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Acoustic and Volumetric Virial Coefficients of Nitrogen

J. F. Estela-Uribe[1] and J. P. M. Trusler[2, 3]

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Speeds of sound in nitrogen were measured at temperatures between 170 and 400 K at amount-of-substance densities between 40 and 400 $\mathrm{mol \cdot m^{-3}}$. From these measurements, second and third acoustic virial coefficients were obtained. The parameters of two- and three-body isotropic intermolecular potential-energy models were optimized in a simultaneous fit to the second and third acoustic virial coefficients and the ordinary second and third virial coefficients of nitrogen reported by Nowak et al. The results, which shows that the acoustic and ordinary virial coefficients are mutually consistent, may be used to predict second and third virial coefficients, and their acoustic counterparts, over a wide range of temperatures. The parameters of an anisotropic site-site potential-energy model were also obtained from a fit to the acoustic and ordinary second virial coefficients alone.

KEY WORDS: intermolecular potential; nitrogen; speed of sound; virial coefficients.

1. INTRODUCTION

The second virial coefficient B of nitrogen is known with high accuracy over an extended range of temperatures [1]. The corresponding second acoustic virial coefficient β_a is also known from previous measurements with high accuracy at temperatures between 80 and 373 K [2]. β_a is given by

$$\beta_a = 2B + 2(\gamma_0 - 1)\, T(dB/dT) + \{(\gamma_0 - 1)^2/\gamma_0\}\, T^2(d^2B/dT^2) \tag{1}$$

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[1] Facultad de Ingeniería, Universidad Javeriana, Calle 18 118-250, Cali, Colombia.

[2] Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BY, United Kingdom.

[3] To whom correspondence should be addressed.

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where γ_0 is the ratio of the perfect-gas heat capacity at constant pressure to that at constant volume. It has been demonstrated clearly that the values of B and β_a for nitrogen obtained in the most careful experiments are mutually consistent to within experimental uncertainties of the order of 0.25 $\mathrm{cm^3 \cdot mol^{-1}}$ [3]. However, it was also noted that previous work had failed to determine the *third* acoustic virial coefficient,

$$\gamma_a = \{(\gamma_0 - 1)/\gamma_0\}\{B + (2\gamma_0 - 1)\,T(dB/dT) + (\gamma_0 - 1)\,T^2(d^2B/dT^2)\}^2 + \gamma_0^{-1}\{(2\gamma_0 + 1)\,C + (\gamma_0^2 - 1)\,T(dC/dT) + \tfrac{1}{2}(\gamma_0 - 1)^2\,T^2(d^2C/dT^2)\} \tag{2}$$

precisely over a wide range of temperatures. Accordingly, one objective of the present study was to make precise measurements of both β_a and γ_a for nitrogen over a wide range of temperatures. A second objective was to test for consistency between the new third acoustic virial coefficients and the most reliable ordinary third virial coefficients C available in the literature. The method by which consistency was judged involved fitting simultaneously the parameters of model two- and three-body intermolecular potential functions to experimental values of β_a, γ_a, B, and C. As an additional benefit, these model potentials are themselves useful tools for interpolating and extrapolating the experimental data.

The experimental measurements of the speed of sound described herein were part of an experimental program intended to validate the development of a new accurate equation of state for natural gas systems [4]. The spherical-resonator technique used in this work is based on a detailed acoustic model [5] which yields the quotient of the speed of sound and the zero-pressure radius of the resonator. The latter is obtained by means of calibration measurements with a gas such as argon or nitrogen for which the zero-density speed of sound is known with high accuracy. Thus, the present measurements were useful also as a means of re-calibrating the radius of our spherical resonator over an extended temperature range.

2. EXPERIMENTAL PROCEDURE AND RESULTS

The measurements were carried out on seven isotherms between 170 and 400 K with a spherical resonator that has been described elsewhere [6]. Typically, seven to ten evenly spaced measurements were made on each isotherm at pressures corresponding to amount-of-substance densities between 40 and 400 $\mathrm{mol \cdot m^{-3}}$. The nitrogen used was supplied by the British Oxygen Company with a certified mole-fraction purity of 0.999999.

