$ in)	$B_{12}$ (perm $\times$ dis)	$B_{12}$ (perm $\times$ sh)	$B_{12}$ (dis $\times$ sh)	$B_{12}$ (T)
- 1.59	- 0.47	0.04	- 1.62	-0.02	- 1.47	- 40.30
- 5.30	- 6.77	0.16	- 5.15	-1.75	- 9.92	-146.79
-22.37	-16.89	0.09	-24.96	-0.68	-30.73	-345.33
-18.25	-13.59	0.07	-20.19	-0.55	-24.16	-314.03
-10.94	-10.39	0.05	-11.96	-0.35	15.25	-195.66

Table 3. Comparison of calculated and experimental interaction second virial coefficient

Mixture	T (K)	$-B_{pq}(T)$ (cm <sup>3</sup> /mole)		
		Calculated	Experimental	Reference for experimental data
CH <sub>3</sub> F + N <sub>2</sub>	198.84	101		
	259.71	56		
	298.00	40	36	a
	353.40	21		
	420.68	5		
CH <sub>3</sub> F + CO <sub>2</sub>	182.75	466		
	225.60	243		
	285.50	165		
	298.00	147	149	a
	372.90	74		
CH <sub>2</sub> Cl + CS <sub>2</sub>	323.00	346	355	b (x)
	325.70	341	346	
	349.41	314	318	
	377.28	262	263	
	402.28	234	225	
	429.86	195	171	

(a) Lunbeck and Boerboom (1961)

(b) Bottomley and Spurling (1967)

(x) At 323 (K) CS<sub>2</sub> is in liquid form, so the measurements, have been done at low pressures.

obtain interaction virial coefficients for unlike molecular interactions. In addition to experimental inaccuracies the values are subject to uncertainties in the isotherm and the degree of polynomial used. Consequently, the experimental data available in the literature are very scanty and at the same time not very precise. For CH<sub>3</sub>F+N<sub>2</sub> and CH<sub>3</sub>F+CO<sub>2</sub> the experimental data are available only at one temperature 298 (K). In view of these uncertainties the agreement found by us between theory and experiment is very satisfactory. Our calculation provides a check on the combination rules and on the consistency of the original potential parameters of the pure gases. Further, the calculation demonstrates explicitly the effect of various branches of nonspherical interactions on the interaction second virial coefficient of polar-quadrupolar gas mixtures.

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