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Direct Determination of the Second Refractivity Virial Coefficient of Methane, Nitrogen, and Five of Their Mixtures[1]

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The experimental technique for the direct determination of the second refractivity virial coefficient is described. The absolute measurement of the refractive index n combined with an expansion technique for obtaining the higher-order coefficients of the Lorentz–Lorenz expansion

$$\mathrm{LL} = [(n^2-1)/(n^2+2)]\,\rho^{-1} = A_n + B_n\rho + C_n\rho^2 + \cdots$$

leads to precise values of density ρ. A_n is the ideal molar refractivity, which is readily determined from the absolute measurements of n in terms of pressure, whereas B_n, C_n,... are the higher-order molar refractivity virial coefficients, which are obtained from expansion experiments. The expansion method consists in measuring the sum of optical path lengths of two similar cells: one of them is filled with the gas at density ρ, and the other is evacuated. After the expansion the density is nearly halved and one measures again the optical path lengths. In order to cancel the small differences in volume and path lengths between the two cells, the process is reversed. Because the linear term in density remains the same before and after the expansion and only the quadratic and higher-order terms change, we can determine the refractivity virial coefficients B_n, C_n,... from the change in the optical path lengths. The measurements for the determination of B_n and C_n for methane, nitrogen, and five mixtures were carried out at 323.15 K and pressures up to 450 bar. The mixed-interaction constant for methane and nitrogen derived from the experimental second refractivity virial coefficient is compared with those obtained from the geometric and linear mixing rule as well as Lorentz combination.

KEY WORDS: expansion technique; Lorentz–Lorenz function; mixed interaction; refractive index; refractivity virial coefficient.

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1. INTRODUCTION

The Lorentz–Lorenz equation can be expressed in a virial form [1, 2] as

$$\mathrm{LL} = [n^2 - 1)/(n^2 + 2)]\, \rho^{-1} = A_n + B_n \rho + C_n \rho^2 + \cdots \tag{1}$$

where n is the refractive index, ρ is the molar density, and A_n, B_n, and C_n are, respectively, the first, the second, and the third refractivity virial coefficients. The refractivity virial coefficients of the mixture are related to the refractivity virial coefficients of the components [3, 4, 5] as

$$B_n = \sum \sum x_i x_j (B_n)_{ij} \tag{2}$$

$$C_n = \sum \sum \sum x_i x_j x_k (C_n)_{ijk} \tag{3}$$

In Eqs. (2) and (3), constants with repeated suffixes, such as $(B_n)_{11}$, refer to pure components, and their values are known. Those with dissimilar suffixes, such as $(B_n)_{12}$, are properties of the mixture, arising from interaction between unlike molecules; these may be termed mixed-interaction constants.

The measurements of B_n and C_n have been carried out using a differential technique. The advantage of the differential technique is that the second refractivity virial coefficient is measured directly compared to the absolute method, where one finds $B_n \rho$ as a small correction to A_n. Most of the values of B_n have been deduced by measuring the refractive index of a gas as a function of its density. As the second term in Eq. (1) contributes a very small fraction, a small error in density may easily lead to errors as high as 100% in B_n [6, 7]. The technique of direct determination of B_n was first developed by Buckingham et al. [8] in the determination of the second dielectric virial coefficient and applied to the measurement of refractive index by St-Arnaud and Bose [1, 9] and Buckingham and Graham [10].

2. EXPERIMENTAL

The expansion technique consists in measuring the sum of optical path lengths of two similar cells (Fig. 1), where one of them is filled with gas at density ρ and the other is evacuated. When the valve between the two cells is opened, the density is nearly halved and one measures again the optical path lengths. Because the linear term in density remains the same before and after the expansion and only the quadratic and higher orders change, we can determine B_n and C_n from the change in the optical path lengths.

The Lorentz–Lorenz equation for the refractive index of a gas is given by Eq. (1). If we now develop $(n-1)\, \rho^{-1}$ as a function of density, we find

$$(n-1)\, \rho^{-1} = A_m + B_m \rho + C_m \rho^2 + \cdots \tag{4}$$

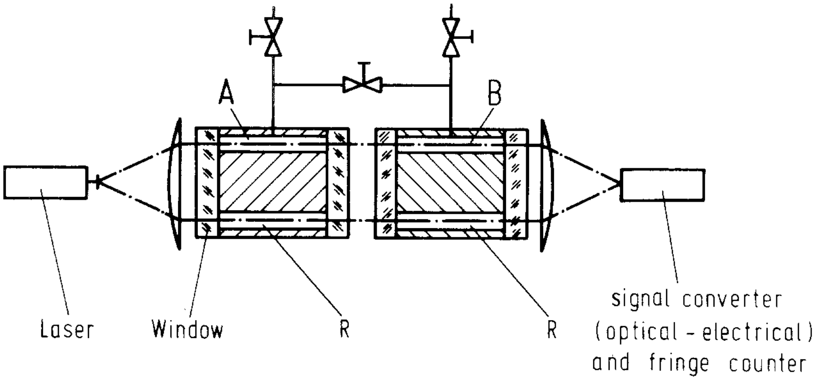

Fig. 1. Schematic view of the apparatus for the measurement of the refractive index: A and B are two measuring cells; R is the reference cell.

