NOTIZEN

Second Virial Coefficients of Ground State Nitrogen Atoms

C. Guidotti and G. P. Arrighini
Istituto di Chimica fisica dell'Università di Pisa, Italy
M. Capitelli and U. T. Lamanna
Dipartimento di Chimica dell'Università di Bari, Italy

(Z. Naturforsch. **31 a,** 1722–1724 [1976]; received July 27, 1976)

Second virial coefficients of ground state nitrogen atoms have been calculated in the temperature range 6000–20000 K. The results have been obtained using experimental potentials for the states $^1\Sigma_g^+$, $^3\Sigma_u^+$ and $^5\Sigma_g^+$ of the nitrogen molecule and an ab initio Heitler-London potential for the $^2\Sigma_u^+$ repulsive potential.

Differences up to a factor of 5 are found between the present second virial coefficients and the corresponding values of Kessel'man et al.

The thermodynamic properties of high temperature-low pressure ideal nitrogen plasmas are well known [1], while minor work exists on the corresponding properties at high pressures, despite their importance in many applications [2]. In this note we examine the first step in the calculation of thermodynamic properties of high temperature-high pressure nitrogen plasmas i. e. the calculation of the second virial coefficients of nitrogen atoms in the ground state N(^{4}S). These quantities can be evaluated from knowledge of the potentials $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$, $^7\Sigma_u^+$ arising in the N(^{4}S) + N(^{4}S) collision.

One can, in fact, write [3–5]

$$\overline{B}_{ij} = \sum_k g_k B_{ij}^k / \sum_k g_k \tag{1}$$

$$B_{ij} = 2\pi N \int_0^\infty [1 - \exp\{-\Phi_{\text{eff}}(r)/kT\}]\, r^2\, \mathrm{d}r \tag{2}$$

$$\Phi_{\text{eff}}(r) = \Phi(r) \quad \text{for} \quad \Phi(r) > 0 \tag{3}$$

$$\Phi_{\text{eff}}(r) = \Phi(r) - KT \ln[1 - F(r)] \quad \text{for} \quad \Phi(r) < 0 \tag{4}$$

$$F(r) = \gamma(\tfrac{3}{2}, -\Phi(r)/KT)/\Gamma(\tfrac{3}{2}) \tag{5}$$

where $\gamma(\frac{3}{2}, x)$ is the incomplete gamma function.

It should be noted that Eq. (2) calculates the so called B_{free} contribution i. e. the contribution due to the atoms which interact, but are free to separate after the interaction [3–5]. The definition of B_{free}, for an attractive potential, through Eqs. (2) – (5), is useful since the corresponding B_{b} term (i. e. the contribution related to the formation of bound molecules) is generally taken into account in the equilibrium constant of the dissociation process [3–5]. It should be, however, pointed out that only $B_{\text{tot}} = B_{\text{free}} + B_{\text{b}}$ can be, in principle, experimentally determined (even if very difficult to do).

The $\Phi(r)$ potentials corresponding to $^1\Sigma_g$ and $^3\Sigma_u$ potentials are strongly attractive; they can be expressed by means of a Morse function, the parameters of which, based on experimental spectroscopic potentials, can be found in Reference [6]. The same function, with parameters in Ref. [7], can be used for the $^5\Sigma_g$ potential; it is based on the predissociation analysis made by McCarrol in Reference [8]. The $^7\Sigma_u$ potential is very important in determining $\overline{B}$, due to its large statistical weight as compared with the corresponding statistical weights of other states. Two independent calculations have been performed on this potential, using a delta function model [9, 10]. The results are expressed by means of an exponential repulsive function

$$\Phi(r) = \Phi_0 \exp\{-b\, r\} \tag{6}$$

with parameters $\Phi_0 = 317.8$ eV, $b = 2.753$ Å^{-1} from Ref. [9] and $\Phi_0 = 253.9$ eV, $b = 2.717$ Å^{-1} from Reference [10].

