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Determination of the Interaction Second Virial Coefficients for the Carbon Dioxide–Ethane System from Refractive Index Measurements

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The compressibility behavior of the CO_2–C_2H_6 system was investigated experimentally. In this work, the refractive indexes of the pure gases and the mixtures were measured using an optical apparatus. On the basis of these data, density and compressibility factors were computed using the Lorentz–Lorenz law. For the pure components, carbon dioxide and ethane, the data from the optical system were slightly adjusted by a fit to Burnett apparatus data measured separately. The experiments produced very accurate virial coefficients and refraction virial coefficients. This paper reports on the effect of temperature on the second and third virial coefficients. For the first refraction virial coefficient, no influence of temperature was found with the equipment used. The interaction second virial coefficient B_{12} (as a function of temperature) was computed from experimental data for the CO_2–C_2H_6 binary system. The data, for which an accuracy of $\pm 1.5\,\mathrm{cm^3 \cdot mol^{-1}}$ was estimated, are in agreement with the data published by Holste et al. [*AIChE J.* **28**:807 (1982)].

KEY WORDS: carbon dioxide; ethane; Lorentz–Lorenz law; mixtures; refraction virial coefficient; interaction second virial coefficient; compressibility factor.

1. INTRODUCTION

Exact information on the compressibility behavior of natural gases is essential for sales gas metering. To determine gas volumes, compressibility factors must be predicted accurately from an equation of state.

Existing methods of prediction [1, 2] do not provide the accuracy required and are sufficiently accurate only in a very narrow range [2, 3].

Both the European Gas Research Group (GERG) and the Gas Research Institute (GRI) of Chicago have therefore sponsored projects

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calling for the development of a highly accurate equation of state. Preliminary results of the GERG work [4, 5] and the GRI work [6] have been published. Both new equations have been derived exclusively from data for pure gases and their binary mixtures. For this work, a substantial–experimental data base has been developed by the GERG [7–9]. Further experimental work has been sponsored by the GRI [10, 11].

A system of major importance for natural gas measurement is the carbon dioxide–ethane binary system, since the pure gases are major constituents of natural gases. To determine the interaction parameters, which have an impact on equations of state, accurate experimental data are required.

This paper reports such experimental work.

2. MEASUREMENT METHODS

The compressibility of carbon dioxide and ethane was investigated using the Burnett apparatus and an optical system.

The Burnett method does not involve direct measurement of a gas volume or a gas mass. It is sufficient to measure pressure during a series of isothermal expansions from one chamber filled with a gas sample into a second chamber which is then evacuated [12].

The optical method does not necessitate direct gas volume or mass measurement either, since the density of the gas is derived from a known correlation between the index of refraction n and the density ρ. The method is, above all, fast, allowing a series of experimental data to be obtained in rapid succession.

The accuracy of the optical method is limited, since the specific refraction in the Lorentz–Lorenz law

$$r = \frac{n^2 - 1}{n^2 + 2}\frac{1}{\rho} \tag{1}$$

from which the density is predicted is not constant, but depends on the density and temperature T [13–16]. It is, however, possible to predict by calibration the part of the specific refraction which depends on density. For this purpose the data of another accurate test method, such as the Burnett apparatus, were used.

During a series of Burnett expansions, the experimental data for the isothermal line decrease as the pressure increases. For this reason, several series of expansion tests would be necessary for each isothermal line to obtain sufficient experimental data at high pressures. This approach therefore takes considerable time and is hence inefficient. The optical method is much better suited to generate a sufficiently dense set of data at high pressures. To calculate the density from the optical test data, the specific refraction is expanded in a virial series. The refraction virial coefficients were adjusted by a fit to the Burnett data.

Further, if both the Burnett apparatus and the optical system are used, a wide range of conditions can be covered by experiments. Whereas the Burnett apparatus can be employed in the gaseous phase above critical conditions, optical-system experiments can approach the vapor pressure curve of a pure gas or the two-phase region of a binary mixture.

Since the Burnett method is well known, this paper merely presents the optical method of measurement used for investigating the carbon dioxide–ethane system.

3. OPTICAL SYSTEM

The optical system exploits the simple correlation between the refractive index n and the density ρ expressed by the Lorentz–Lorenz law.

The optical apparatus consists essentially of two connected interferometers. One interferometer measures the refractive index of the sample gas, while the second instrument determines the refractive index of nitrogen at a fixed temperature. The two instruments are interconnected to adjust the nitrogen pressure to the pressure of the sample gas. The nitrogen interferometer was calibrated using the deadweight tester of the Burnett apparatus. For this reason, the sample gas pressure could be determined rapidly from the refractive index of nitrogen.

Figure 1 is a schematic of the grating interferometer incorporated in the optical apparatus. The interferometer consists of a sample gas chamber and a reference chamber. The refractive index of the sample gas is determined at a given temperature T and a pressure p of the sample gas in the test chamber (3) and under vacuum conditions while the gas in the reference chamber (4) is always under atmospheric conditions.