The speeds of sound u were determined from the resonance frequencies of the lower four radial modes according to the acoustic model [5, 6]:

$$u/a_0 = (2\pi a/a_0)\left(f_{0n} - \sum_j \Delta f_j\right)\Big/ \nu_{0n} \tag{3}$$

Here, a is the radius of the resonator at the temperature and pressure in question, a_0 is the corresponding zero-pressure radius, f_{0n} is the observed resonance frequency of the radial mode designated $(0, n)$, ν_{0n} is the corresponding eigenvalue, and Δf_j are corrections to the resonance frequency due to departures from a zeroth-order model. These corrections arise from the thermal boundary layer at the wall of the resonator, coupling between gas and shell motion, dissipation in the bulk of the fluid, and geometric imperfections. The thermodynamic and transport properties required in the calculation of these corrections were taken from the Lee–Kesler equation of state [7] and correlation of Vesovic et al. [8], respectively. The agreement between the speeds of sound obtained from the individual radial modes was always better than $\pm 5 \times 10^{-6}\langle u \rangle$ in this work.

In the case of nitrogen, the speeds of sound obtained from Eq. (3) are not exactly equivalent to the thermodynamic quantity $u_0 = [(\partial p/\partial \rho)_S]^{1/2}$. This condition arises because the vibrational relaxation time of nitrogen is exceptionally long [9], with the consequence that the vibrational degree of freedom is not in thermal equilibrium with the translational and rotational modes during the acoustic cycle. Under these conditions, the measured speed of sound cannot be compared directly with the predictions of an equation of state. The extent of this effect in nitrogen is detailed elsewhere [10], and it turns out that the period of the sound waves used in our experiments far exceeds the vibrational relaxation time at all temperatures and pressures. Consequently, the experimental speeds of sound u are related to u_0 by the simple formula [10]:

$$(u/u_0)^2 = (C_V/C_p)(C_p - C_{\text{vib}})/(C_V - C_{\text{vib}}) \tag{4}$$

Here, C_V and C_p are the isochoric and isobaric molar heat capacities of the real gas and C_{vib} is the vibrational contribution to C_V. Values of the real-gas heat capacities at each state point were calculated with the AGA8-DC92 model [11]. C_{vib} was calculated at each temperature from the harmonic oscillator model with vibrational characteristic temperature $\theta_{\text{vib}} = 3395$ K [12]. As C_{vib} increases rapidly with temperature, the extent of the correction calculated from Eq. (4) also increases with temperature. Indeed, the correction is negligible for temperatures below 190 K but it reaches about 0.08 per cent at $T = 400$ K.

The mean values $\langle u_0/a_0 \rangle$ of (u_0/a_0) obtained from the four radial modes were analyzed on each isotherm in terms of the virial-like expansion

$$\langle u_0/a_0 \rangle^2 = (A_0/a_0^2)(1 + \beta_a \rho_n + \gamma_a \rho_n^2 + \cdots) \tag{5}$$

Here, $A_0 = RT\gamma_0/M$, M is the molar mass, and ρ_n is the amount-of-substance density. We choose an expansion in powers of ρ_n, rather than one in the experimental quantity p, because the former usually converges more rapidly than the latter, particularly at low temperatures. The amount-of-substance densities were calculated at the experimental temperatures and pressures from the virial equation of state truncated after the third virial coefficient. The second and third virial coefficients used here were calculated from the isotropic Maitland–Smith potential and the Axilrod–Teller triple-dipole potential described below with parameters from Ref. 3. An analysis shows that errors in these virial coefficients do not affect the values of β_a obtained from Eq. (5). The value of γ_a obtained is also unaffected by errors in C but it will be in error by $\delta B \cdot \beta_a$ if there is an error δB in the second virial coefficient. In the present case, plausible errors in B are less than 1 $\text{cm}^3 \cdot \text{mol}^{-1}$ and the consequences for γ_a are therefore small. Three-term fits sufficed to accommodate the experimental data to better than $1.5 \times 10^{-6} \langle u_0/a_0 \rangle$, and from these (A_0/a_0^2), β_a and γ_a were obtained.