To check the reliability of these calculations, we have done an "ab initio" quantum mechanical determination of the $^7\Sigma_u$ potential, by using the valence bond type wave function (7):

Table 1. Values of $\Phi(r)$ relative to $^7\Sigma_u$ potential.

r(Å)	Φ(eV) [a]	Φ [9]	Φ [10]
1.09	38.91		
1.59	6.92	3.99	3.38
1.85	2.68	1.95	1.66
3.17	9.7(−3)	5.15(−2)	4.6(−2)
4.0	8.3(−4)		

9.7(−3) ≡ 9.7×10^{-3}; [a] present results.

Reprint requests to Prof. C. Guidotti, Istituto di Chimica fisica dell'Università, Via Risorgimento, 35, *I-56100 Pisa* (Italy).

T °K	$^1\Sigma_g$[6]	$^3\Sigma_u$[6]	$^5\Sigma_g$[9]	$^5\Sigma_g$[8]	$^7\Sigma_u$[9]	$^7\Sigma_u$[10]	$^7\Sigma_u$[a]
6000	−43.1	−26.5	3.42	2.43	22.9	21.8	17.6
7000	−37.4	−23.5	3.44	2.50	21.6	20.4	16.8
8000	−35.8	−21.1	3.44	2.55	20.4	19.3	16.1
9000	−33.5	−19.2	3.45	2.59	19.4	18.4	15.6
10000	−30.5	−17.7	3.45	2.62	18.6	17.5	15.1
15000	−22.5	−12.6	3.43	2.67	15.6	14.6	13.3
20000	−18.0	−9.8	3.40	2.67	13.6	12.7	12.1

Table 2. Second virial coefficients (cm^3/mole) corresponding to different potentials.
[6]: derived from potentials of Ref. [6];
[a]: derived from the present calculated potential.

$$\begin{aligned}\Psi({}^7\Sigma_u) = {} & 0.22360680\ \Psi_{\mathrm{A}}(0,0,15/4,-3/2) \cdot \Psi_{\mathrm{B}}(0,0,15/4,3/2) \\ & + 0.67082039\ \Psi_{\mathrm{A}}(0,0,15/4,-1/2) \cdot \Psi_{\mathrm{B}}(0,0,15/4,1/2) \\ & + 0.67082039\ \Psi_{\mathrm{A}}(0,0,15/4,1/2) \cdot \Psi_{\mathrm{B}}(0,0,15/4,-1/2) \\ & + 0.22360680\ \Psi_{\mathrm{A}}(0,0,15/4,3/2) \cdot \Psi_{\mathrm{B}}(0,0,15/4,-3/2)\end{aligned} \tag{7}$$

where Ψ_{A} and Ψ_{B} represent Slater determinantal atomic functions centered on atoms A and B respectively, which are eigenfunctions of the operators $\mathcal{L}^2$, $\mathcal{L}_z$, S^2, S_z with the corresponding eigenvalues in the brackets. The molecular eigenfunction is, of course, an eigenstate of $\mathcal{L}_z$ and of the spin operators. The determinantal atomic function Ψ_{A} and Ψ_{B}, have been built with the following minimal STO basis $\mathscr{Z}$ (1s) $= 6.70$, $\mathscr{Z}$ (2s and 2p) $= 1.95$. The potential energy has been therefore calculated as

$$\Phi(r) = \langle \Psi({}^7\Sigma_u) | \mathcal{H} | \Psi({}^7\Sigma_u) \rangle - 2E[\mathrm{N}({}^4\mathrm{S})] \tag{8}$$

where $E[\mathrm{N}({}^4\mathrm{S})] = -54.26512$ a. u.

Results of these computations are reported in Table 1; they can be fitted, in the energy range $10^{-2} - 7$ eV, with a satisfactory approximation to Eq. (6), with parameters $\Phi_0 = 5572$ eV, $b = 4.170$ Å^{-1}. It should be noted that the wavefunction (7) can be considered a satisfactory representation of the $^7\Sigma_u$ potential, since it represents the only "covalent" configuration of this state in the framework of the atomic basis set utilized [11].