The coefficients of Eq. (4) are related to those of Eq. (1) through the following relations:

$$A_n = (2/3)\,A_m \tag{5}$$

$$B_n = (2/3)\,B_m - (1/9)\,A_m^2 \tag{6}$$

$$C_n = (2/3)\,C_m - (2/9)\,A_m B_m - (4/27)\,A_m^3 \tag{7}$$

Consider the volumes A and B (Fig. 1) to be given by $V_A = V(1+\delta)$ and $V_B = V(1-\delta)$, where δ is small. Let the optical path length of each volume be given by $l_A = l(1+\Delta)$ and $l_B = l(1-\Delta)$, where Δ is also small. If A initially contains a gas of refractive index n_A, at a density ρ_A, while B is evacuated, one observes a change (D_A) in refractive index on opening the valve between cell A and cell B. D_A is defined by the relation

$$D_A = (n_A - 1)(1+\Delta) - 2(n_{AB} - 1) \tag{8}$$

where n_{AB} is the refractive index in both cells after the expansion. One then gets

$$D_A = A_m(\Delta - \delta)\,\rho_A + \frac{B_m}{2}\,[1 + 2(\Delta - \delta)]\,\rho_A^2 + \frac{C_m}{4}\,[3 + (4\Delta - 3\delta)]\,\rho_A^2 + \cdots \tag{9}$$

Similarly, if B contains a gas with refractive index n_B and density ρ_β and if A is evacuated, the expansion from B to A leads to a corresponding change

D_B in the index of refraction. D_B, defined in the same way as D_A, is given by

$$D_B = -A_m(\Delta-\delta)\,\rho_B + \frac{B_m}{2}[1-2(\Delta-\delta)]\,\rho_B{}^2 + \frac{C_m}{4}[3-(4\Delta-3\delta)]\,\rho_B{}^3 + \cdots \tag{10}$$

From Eq. (4), ρ_A and ρ_B can be expressed in terms of n_A-1 and n_B-1 as

$$\begin{aligned}\rho_A &= (n_A-1)/A_m - (n_A-1)^2 B_m/A_m{}^3\\ &\quad + (n_A-1)^3[(2B_m{}^2 - A_m C_m)/A_m{}^5] + \cdots \end{aligned}\tag{11}$$

$$\begin{aligned}\rho_B &= (n_B-1)/A_m - (n_B-1)^2 B_m/A_m{}^3\\ &\quad + (n_B-1)^3[(2B_m{}^2 - A_m C_m)/A_m{}^5] + \cdots \end{aligned}\tag{12}$$

On replacing ρ_A and ρ_B in Eqs. (9) and (10) with Eqs. (11) and (12), one gets by combining Eqs. (9) and (10)

$$\begin{aligned}&D_A/(n_A-1) + D_B/(n_B-1)\\ &\quad = (B_m/2A_m^2)[(n_A-1)+(n_B-1)]\\ &\qquad + [(3A_m C_m - 4B_m{}^2)/4A_m{}^4][(n_A-1)^2+(n_B-1)^2]\end{aligned}\tag{13}$$

Equation (13) can be written in a more convenient form:

$$\begin{aligned}F = (\Delta K_{AB})/K_A + (\Delta K_{BA})/K_B &= [B_m/(2A_m{}^2)](\lambda/l)[K_A+K_B]\\ &\quad + [(3A_m C_m - 4B_m{}^2)/4A_m{}^4](\lambda/l)^2[K_A{}^2+K_B{}^2] + \cdots\end{aligned}\tag{14}$$

where K_A and K_B correspond to the absolute number of fringes in cells A and B before expansion; ΔK_{AB} and ΔK_{BA} are, respectively, the number of fringes observed during the expansion from A to B and from B to A. The total fringe count to vacuum, such as K_A, is related to the absolute value of the refractive index n_A, by means of the formula

$$n_A = (K_A\lambda/l_A) + 1 \tag{15}$$

where λ is the vacuum wavelength of light and l_A is the spacer length at the temperature of the fluid.