As discussed in Refs. 2 and 10, the molar mass of nitrogen may be evaluated from experimental measurements of isotopic composition, together with the masses of the ^{14}N and ^{15}N atoms, with an uncertainty of about $1 \times 10^{-6} M$. The perfect-gas heat capacities may be evaluated with similarly small uncertainty [2, 10] from spectroscopic data including the rotational constant, centrifugal distortion constant, and the vibrational characteristic temperature. Consequently, A_0 may be obtained for nitrogen with much the same accuracy as for argon and thus the values of (A_0/a_0^2) form an excellent basis for the determination of the zero-pressure radius of the resonator. Accordingly, we obtained a_0 in that way and proceeded to compute absolute values of the "thermodynamic" (zero-frequency) speeds of sound from $\langle u_0/a_0 \rangle$; the results are given in Table I. Three of the isotherms investigated in this work ($T = 250$, 300, and 350 K) were also studied by Costa Gomes and Trusler [10]. We note that present results agree with values interpolated from the data of Costa Gomes and Trusler to within ±0.001 per cent in all cases.

The acoustic virial coefficients are reported in Table II together with uncertainties which include two standard deviations, as estimated from the variance-co-variance matrix, and allowances for systematic uncertainties. A comparison between our results at $T = 190$ K and those of Ewing and Trusler [2] at $T = 189.99$ K, reveals a difference in β_a of just (0.05 ± 0.12)

Table I. Zero-Frequency Speeds of Sound in Nitrogen

p (MPa)	u_0 $(\mathrm{m \cdot s^{-1}})$	p (MPa)	u_0 $(\mathrm{m \cdot s^{-1}})$
	$T = 170$ K		
0.49971	263.828	0.19945	264.984
0.44987	264.017	0.14963	265.179
0.39990	264.209	0.09981	265.375
0.34971	264.402	0.04984	265.573
0.29961	264.595	0.02502	265.672
0.24941	264.790		
	$T = 190$ K		
0.60346	279.678	0.24033	280.437
0.50913	279.869	0.15108	280.632
0.41925	280.055	0.06067	280.833
0.32881	280.247		
	$T = 215$ K		
0.68335	298.418	0.27080	298.674
0.57520	298.478	0.17258	298.746
0.46912	298.542	0.07053	298.825
0.36320	298.611		
	$T = 250$ K		
0.80204	322.771	0.43900	322.528
0.67789	322.686	0.31851	322.456
0.66986	322.684	0.21026	322.395
0.55883	322.605	0.06962	322.322
	$T = 300$ K		
0.89729	354.462	0.29907	353.476
0.79755	354.292	0.19952	353.320
0.69760	354.124	0.14918	353.242
0.59787	353.959	0.09947	353.166
0.49852	353.796	0.04979	353.090
0.39860	353.635		
	$T = 350$ K		
1.20587	383.809	0.47750	382.207
1.01607	383.384	0.29825	381.826
0.83620	382.986	0.11920	381.450
0.65531	382.591		
	$T = 400$ K		
1.41522	410.773	0.55642	408.646
1.18476	410.195	0.34174	408.126
0.97459	409.672	0.13539	407.631
0.77004	409.168		

Table II. Second β_A and Third γ_A Acoustic Virial Coefficients of Nitrogen

T (K)	β_a ($\mathrm{cm^3 \cdot mol^{-1}}$)	γ_a ($\mathrm{cm^6 \cdot mol^{-2}}$)
170	-42.29 ± 0.10	5210 ± 200
190	-25.51 ± 0.10	4780 ± 200
215	-9.79 ± 0.10	4580 ± 200
250	6.14 ± 0.10	4250 ± 200
300	21.31 ± 0.10	4170 ± 200
350	31.56 ± 0.10	3880 ± 200
400	38.73 ± 0.10	3720 ± 200

$\mathrm{cm^3 \cdot mol^{-1}}$ and a difference in γ_a of (220 ± 500) $\mathrm{cm^6 \cdot mol^{-2}}$. Similarly close agreement in β_a is found at all temperatures but the agreement in γ_a deteriorates somewhat at higher temperatures where the results of Ewing and Trusler approach a nearly constant value of around 4000 $\mathrm{cm^6 \cdot mol^{-2}}$ at $T \geqslant 240$ K while the values obtained in this work decrease steadily with temperature. It is our opinion that the higher densities included in the present study (approximately twice the greatest density studied by Ewing and Trusler) make the present results for γ_a the more reliable.

