

## Second virial coefficient for a mixture of nonspherical molecules of arbitrary symmetry

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**Abstract.** The mixture and interaction second virial coefficients of a binary gas mixture of nonspherical molecules of arbitrary symmetry have 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 molecular anisotropy of very general type has been accounted. The relative contribution of each branch of interactions has been evaluated as a function of temperature. The theoretical values of interaction second virial coefficient have been compared with the experimental data of  $N_2+A$ ,  $N_2+He$ ,  $N_2+H_2$ ,  $N_2+O_2$ ,  $N_2+C_2H_4$ ,  $N_2+C_2H_6$ ,  $CO_2+A$ ,  $CO_2+H_2$ ,  $CO_2+N_2$ ,  $CO_2+O_2$ ,  $CO_2+CO$ ,  $CO_2+C_2H_4$ ,  $CO_2+C_2H_6$ ,  $O_2+A$  and  $H_2+CO$ . The agreement between theory and experiment is satisfactory for all the systems. Numerical estimations of the mixture second virial coefficients as a function of temperature and composition are given for the systems  $CO_2+A$ ,  $CO_2+H_2$ ,  $CO_2+N_2$ ,  $CO_2+O_2$  and  $CO_2+CO$ .

**Keywords.** Mixture second virial coefficients; electric multipole moments; perturbation method; nonpolar mixtures.

### 1. Introduction

The extent to which the molecular anisotropy contribute to the equilibrium properties of polyatomic fluids has been a subject of growing interest in recent past (Singh 1975; Ananth *et al* 1974; Shukla *et al* 1976). It has been shown (Singh and Singh 1976, 1977; Singh 1977) that the virial coefficients and dilute gas viscosity of single-component polyatomic gas mixtures can be satisfactorily explained with one set of force parameters provided that the molecular asymmetry is explicitly accounted in the calculations of virial coefficients and that almost all branches of anisotropic interactions are important. Such systematic attempts to a gas mixture of different species have not yet been made. Since the calculation of mixture properties such as mixture virial coefficients is a stringent test of the validity of a set of potential parameters, its calculation using the usual mixing rules which relate the force parameters between unlike molecules to those between like molecules will be of considerable importance. We report in this paper the calculation of mixture second virial coefficient  $B_M$  and interaction second virial coefficient  $B_{12}$  for fifteen binary nonpolar gas mixtures of non-spherical molecules. From a systematic study of this kind, valuable information about the anisotropic interactions between unlike molecules can be derived, which are often required for the proper correction of thermodynamic functions of mixtures.

For a binary system the mixture second virial coefficient is of the form

$$B_M = X_1^2 B_{11} + 2X_1 X_2 B_{12} + X_2^2 B_{22} \quad (1)$$

where  $X_i$  represents the mole fraction of  $i$ -th component of the mixture. The coefficients  $B_{11}$  and  $B_{22}$  which are the second virial coefficients of pure components, are related to the potential between the similar molecules of 1 and 2, respectively. The interaction second virial coefficient,  $B_{12}$ , is connected to the potential between a molecule of 1 and a molecule of 2. Although the coefficients  $B_{11}$ ,  $B_{22}$  and  $B_{12}$  are functions of the temperature only, the mixture second virial coefficient is obviously a function of composition as well as temperature.

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

$$B_{12}(T) = - 2\pi N \int_0^\infty \int_{\omega_1} \int_{\omega_2} (\exp [-\beta U(r_{12}, \omega_1, \omega_2)] - 1) \\ \times r_{12}^2 dr_{12} d\omega_1 d\omega_2. \quad (2)$$

Here  $\beta = 1/kT$  and  $\omega_i$  represents the Euler angles  $\theta_i$ ,  $\phi_i$  and  $\psi_i$  which specify the orientation of molecule  $i$ .

