

SECOND VIRIAL COEFFICIENTS FOR NONSPHERICAL MOLECULES  
AND THEIR EXPERIMENTAL MEASUREMENTS

A.Boushehri\*

S.H.Moosavipour

*Department of Chemistry, Shiraz University, Shiraz, Iran*

( Received 28th Oct. 1989 )

( Approved 14th May 1990 )

## ABSTRACT

The virial coefficients can be obtained from statistical mechanics in connection with the intermolecular potentials. The intermolecular potential of polyatomic molecules is usually assumed to consist of a spherically symmetric component plus a contribution due to asphericity of the molecular charge distribution. In this study, the second virial coefficients have been calculated for  $N_2$ , CO, and  $SF_6$  from the Lennard-Jones(6-12) potential. The results are in good agreement with those obtained experimentally.

## INTRODUCTION

The intermolecular potential energy of polyatomic molecules is usually assumed to consist of a spherically symmetric component plus a contribution due to the asphericity of the molecular charge distribution. The latter contribution is less important in spherically symmetric molecules. Yet much progress has been made in describing the forces between spherically symmetric molecules like those of Noble gases. Lennard-Jones proposed for interpretation of these

systems his famous potential energy model in 1924[1]. Subsequently a few other potential models have been presented by other investigators, e.g. "11-6-8" model of Klein and Hanley[2].

The extended law of corresponding states of Kestin, Ro, and Wakeham[3] has provided the correlation of low-density equilibrium and transport properties of the monatomic gases and their mixtures with an uncertainty commensurate with the experimental accuracy. A semiempirical potential formula for Argon with new parameters

\*Corresponding author

has been formulated by Ahlrichs and coworkers[4]. Aziz and Chen[5] have proposed six models HFD-A, HFD-B, HFD-C, HFD-D, HFD-1, and HFD-II which are in more consistent with theoretical and experimental results. Based upon comparison of theoretical and experimental results, they preferred the HFD-C for moderate and high temperatures.

While much progress has been made in describing the thermodynamic properties of assemblies of molecules with spherical symmetry, there are many molecules whose force fields depend on their relative orientations. In this regard, molecules possessing permanent dipole moments form an important class. Their interactions have been discussed in terms of an intermolecular energy represented by a central force term together with the interaction of point dipoles. Such a model was first used by Stockmayer[6] who supposed that the central forces were of the Lennard-Jones type, that is, an  $r^{-6}$  term describing the attractive dispersion forces and an  $r^{-s}$  term ( $s > 6$ ) representing the repulsive forces of short range caused by the overlap of electron clouds. However, the Stockmayer force field is a simplification of the true position. Buckingham and Pople [7] proposed that in addition to the interaction of permanent dipoles, other orientation forces, such as dipole-induced dipole interaction, quadrupole

forces, and the effect of molecular shape may be important.

Spurling and Mason[8] analyzed the viscosity data for nine quadrupolar gases with the collision integrals for a 12-6-5 potential in order to obtain the parameters of the spherical component of the potential. These parameters were then used in conjunction with experimental second virial coefficients to determine the quadrupole moments and shape parameters of the molecules. Boushehri and Attaran[9] calculated the second virial coefficients of polyatomic gases from the potential model HFD-I.

In this study, second virial coefficients of some polyatomic gases ( $N_2$ , CO,  $SF_6$ ) have been calculated using the Lennard-Jones (6-12) potential. The results are in satisfactory agreement with presently available experimental data.

## CALCULATIONS

If two nonspherical molecules interact, the potential energy will depend on the relative spatial orientations of the molecules as well as on their separation distance. The goal of the present paper is to calculate the second virial coefficients for  $N_2$ , CO, and  $SF_6$  gases by taking into account the following terms of potential model used by Buckingham and Pople [7].

$$B^*(T^*) = B^*(12-6) + B^*(\text{quad}) + B^*(\text{anis}) + B^*(\text{quad-dipole}) + B^*(\text{quad-ind dipole}) + B^*(\text{quad} \times \text{anis}) + \dots$$

(1)