3. INTERMOLECULAR POTENTIALS AND VIRIAL COEFFICIENTS

Intermolecular potential parameters were fitted for both site–site and isotropic Maitland–Smith intermolecular potential models. The site–site model gives the pair-wise intermolecular potential $U(r, \Omega)$ in the form

$$U(r, \Omega) = \tfrac{1}{4} \sum_{i=1}^{2} \sum_{j=1}^{2} U_{SS}(r_{ij}) \tag{6}$$

where r is the separation of the centres of mass, Ω denotes the set of co-ordinates which specify the relative orientation of the two molecules, and r_{ij} is the distance between site i on molecule 1 and site j on molecule 2. In the present case, the two sites on each molecule were located on the atomic centres 109 pm apart. The site–site interaction potential used was the Maitland–Smith function [13]

$$U_{SS}(r) = \varepsilon \left[\left(\frac{6}{n(r) - 6} \right) \left(\frac{r_\mathrm{m}}{r} \right)^{n(r)} - \left(\frac{n(r)}{n(r) - 6} \right) \left(\frac{r_\mathrm{m}}{r} \right)^{6} \right] \tag{7}$$

where r_m is the separation at which the potential reaches its minimum of $-\varepsilon$. The exponent $n(r)$ is given by

$$n(r) = m + \gamma\{(r/d) - 1\} \tag{8}$$

where $d = r_m(6/m)^{1/(m-6)}$ is the separation at which the potential crosses zero. The adjustable parameters are therefore d (or r_m), ε, γ, and m. In the present case, γ was constrained to the value 12 and the remaining parameters were fitted to the β_a data consolidated from the present work and that of Ewing and Trusler, covering temperatures from 80.05 to 400 K. A non-linear optimization method was used which minimized the statistic

$$\chi^2 = \frac{1}{(N-m)}\left[\sum_{i=1}^{N}\left[(y_i - y_{\text{fit},i})/\sigma_i\right]^2\right] \tag{9}$$

where σ_i is the standard deviation associated with the ith experimental datum y_i, $y_{i,\text{fit}}$ is the corresponding value calculated form the model, N is

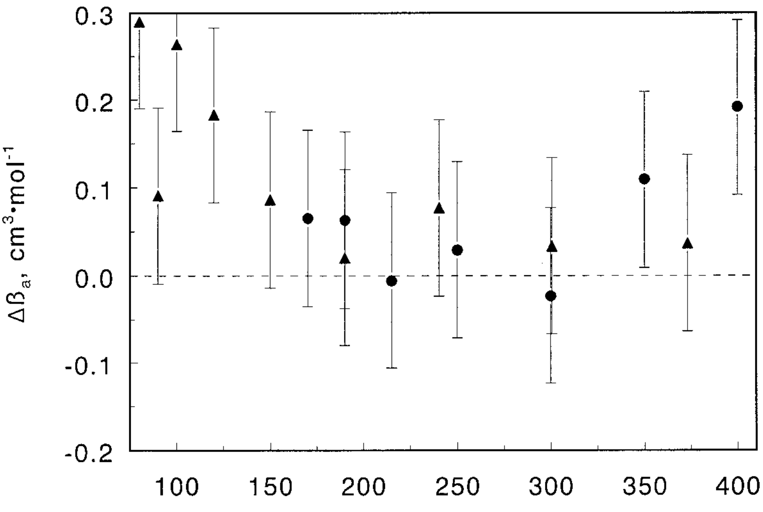

Fig. 1. Deviations $\Delta\beta_a = \beta_a(\text{exp}) - \beta_a(\text{fit})$ of second acoustic virial coefficients of nitrogen with respect to those calculated from a site–site MS intermolecular potential. ▲ Ewing and Trusler [2]; ● this work.