Values of B_{ij} relative to the present $^7\Sigma_u$ potential, are reported in Table 2, and compared with the corresponding results obtained by using the potential of References [9, 10]. One can note the agreement between the B_{ij} values obtained from the different potentials (maximum deviation being of the order of 25%), even though the potentials can strongly differ (see Table 1). These differences become smaller when one adds the $^7\Sigma_u$ contribution to the remaining contributions. In the same table we also report the contributions coming from the other potentials. The average second virial coefficients of nitrogen atoms calculated by Eq. (1) have been compared in Table 3 with the corresponding values of Reference [4]. The strong differences (up to a factor 5) between the present results and the Kessel'man ones, are due to a different choice of the potentials, since the same equations [i. e. Eqs. (1) to (5)] were used for evaluating the second virial coefficient. In particular Kessel'man et al. [4] used a Morse potential for the $^5\Sigma_g$ state, based on the Vanderslice et al. results [9], which is indeed an approximation as compared with the present $^5\Sigma_g$ choice. Moreover he presumably used the $^7\Sigma_u$ potential of Ref. [9], while he fitted with the Hulburt-Hirschfelder function the remaining potentials (i. e. the states $^1\Sigma_g$, $^3\Sigma_u$).

It should be noted that the trend of $\bar{B}$ values versus temperature, calculated in the present work is also different from that reported in Reference [4]. The two series of results of Table 3, can be explained noting that Kessel'man et al. overestimate the contributions coming from $^5\Sigma_g$ and $^7\Sigma_u$ states, as compared with the present results (see Table 2), underestimating at the same time those from $^1\Sigma_g$ and $^3\Sigma_u$ states.

T °K	$\bar{B}$[a]	$\bar{B}$[4]
6000	0.79	5.05
7000	1.39	5.10
8000	1.65	5.11
9000	1.92	5.10
10000	2.19	5.05
11000	2.39	
12000	2.54	
13000	2.67	
14000	2.78	
15000	2.87	
16000	2.95	
17000	3.01	
18000	3.07	
19000	3.11	
20000	3.15	

Table 3. Average virial coefficient $\bar{B}$ (cm^3/mole).
[a] Present work.

Acknowledgements

The authors thank the "Laboratorio di Chimica quantistica ed energetica molecolare del C.N.R." of Pisa, and the "Centro di Studio per la Chimica dei Plasmi del C.N.R." of Bari for financial support of this work.

---

[1] M. Capitelli, E. Ficocelli, and E. Molinari, Z. Naturforsch. **26 a**, 672 [1971].

[2] P. P. Kulic, AIAA 9th Electric Propulsion Conference, Bethseda 1971.

[3] T. L. Hill, J. Chem. Phys. **23**, 617 [1955].

[4] P. M. Kessel'man, A. S. Bestuzkev, and Y. I. Blank, Teplofizika Vysokikh Temperatur **6**, 348 [1968].

[5] M. Capitelli and U. Lamanna, Chem. Phys. **14**, 261 [1976].

[6] D. D. Konowaloff and J. O. Hirschfelder, Phys. Fluids **4**, 637 [1961].

[7] M. Capitelli and R. S. Devoto, Phys. Fluids **16**, 1835 [1973].

[8] P. K. McCarrol, J. Chem. Phys. **37**, 805 [1962].

[9] J. T. Vanderslice, E. A. Mason, and E. R. Lippincott, J. Chem. Phys. **30**, 129 [1959].

[10] W. E. Meador, NASA, TR-R-68 [1960].

[11] We want to stress the importance of the present $^7\Sigma_u$ potential, which represents, to our knowledge, the first ab initio potential. The present potential can be used either for calculating the collision integrals (transport cross sections) of nitrogen atoms, or for generating the $N-N_2$, N_2-N_2 potentials according to the method outlined in Reference [9].