The potential energy of a pair of molecules has the form

$$U(1, 2) = \Phi_{12}(r_{12}) + V_{12}(r_{12}, \omega_1, \omega_2) \quad (3)$$

where  $\Phi_{12}$  is the central potential between a molecule of 1 and a molecule of 2 and  $V_{12}$  arising from tensor forces, contains all of the angle-dependence of pair interaction. For this interaction, we write

$$V_{12} = V_{12}^{\text{perm}} + V_{12}^{\text{in}} + V_{12}^{\text{dis}} + V_{12}^{\text{sh}} \quad (4)$$

where  $V_{12}^{\text{perm}}$  is the interaction between the permanent multipole moments of the molecules,  $V_{12}^{\text{in}}$  the interaction of induced multipole moments in one molecule with the permanent moments of the other molecule,  $V_{12}^{\text{dis}}$  the interaction between anisotropic dispersion forces of the molecules, and  $V_{12}^{\text{sh}}$  the angle-dependent overlap interaction. For our calculation we take the functional form of these interactions as summarized by us (Singh and Singh 1976) (hereinafter referred to as I). Our calculation differs in two respects from that of earlier workers: (i) we include more branches of anisotropic pair interaction, and (ii) the values of electric multipole moments are taken from independent experimental measurements.

The contribution of different branches of pair interaction to the second virial coefficients have been calculated by using a perturbation method in which tensor forces  $V_{12}$  are taken as perturbation of the pair central potential  $\Phi_{12}$ . The series expansion has been carried out to sufficient length so that the proper convergence is achieved to a sufficient degree of accuracy.

The unlike potential parameters  $\sigma_{12}$ ,  $\epsilon_{12}$  and  $D_{12}$  have been obtained from the force parameters for like interactions by using combination rules. These combination rules are semiempirical and have little theoretical justification. For energy  $\epsilon_{12}$  and size  $\sigma_{12}$  the most commonly used combination rules are

$$\begin{aligned}\sigma_{12} &= \frac{1}{2} (\sigma_{11} + \sigma_{22}) \\ \epsilon_{12} &= (\epsilon_{11} \epsilon_{22})^{\frac{1}{2}}.\end{aligned}\quad (5)$$

Several attempts have been made in the past to modify these rules without much success (Calvin and Reed 1971, 1972). For the shape parameter we use

$$D_{12} = (D_{11} D_{22})^{1/2}.\quad (6)$$

In general  $\epsilon_{12}$ ,  $\sigma_{12}$  and  $D_{12}$  have intermediate values between  $\epsilon_{11}$  and  $\epsilon_{22}$ ,  $\sigma_{11}$  and  $\sigma_{22}$  and  $D_{11}$  and  $D_{22}$ . The like potential parameters for the pure gases (A, He, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>) are given in table 1. These parameters are as those obtained by us in I from the dilute gas viscosity data and have been found suitable to explain the pressure and dielectric second virial coefficients and pressure

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

Mole- cule	$\sigma$ (A)	$\epsilon/k$ (K)	$(D)$	$\bar{a}(A^2)$	$K$	$\theta \times 10^{26}$ (esu cm <sup>2</sup> )		Ref.
						Value	Method of determination	
A	3.465	116.0	0.00	1.630	0.000	0.00	—	—
He	2.556	10.22	0.00	0.220	0.000	0.00	—	—
H <sub>2</sub>	2.970	37.5	0.22	0.790	0.090	0.651	Induced bi- refringence	a
N <sub>2</sub>	3.650	92.5	0.02	1.730	0.176	-1.40	Induced bi- refringence	a
O <sub>2</sub>	3.440	112.5	0.10	1.590	0.239	-0.40	Induced bi- refringence	a
CO	3.672	95.5	0.10	1.970	0.168	-2.20	Zeeman effect and accurate CI wave function	b, c
CO <sub>2</sub>	3.932	197.5	0.16	2.925	0.257	-4.30	Induced bi- refringence	a
C <sub>2</sub> H <sub>4</sub>	4.468	190.5	0.24	4.269	0.158	2.00	Induced bi- refringence	a
						1.96	Wave function of moderate quality	d
C <sub>2</sub> H <sub>6</sub>	4.144	200.5	0.27	4.470	0.112	2.00	Induced bi- refringence	a

a. Buckingham *et al* (1968); b. Gustafson and Gordy (1970); c. Sin and Davidson (1970); d. Snyder and Basch (1972).

Table 2. Comparison of calculated and experimental interaction second virial coefficient.