Here  $B^*(T^*)$ , the reduced second virial coefficient, depends only on  $T^*$  and is equal to  $B(kT/\epsilon_0)/(2N_0\sigma_0^3/3)$ , where  $\epsilon_0$  is the depth of potential well, and  $\sigma_0$  is the distance in which the repulsive potential equals to the attractive one. Expressions for the first few terms in each of the major contributions to nonspherical portion  $B_{ns}^*$  are given in refs. [7,10]. In Table 1, tabulates the calculated second virial coefficients of  $N_2$ , CO and  $SF_6$  as a function of temperature via equation 1. The scaling parameters and the dimensionless quantities  $T^* = T/(\epsilon_0/k)$ ,  $B^* = B/(2\pi N_0\sigma_0^3/3)$ ,  $\mu^* = \mu/(\epsilon_0\sigma_0^3)^{1/2}$ ,  $\theta^* = \theta/(\epsilon_0\sigma_0^5)^{1/2}$ , and  $\alpha^* = \bar{\alpha}/\sigma_0^3$  are taken from Ref. [11], where  $\mu$  is the dipole moment. The average polarizability  $\bar{\alpha}$  is given by  $\bar{\alpha} = (\alpha^{11} + 2\alpha^1)/3$ , where  $\alpha^{11}$  is the polarizability along the axis of symmetry and  $\alpha^1$  is perpendicular to the axis. The quadrupole moment  $\theta$  is defined by:

$$\theta = \sum_i e_i (Z_i^2 - X_i^2)$$

where  $e_i$  is the  $i$ th element of charge and  $X_i$  and  $Z_i$  are its coordinates in a system where its  $Z$  axis is the symmetry axis and its origin is located in the center of mass. The results for molecules with octupole moments have also been discussed in ref. [12].

Table 1: Second virial coefficient of  $N_2$ , CO, and  $SF_6$ 

$T^\circ K$	$B(T)_{\text{theo.}}$	$B_{\text{exp.}}$
$N_2$		
293.15	-8.321	-6.031
313.15	-4.590	-2.794
333.15	-1.209	+2.961
CO		
293.15	-12.784	-11.972
313.15	-8.540	-5.538
333.15	-4.738	-0.420
$SF_6$		
293.15	-247.919	-252.591
313.15	-216.485	-222.000
333.15	-192.201	-191.040

Dimensional material and effective spherical parameters are given in Table 2.

## EXPERIMENTAL

The apparatus used for the measurement of these data is essentially similar to that employed by Chinese workers [13] where a mercury U-tube used as the differential pressure gauge. One advantage of this arrangement is that the manometer does not have to be in the thermostat bath. A five-junction thermocouple, and a Leeds and Northrup potentiometer ( $\pm 1 \mu V$ ) were used for controlling the bath temperature within  $\pm 0.1^\circ C$ . Pressures were measured with a travelling microscope reading down to

Table 2. Dimensionless material parameters used in calculation of the nonspherical contributions to second virial coefficients along with the effective spherical parameters

	$\mu^{*a}$	$\theta^{*b}$	$\alpha^{*d}$	$\kappa^f$	$\sigma_o$ (nm)	$\epsilon_o/k$ (K)
N <sub>2</sub>	0	0.47 <sup>c</sup>	0.0357	0.131	0.3652	98.4
CO	0.138	0.84	0.0404	0.090	0.3652	98.4
SF <sub>6</sub>	0	0	0.0452 <sup>e</sup>	0	0.5252	207.7
Polarizability anisotropy				$\kappa = (\alpha^{11} - \alpha^1) / 3 \bar{\alpha}$		
The parameters $\sigma_o$ and $\epsilon_o/k$ were determined by fitting accurate viscosity data to the same functional $\Omega(2,2)^*$ as used for the noble gases, in the range $1 \leq T^* \leq 10$ . <sup>g</sup>						

<sup>a</sup>R.D.Nelson, Jr., D.R.Lide, Jr., and A.A.Maryott, U.S. National Bureau of Standards NSRDS-NBS 10 (1967).

<sup>b</sup>D.E.Stogryn and A.P.Stogryn, Mol. Phys. 11, 371 (1966), unless otherwise noted.