The measurements are carried out in such a way that K_A is nearly equal to K_B. The variable in the second term of Eq. (14) can then be written as $(K_A+K_B)^2/2$.

On plotting F against $(K_A + K_B)$, we get B_n and C_n from a least-squares fit of a polynomial of the form

$$y = ax + bx^2 + cx^3 + \cdots \qquad (16)$$

The error in F decreases with pressure and hence the higher-pressure measurements are weighted more.

The first refractivity virial coefficient A_n and the second pressure virial coefficient B_p are obtained by making an absolute measurement of the refractive index as a function of pressure.

Replacing the density ρ in Eq. (1) with

$$P/RT = \rho + B_P \rho^2 + \cdots \qquad (17)$$

we obtain

$$(n^2 - 1)/(n^2 + 2) = A_n P/RT + (B_n - A_n B_P)(P/RT)^2 + \cdots \qquad (18)$$

The refractive index measurements of methane, nitrogen, and five of their mixtures were carried out using a grating interferometer. The advantage of a grating interferometer is that it performs a reversible counting and generates a DC compensated signal from the interference fringes. The details of the grating interferometer and pressure measuring device are given in our other article in this volume [13].

3. RESULTS AND DISCUSSION

Refractive index measurement for methane, nitrogen, and five mixtures of methane and nitrogen were made at 323.15 K and up to pressures of

Table I. Refractivity Virial Coefficients of Methane, Nitrogen, and Methane–Nitrogen Mixtures

Gas (mole fraction)	Temp. (K)	λ (nm)	$A_n \times 10^6$ $(\mathrm{m^3 \cdot mol^{-1}})$	$B_n \times 10^{12}$ $(\mathrm{m^6 \cdot mol^{-2}})$	$C_n \times 10^{18}$ $(\mathrm{m^9 \cdot mol^{-3}})$	Reference No.
N_2	323.15	633.0	4.446 ± 0.001	0.64 ± 0.08	-107 ± 5	Our work
13.52% $CH_4 + N_2$			4.734 ± 0.001	1.0 ± 0.2	-124 ± 13	
25.02% $CH_4 + N_2$			4.979 ± 0.001	1.5 ± 0.3	-152 ± 23	
38.69% $CH_4 + N_2$			5.270 ± 0.001	2.0 ± 0.3	-166 ± 20	
49.92% $CH_4 + N_2$			5.509 ± 0.002	2.6 ± 0.4	-194 ± 42	
89.76% $CH_4 + N_2$			6.358 ± 0.002	5.1 ± 0.4	-296 ± 46	
CH_4			6.576 ± 0.002	5.83 ± 0.15	-326 ± 10	
CH_4	220	546.2	6.613 ± 0.002	6.1 ± 1.0	-320	11
	299	632.8	6.600 ± 0.002	7.15 ± 0.35	—	10
	302	632.8	6.553 ± 0.002	6.60 ± 0.38	—	1
	298	633.0	6.578 ± 0.002	6.14 ± 0.20	-345 ± 15	12

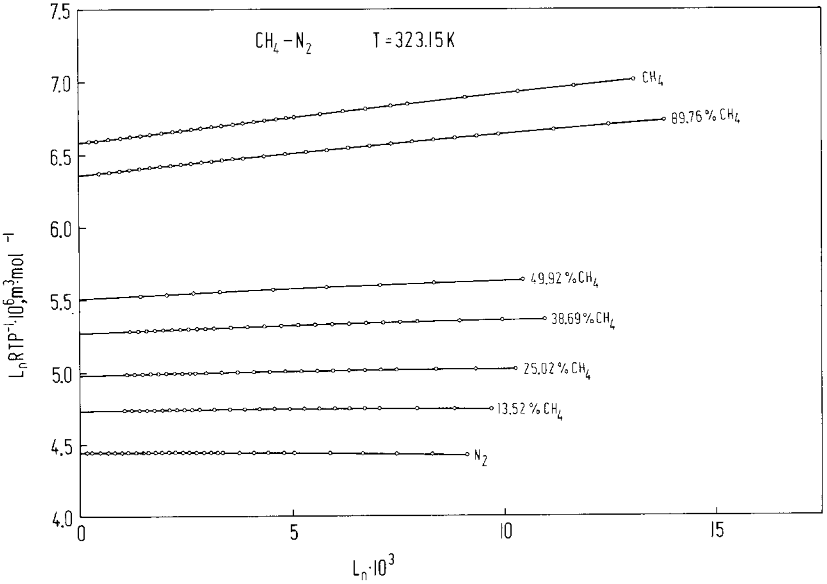

Fig. 2. L_nRT/P of methane, nitrogen, and their mixtures plotted as a function of L_n at 323.15 K. Points are experimental and curves are the least-squares fit.