Mixture	T(K)	$B_{12}(T)$ (cm <sup>3</sup> /mole)		Ref.	
		Calc.	Exptl.		
N <sub>2</sub> +A	148.2	-85.66	-81.60	a	
	173.2	-61.36	-59.10		
	198.2	-44.24	-44.10		
	223.2	-32.04	-32.60		
	248.2	-23.02	-23.70		
	273.2	-15.74	-16.40		
	298.2	-10.22	-10.90		
	323.2	-5.38	-6.20		
N <sub>2</sub> +He	298.0	17.06	17.71	b	
			12.55	c	
	303.0	19.19	21.84	d	
			21.03	e	
N <sub>2</sub> +H <sub>2</sub>	36.0	-257.83	-227.00	f	
	40.0	-208.50	-184.00		
	44.0	-168.59	-150.00		
	48.0	-140.15	-123.00		
	52.0	-118.00	-106.00		
	56.0	-108.40	-95.00		
	60.0	-104.32	-92.00		
	298.0	11.56	13.50		c
			12.80		b
			11.10		g
N <sub>2</sub> +O <sub>2</sub>	90.0	-221.87	-222.20	h	
	303.0	-8.82	-9.70±0.30	i	
N <sub>2</sub> +C <sub>4</sub> H <sub>4</sub>	298.0	-56.85	-59.70	c	
N <sub>2</sub> +C <sub>2</sub> H <sub>6</sub>	277.4	-57.40	-65.40	i	
	310.9	-43.54	-38.60		
	377.6	-21.28	-20.10		
	444.3	-5.96	-3.80		
	510.9	2.79	5.90		
CO <sub>2</sub> +A	303.0	-43.30	-31.80±4.60	k	
	333.0	-33.62	-25.80±4.20		
	363.0	-25.30	-19.60±4.20		
CO <sub>2</sub> +H <sub>2</sub>	298.0	0.70	-1.10	b	
	303.0	1.39	-1.00±3.80	k	
	333.0	4.61	0.40±4.40		
	363.0	7.35	0.00±3.20		
CO <sub>2</sub> +N <sub>2</sub>	298.0	-41.53	-42.60	b	
	303.0	-38.34	-40.47		
			-40.60±0.20		i
			-41.40±6.20		k
	333.00	-27.86	-36.00±4.00		
	363.0	-20.52	-28.50±3.60		
CO <sub>2</sub> +O <sub>2</sub>	298.0	-46.52	-61.25	c	
	303.0	-43.40	-41.50±0.20		i
	333.0	-36.51	-36.80±5.20		k
	363.0	-27.52	-28.40±5.60		
		-25.60±4.40			
CO <sub>2</sub> +CO	303.0	-41.97	-43.60±4.60	k	
	333.0	-32.15	-36.60±4.00		
	363.0	-23.24	-25.70±6.00		
CO <sub>2</sub> +C <sub>2</sub> H <sub>4</sub>	298.0	-118.95	-136.00	c	
	373.0	-82.96	-93.00		l

Table 2 (contd.)

CO <sub>2</sub> +C <sub>2</sub> H <sub>6</sub>	310.9	-101.53	-103.00	m
	344.2	-88.15	-87.50	
	377.5	-72.00	-73.30	
	410.9	-60.30	-60.40	
	444.2	-48.70	-48.20	
	477.5	-36.25	-37.00	
510.8	-27.23	-26.00		
O <sub>2</sub> +A	90.00	-214.35	-233.30	h
H <sub>2</sub> +CO	36.0	-268.56	-256.00	f
	40.0	-220.45	-213.00	
	44.0	-183.60	-179.00	
	48.0	-154.25	-153.00	
	52.0	-136.00	-133.00	
	56.0	-121.50	-117.00	
	60.0	-114.50	-108.00	

a. Brewer and Vaughn (1969)

b. Lunbeck and Boerboom (1951)

c. Edwards and Roseweare (1942)

d. Kramer and Miller (1951)

e. Pfefferle *et al* (1955)

f. Reuss and Beenakker (1956)

g. Michels and Wassenaar (1949)

h. Knobler *et al* (1959)

i. Gorski and Miller (1953)

j. Gunn (1958)

k. Cottrell (1956)

l. Ku and Dodge (1967)

m. Huff and Reed (1963).

third virial coefficient. In table 1, we also list the values of quadrupole moments which in our opinion are most reliable. The method and references from where we took these values are also given.