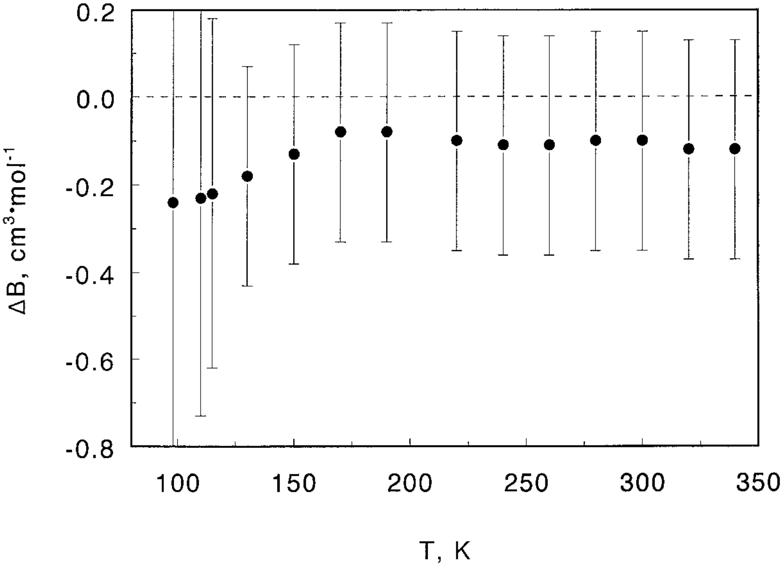

Fig. 2. Deviations $\Delta B = B(\text{exp}) - B(\text{fit})$, of second virial coefficient of nitrogen with respect to those calculated with a site–site MS intermolecular potential. ● Nowak et al. [1].

the number of points in the fit, and m is the number of free parameters. The calculation method of Ewing and Trusler [2] was used to obtain B and its temperature derivatives. The first translational and rotational quantum corrections were included in these calculations. The results obtained were: $d = 0.33375$ nm; $\varepsilon/k = 169.12$ K; $m = 11.553$; $\gamma = 12$; and $\chi^2 = 1.2$.

The experimental and calculated second acoustic virial coefficients are compared in Fig. 1. This comparison shows remarkably good agreement between the present results and those of Ewing and Trusler [2]. Also, the overall agreement with the calculated values is good; the worst discrepancy being only about 0.3 $\text{cm}^3 \cdot \text{mol}^{-1}$ at the lowest temperature. In Fig. 2, we compare ordinary second virial coefficients calculated form the site–site model with the recent highly-accurate experimental data of Nowak et al. [1]; the agreement is good.

Although the site–site model is clearly very satisfactory as a means of correlating second virial coefficients, application of such models to the calculation of third virial coefficients, while perfectly possible, is computationally demanding. Accordingly, in proceeding to a full simultaneous analysis of both second and third virial coefficients (ordinary and acoustic), the site–site potential was abandoned in favor of an isotropic Maitland–

Smith potential. The repulsive exponent $n(r)$ used in this case was written in the slightly different form

$$n(r) = m + \gamma\{(r/r_{\mathrm{m}}) - 1\} \tag{10}$$

The parameter γ was constrained to the constant value adopted in Ref. 3. In computing the potential energy of clusters of three molecules, the non-additive Axilrod–Teller triple-dipole potential ΔU was included:

$$\Delta U = \psi_{123}(r_{12} r_{13} r_{23})^{-3}\,(1 + 3\cos\theta_1 \cos\theta_2 \cos\theta_3) \tag{11}$$

Here, r_{ij} is the distance between molecules i and j, θ_i is the angle at molecule i subtended by molecules j and k, and ψ_{123} is the three-body dispersion coefficient which we treated as an adjustable parameter. The calculation method has been described elsewhere [3, 14]. The leading translational quantum corrections to both B and C (and β_{a} and γ_{a}) were implemented. The data used in the fit were the second and third virial coefficients of Nowak et al. [1], the second and third acoustic virial coefficients of the present work, and the second acoustic virial coefficients of Ewing and Trusler [2]. The results obtained were $r_{\mathrm{m}} = 0.39224$ nm; $\varepsilon/k = 134.91$ K; $\gamma = 18$; $m = 18.236$; $y_{123}/k = 1.008 \times 10^{-3}$ $\mathrm{K} \cdot \mathrm{nm}^9$; and $\chi^2 = 1.9$.