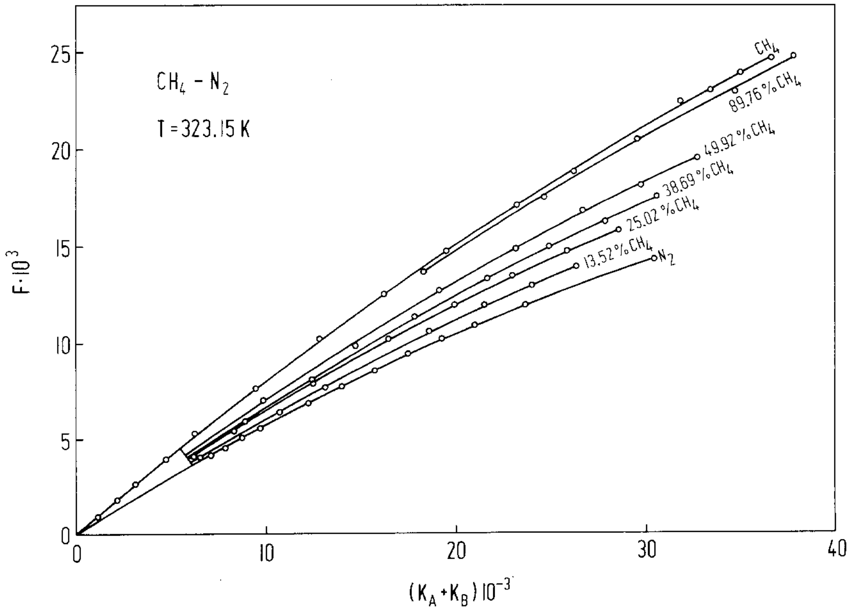

Fig. 3. Plots of the refractive index expansion function F against $K_A + K_B$. Points are experimental and curves are the least-squares fit.

450 bar. Table I gives the experimental values of A_n, B_n, and C_n of the pure gases and those of the mixtures. Figure 2 shows the function $L_n RT/P$ plotted in terms of L_n. The various A_n values are determined from the intercepts using the least-squares fit. In Fig. 3 we plot F against $K_A + K_B$ [Eq. (14)] and determine B_n and C_n from the least-squares fit for pure gases as well as the mixtures.

The values of the second and third refractivity virial coefficients, B_n and C_n, are plotted in Figs. 4 and 5 against the mole fraction x of N_2 in CH_4–N_2 mixtures.

The only criteria for precision of the mixed virial coefficient values are consistency as indicated by the error estimates listed in Table I, which are three standard deviations of the coefficients for the best least-squares fit, and the accuracy with which the results can be represented by the expected

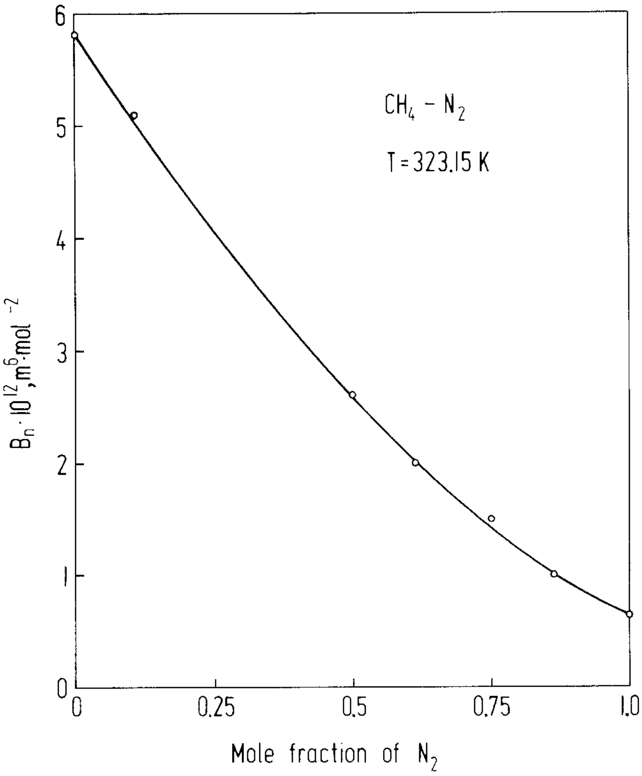

Fig. 4. Dependence of second refractivity virial coefficient B_n on mole fraction x of N_2 in CH_4–N_2 mixtures at 323.15 K.