Calculated values of interaction second virial coefficient are compared with the values obtained from the experimental data in table 2. Except for N<sub>2</sub>-H<sub>2</sub> and CO<sub>2</sub>-H<sub>2</sub> the agreement between calculated and experimental values are good for all the systems investigated here. For checking the convergence of the perturbation series, we calculated  $B_{12}$  at temperature  $T=298$  K for CO<sub>2</sub> + N<sub>2</sub> by solving numerically eq. (2) and obtained the value  $-42.15$  (cm<sup>3</sup>/mole) which is in good agreement with the value found from the perturbation series  $-41.53$  (cm<sup>3</sup>/mole). For N<sub>2</sub>+H<sub>2</sub> and CO<sub>2</sub>+H<sub>2</sub> the calculated values are always greater than the experimental values. The cause of this discrepancy between calculated and experimental values may be attributed to the quantum effect, which is quite significant at low temperatures. It has been shown (Singh and Datta 1970; Rakshit and Chowdhary 1971) that the second virial coefficient of D<sub>2</sub>, H<sub>2</sub> and HD can be explained satisfactorily provided the quantum corrections are included in the calculation. The contribution of the quantum correction term to the second virial coefficient has been found to be positive. Therefore, if included in the present calculation the values of the interaction second virial coefficient for N<sub>2</sub>+H<sub>2</sub> and CO<sub>2</sub>+H<sub>2</sub> will be in more close agreement to the experimental values.

Table 3 lists the contribution of different branches of pair interaction at two temperatures for the mixtures N<sub>2</sub> + O<sub>2</sub>, N<sub>2</sub>+C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub> + N<sub>2</sub>, CO<sub>2</sub> + O<sub>2</sub>, CO<sub>2</sub> + CO and CO<sub>2</sub> + C<sub>2</sub>H<sub>6</sub>. It can be seen from table 3 that all branches of anisotropic interaction contribute significantly throughout the temperature range of our investigation. While the direct anisotropic dispersion and overlap terms are large, they are of opposite sign to the dispersion overlap term, resulting in considerable cancellation.

Table 3. Contribution of different branches of pair interactions to the second virial coefficient.

Mixture	T(K)	$B_{12}$ (12-6)	$B_{12}$ (quad)	$B_{12}$ (quad in dip)	$B_{12}$ (dis)	$B_{12}$ (sh)	$B_{12}$ (quad $\times$ quad in dip)	$B_{12}$ (quad $\times$ sh)	$B_{12}$ (sh $\times$ dis)	$B_{12}$ (T)
$N_2+O_2$	90.0	-214.50	-0.66	-1.57	-11.32	-0.89	0.02	0.11	5.52	-221.87
$N_2+C_2H_6$	303.0	-8.28	-0.04	-0.27	-0.66	-0.11	0.00	0.01	0.45	-8.82
$CO_2+N_2$	298.0	-37.56	-2.69	-2.27	-1.62	-0.32	0.03	0.57	1.22	-41.53
	363.0	-17.69	-1.79	-1.60	-1.09	-0.25	0.02	0.36	0.78	-20.52
$CO_2+O_2$	298.0	-40.70	-2.61	-3.82	-2.29	-1.02	0.01	0.85	2.57	-46.52
	363.0	-23.03	-1.77	-3.11	-1.58	-0.79	0.00	0.55	1.88	-27.52
$CO_2+CO$	303.0	-36.13	-6.27	-2.97	-1.57	-1.60	0.07	1.53	3.35	-41.97
	363.0	-18.40	-4.26	-2.39	-1.09	-1.26	0.03	0.91	2.31	-23.24
$CO_2+C_2H_6$	310.9	-96.02	-3.32	-4.22	-3.10	-8.50	0.04	3.93	8.41	-101.53
	510.8	-23.70	-1.15	-2.31	-1.10	-4.20	0.02	1.28	3.49	-27.23

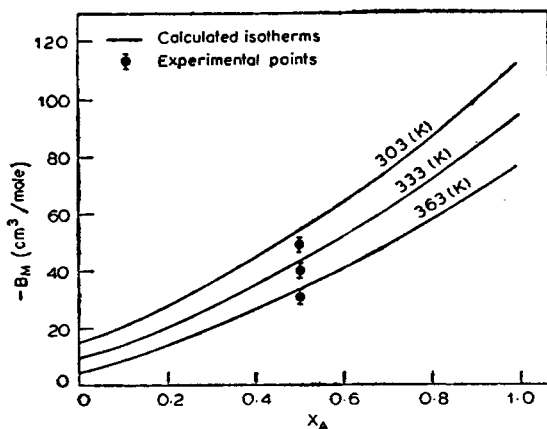


Figure 1. Comparison of calculated and experimental mixture second virial coefficients for the  $\text{CO}_2+\text{A}$  system: (Cottrell 1956).