Deviations with respect to the fit are presented in Figs. 3 to 6. Figure 3 shows the deviations of the second acoustic virial coefficients. The agreement with the model is within $\pm 0.25\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$, except at the lowest temperature where the datum of Ewing and Trusler differs from the model by about $0.5\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$. This pattern of deviations is quite similar to that reported by Trusler et al. [3], who obtained a similar set of potential parameters from the second acoustic virial coefficients of Ewing and Trusler alone. Comparing Figs. 1 and 3, we see that there is evidence that the isotropic potential model is not quite as accurate as the site–site model; however, the deterioration is slight.

Figure 4 shows good agreement between the third acoustic virial coefficients of this work and the model throughout the temperature range from 170 to 400 K. The data of Ewing and Trusler (which were not included in the fit) are also represented reasonably well at temperatures down to 120 K. At temperatures below 100 K, the model deviates considerably from the experimental results.

Figure 5 compares the ordinary second virial coefficients of Nowak et al. with the predictions of the model. The agreement at temperatures less than 170 K is not as good as in the case of the site–site potential; nevertheless, the overall agreement is still quite satisfactory. Finally, Fig. 6 show good agreement of the experimental third virial coefficients.

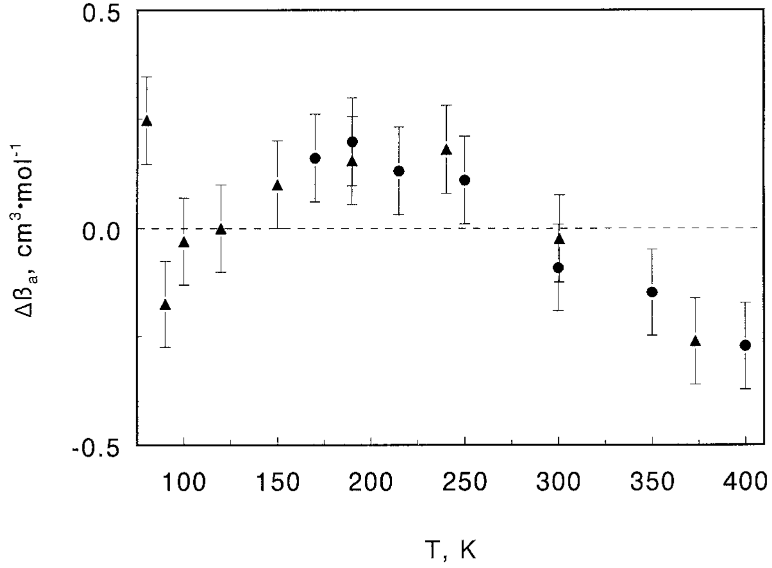

Fig. 3. Deviations $\Delta\beta_a = \beta_a(\exp) - \beta_a(\text{fit})$ of second acoustic virial coefficients of nitrogen with respect to those calculated with an isotropic MS intermolecular potential. ▲ Ewing and Trusler [2]; ● this work.

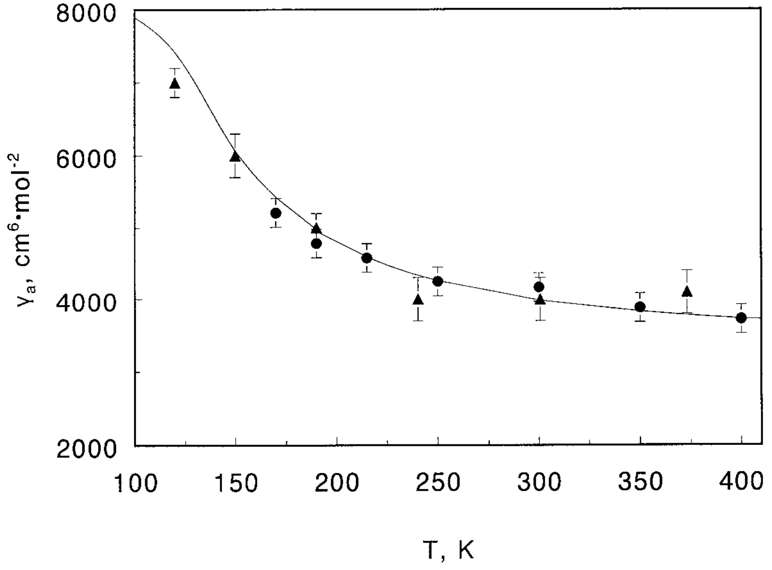

Fig. 4. Third acoustic virial coefficient γ_a of nitrogen. ▲ Ewing and Trusler [2]; ● this work; —— isotropic Maitland–Smith intermolecular potential.