<sup>c</sup>A.D.Buckingham, R.L.Disch, and D.A.Dunmur, J. Am. Chem. Soc. 90, 3104 (1968). See comments by F.P.Billingsley II and M.Krauss, J. Chem. Phys. 60, 2767 (1974).

<sup>d</sup>A.A.Maryott and F.Buckley, Natl. Bur. Stand. Circ. (U.S.), 537, (1953), unless otherwise noted. The molecular polarizability includes both electronic and atomic contributions; see E.A.Gislason, F.E.Budenhöfzer, and A.D.Jorgensen, Chem. Phys. Lett. 47, 434 (1977).

<sup>e</sup>A.B.Tipton, A.P.Deam, and J.E.Boggs, J. Chem. Phys. 40, 1144 (1964).

<sup>f</sup>N.J.Bridge and A.D.Buckingham, Proc. R. Soc. London, Ser. A 295, 334 (1966).

<sup>g</sup>B.Najafi, E.A.Mason, and J.Kestin, Physica 119A, 387 (1983).

0.05 mm. The experiments were carried out at 20, 40 and 60°C for each of the N<sub>2</sub>, CO, and SF<sub>6</sub> gases. The second virial coefficients of these gases at mentioned temperatures were ob-

tained using equation (3.3.7) of Ref. [10]. Experimental results are tabulated in table 1. Nitrogen, carbon monoxide, and sulphur hexafluoride were supplied by the Matheson Co.

The minimum purities were 99%.

## RESULTS AND DISCUSSION

When a gas is kept at relatively high pressures and low temperatures, its behaviour can be expressed by "The virial equation of state". The virial coefficients can be obtained from statistical mechanics and intermolecular potentials as well as from the experimental measurements.

The intermolecular potential of molecules is usually assumed to consist of a spherically symmetric component  $U_0(r)$  as well as a contribution due to the asphericity of the molecular charge distribution  $U_{ns}$ .  $U_0(r)$  can be directly calculated from potential models like Lennard-Jones (6-12) Potential.  $U_{ns}$  is also divided into two categories: long-range and short-range forces.

In this study, the second virial coefficients of some polyatomic gases has been calculated using the Lennard-Jones (6-12) potential. The second virial coefficients has been calculated for gaseous molecules ( $N_2$ ,  $CO$ , and  $SF_6$ ). The results are in satisfactory agreement with the experimental data as shown in Table 1. In short, there are many reported calculations of the virial coefficient but none of them consider all the terms (including  $B^*(12-6)$  in eq. (1)).

## Acknowledgement

We are thankful to Shiraz University Research Council for the support of this work through Grant No 66-SC-468-241.

## REFERENCES

1. J. E. Lennard-Jones, *Proc. Roy. Soc. A* 106, 441 (1924).
2. H. J. M. Hanely and M. Klein, *J. Chem. Phys.* 53, 4722 (1970).
3. J. Kestin, S. T. Ro and W. Wakeham, *Physica* 58, 165 (1972).
4. R. Ahlrichs, P. Penco and G. Scoles. *J. Chem. Phys.* 19, 11 (1976).
5. A. R. Aziz and H. H. Chen, *J. Chem. Phys.* 67, 5719 (1977).
6. W. H. Stockmayer, *J. Chem. Phys.* 9, 398 (1941).
7. A. D. Buckingham and J. A. Pople, *Trans. Faraday, Soc.* 51, 1173 (1955).
8. T. H. Spurling and E. A. Mason, *J. Chem. Phys.* 64, 322 (1967).
9. A. Boushehri and A. M. Attaran, *Bull. Chem. Soc. Japan.* 61, 1743 (1988).
10. E. A. Mason and T. H. Spurling, " *The Virial Equation of State*", Pergamon, Oxford (1969).
11. A. Boushehri, J. Bzowski, J. Kestin and E. A. Mason, *J. Phys. Chem. Ref. Data* 16, 445 (1987); Erratum, 17, 255 (1988).
12. S. Kielich, *Physica* 28, 511 (1962).
13. Y. C. Chang, H. T. Wang, and T. Huang, *K'o-hsueh T, ung-pao*, No. 5, 437 (1965).