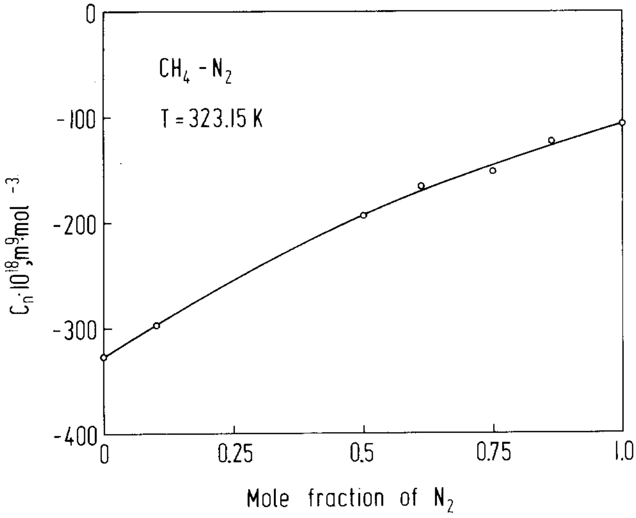

Fig. 5. Dependence of third refractivity virial coefficient C_n on mole fraction x of N_2 in CH_4–N_2 mixtures at 323.15 K.

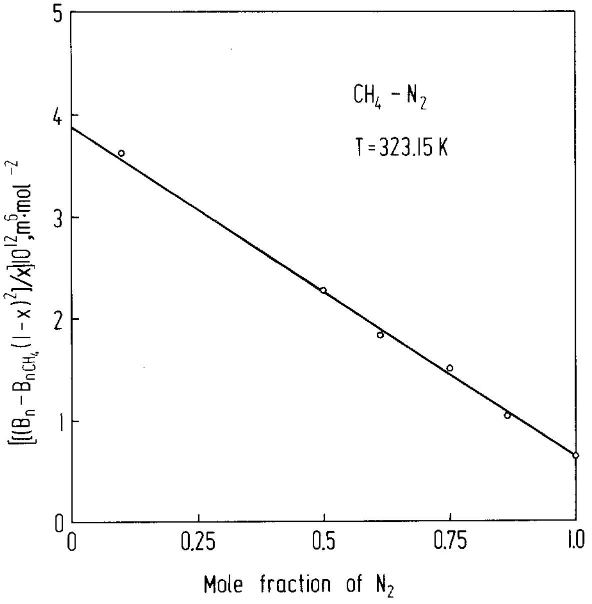

Fig. 6. Plot of $[B_n - B_{n\mathrm{CH}_4}(1-x)^2]\,x^{-1}$ as a function of mole fraction of x of N_2 in CH_4–N_2 mixtures at 323.15 K.

Table II. Mixed Second Refractivity Virial Coefficient from CH_4–N_2 Mixtures

		$(B_n)_{12}\,10^{12}\,(m^6 \cdot mol^{-2})$			
		expt.	Calculated		
Gas mixtures	Temp. (K)		Geometric rule	Linear rule	Lorentz combination
CH_4–N_2	323.15	1.95	1.93	3.23	2.36

form of dependence on composition, expressed by Eq. (2). On expanding Eq. (2), one gets

$$B_n = (B_n)_{11}(1-x)^2 + 2(B_n)_{12}\,x(1-x) + (B_n)_{22}\,x^2 \qquad (19)$$

where B_n is the second refractivity virial coefficient of the mixture, x is the mole fraction of nitrogen, $(B_n)_{11}$ and $(B_n)_{22}$ are, respectively, the second refractivity virial coefficients of methane and nitrogen, and $(B_n)_{12}$ is the mixed-interaction constant.

A plot of $[B_n - (B_n)_{11}(1-x)^2]\,x^{-1}$ against x is shown in Fig. 6. The intercept of the straight-line fit gives $(B_n)_{12} = 1.95 \times 10^{-12}\ m^6 \cdot mol^{-2}$.

The observed value (Table II) of the mixed-interaction constant $(B_n)_{12}$ agrees within 1% with the combination rule given by

$$(B_n)_{12} = [(B_n)_{11} \cdot (B_n)_{22}]^{\frac{1}{2}} \qquad (20)$$

The agreement is much worse with the linear mixing rule

$$(B_n)_{12} = [(B_n)_{11} + (B_n)_{22}]/2 \qquad (21)$$

or the Lorentz combination rule given by

$$(B_n)_{12} = [(B_n)_{11}^{\frac{1}{3}} + (B_n)_{22}^{\frac{1}{3}}]^3/8 \qquad (22)$$

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