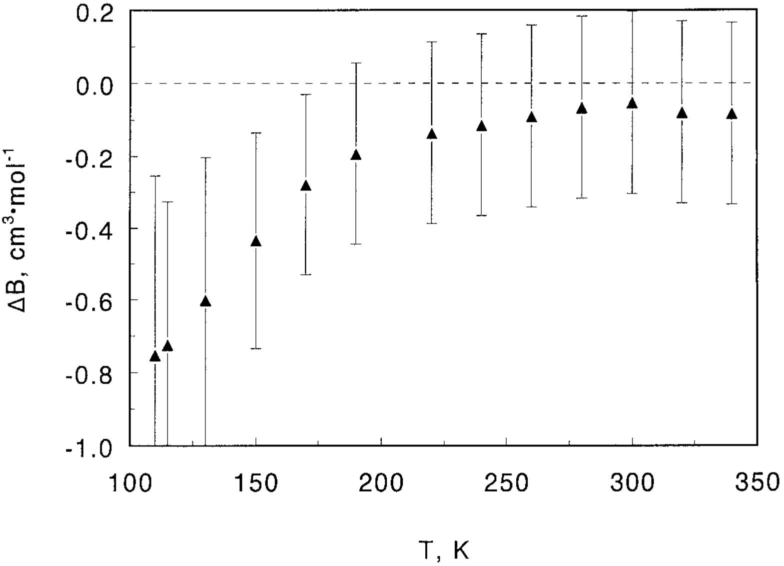

Fig. 5. Deviations $\Delta B = B(\exp) - B(\mathrm{fit})$, of second virial coefficient of nitrogen with respect to those from an isotropic MS intermolecular potential. ▲ Nowak et al. [1].

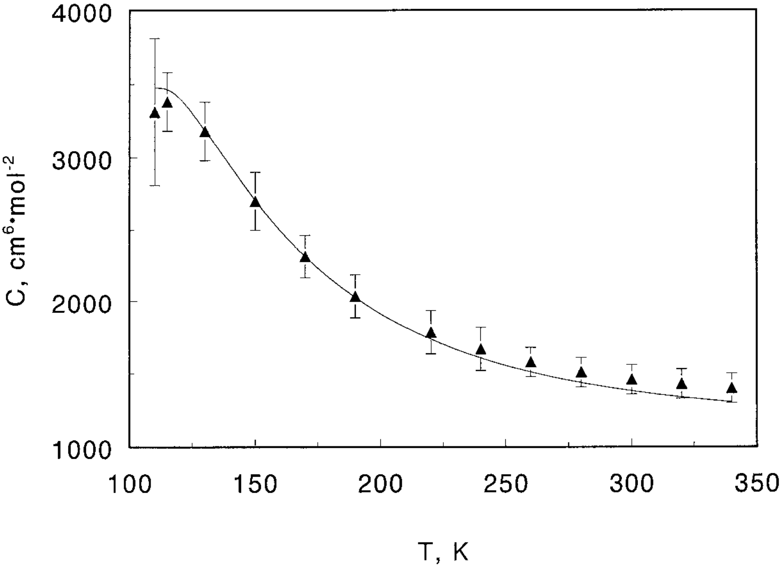

Fig. 6. Third virial coefficient C of nitrogen. ▲ Nowak et al. [1]; —— isotropic Maitland–Smith intermolecular potential.

4. CONCLUSION

Reliable second and third acoustic virial coefficients have been obtained for nitrogen in the temperature range 170 to 400 K. The latter are of notably higher accuracy than previous determinations. The calculations presented in this paper lead to the conclusion that both isotropic and anisotropic intermolecular potential models are able to represent the experimental ordinary and acoustic second virial coefficients almost within the experimental uncertainties. The site–site model is slightly better but has the disadvantage of being difficult to apply to the third virial coefficients. On the other hand, the isotropic model does not fit β_{a} quite as well but it is nevertheless good and can be used easily for C and γ_{a} with good accuracy. The available third acoustic virial coefficients are consistent with the ordinary third virial coefficients of Nowak et al. in the overlapping temperature range.

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