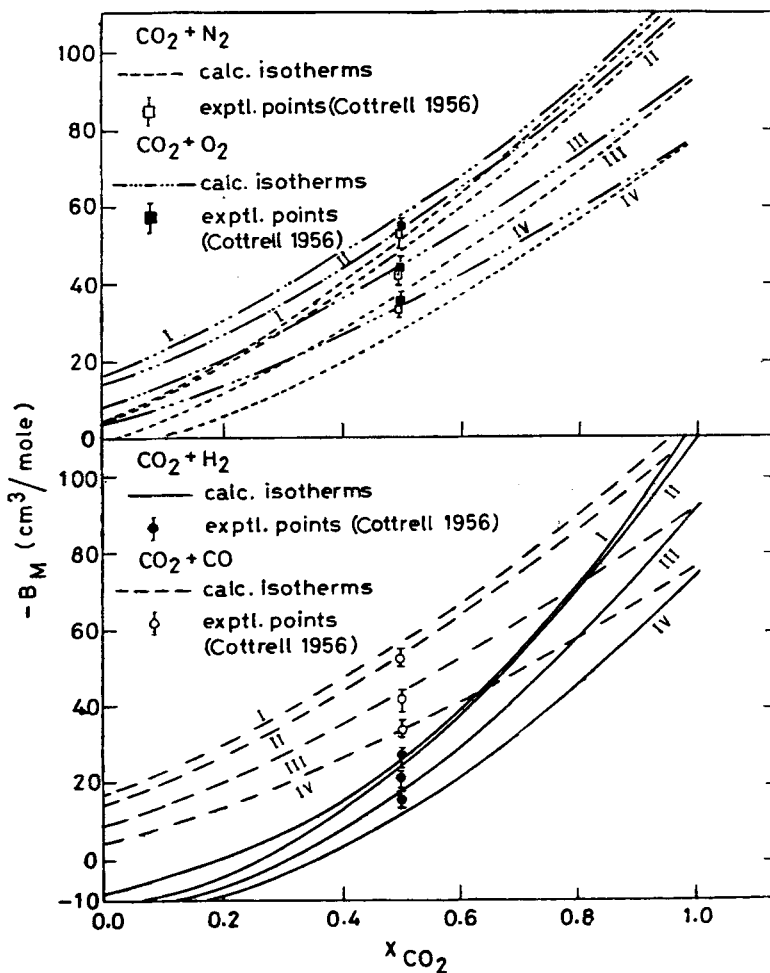


Figure 2. Comparison of calculated and experimental mixture second virial coefficients for the  $\text{CO}_2+\text{H}_2$ ;  $\text{CO}_2+\text{CO}$ ;  $\text{CO}_2+\text{N}_2$  and  $\text{CO}_2+\text{O}_2$ .

Figures 1 and 2 show the variation of mixture second virial coefficient with composition and temperature and compare the calculated values with the values obtained from experimental data for  $\text{CO}_2 + \text{A}$  and  $\text{CO}_2 + \text{H}_2$ ,  $\text{CO}_2 + \text{N}_2$ ,  $\text{CO}_2 + \text{O}_2$  and  $\text{CO}_2 + \text{CO}$ . Experimental points which are given in the figures are those as determined by Cottrell (1956). 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 obtain interaction virial coefficients for unlike molecular interactions. Thus in addition to experimental inaccuracies the values are subject to uncertainties in the isotherm and the degree of polynomial used. 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; the calculation shows explicitly the effect of various branches of nonspherical interactions on the second virial coefficient of a binary gas mixture.

From our calculation it appears that depending upon the relative magnitudes of the potential parameters of the components, the binary gas mixtures may behave in two different ways. If both the force constants (size and energy) of one component are greater than those of the other, the interaction second virial coefficient is higher within a certain temperature range than the pure component second virial coefficient. On the other hand, if one parameter is greater and the other smaller for one component than for the other, then within a certain temperature range the interaction second virial coefficient is lower than either of the pure component values. Mixture of first kind may be less compressible at certain temperatures and compositions than either of the pure components while those of the second type can be more compressible.

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