To measure the refractive index n of the sample gas, a laser beam is split into a test beam and a reference beam by diffraction grating. After traveling through the two chambers, the two coherent beams are reunited and display interference. If the path of the laser beam is changed in the test chamber by one wavelength, a full bright–dark–bright interference fringe will be produced. The second diffraction grating (10) before the reunification of the beam splits the interference pattern to show whether the phase difference is increasing or decreasing. The refractive index n is calculated from the interference fringe numbers k_n according to

$$n = \frac{\lambda}{l_0(1+\alpha t)} k_n + 1 \tag{2}$$

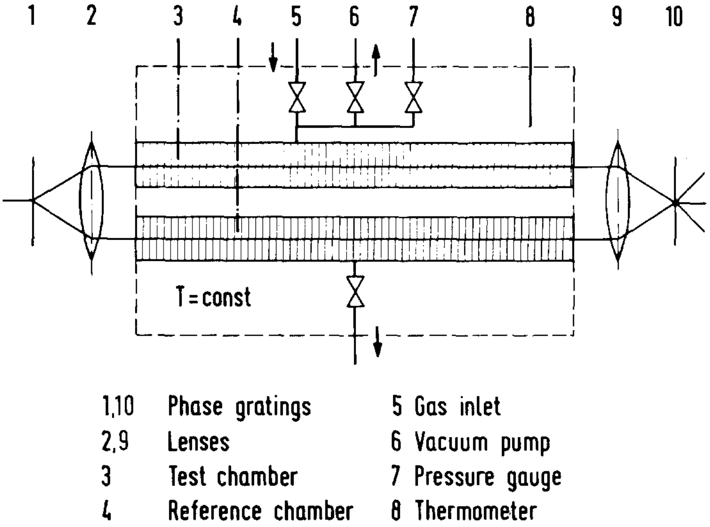

Fig. 1. Schematic diagram of the optical measuring device.

where λ is the wavelength (632.99 nm for the helium–neon laser used for the experiments), l_0 is the effective length of the test chamber at 0°C, and t is the temperature in degrees centigrade. In the experiments, the effective length l_0 of the test chamber was 249.897 mm and the coefficient of linear thermal expansion of the stainless-steel test chamber was $\alpha = 16.5 \times 10^{-6}\ \mathrm{K}^{-1}$. The number of the interference fringes from vacuum to the density measured in the test chamber is represented by k_n.

Temperature was measured and controlled using platinum resistance thermometers and mercury thermometers. The test apparatus is designed for a temperature range from 0 to 80°C. The uncertainty of temperature measurements is ± 0.01 K. For pressure measurement, the largest part of the uncertainty in the upper part of the pressure range is determined by the uncertainty of the deadweight tester. At a pressure above 6 bar, the uncertainty is 10^{-4}. In this pressure range, the resolution of the interferometer is by as much as 10^2 greater. Below 6 bar, the uncertainty is only 0.6 mbar. The accuracy of the refractive index measurement has been estimated to be approximately 1.5×10^{-4} above 5 bar. As for pressure measurement, the resolution of the interferometer is much greater.

4. OPTICAL-TEST DATA

The compressibility factor Z

$$Z = \frac{p}{RT\rho} \tag{3}$$

(where p is the pressure, R is the universal gas constant, T is the temperature, and ρ is the molar density) may be computed from the refractive index n, if the specific refraction

$$r = \frac{n^2 - 1}{n^2 + 2} \frac{1}{\rho} = \frac{L_n}{\rho} \tag{4}$$

(where L_n is the refraction) as defined by the Lorentz–Lorentz law is known. The dependence of the Lorentz–Lorentz law on density is normally described by the virial equation

$$r = A_n + B_n \rho + C_n \rho^2 + \cdots \tag{5}$$

where A_n, B_n, C_n,..., are the first, second, third, and further refraction virial coefficients. If the series is truncated after the third term, then on the basis of Eqs. (3) to (5),

$$\rho = \frac{L_n}{A_n} - \frac{L_n}{A_n} \left(\frac{B_n}{A_n} \right)^2 + \frac{2B^2{}_n - A_n C_n}{A^2{}_n} \left(\frac{L_n}{A_n} \right)^3 \tag{6}$$

and

$$Z = \frac{p}{RT} \left(\frac{A_n}{L_n} + \frac{B_n}{A_n} + \frac{A_n C_n - B_n^2}{A_n^3 L_n} \right) \tag{7}$$

To compute the density ρ or the compressibility factor Z, the refraction virial coefficients must be known. The first refraction virial coefficient A_n is determined directly from the measured isothermal refractive indexes. The ratios of refraction L_n over pressure p are for this purpose computed and plotted as a function of pressure. Including the known universal gas constants R for each isothermal line, A_n is expressed by the following limit:

$$A_n = RT \lim_{p \to 0} \{L_n/p\} \tag{8}$$

A_n hence represents the intercept of the $(RT\, L_n/p)$ versus pressure curve.

The first approximation of the density ρ and—if p, R, and T are added—the compressibility factor Z from the refractive index are obtained using the first refraction virial coefficients only. The analysis of the experimental data shows that the accuracy of A_n is better than 6×10^{-4}. The agreement between the densities and the compressibility factors determined using the first virial coefficient with the true density and compressibility factors is usually better than 0.3% for pressures up to 60 bar. The results obtained by this approach were corrected by a fit using data from the Burnett apparatus. For this purpose, B_n and C_n were varied.

In the final analysis, the overall accuracy of the experimental data depends on the accuracy of the Burnett data. On the basis of a conservative estimate, this accuracy was better than 0.1%.

5. EXPERIMENTAL DATA

The compressibility factors of pure carbon dioxide, pure ethane, and three binary carbon dioxide–ethane mixtures were measured by the optical apparatus at least for the 0, 20, 40, and 80°C isothermal lines at pressures up to 60 bar.

The purity of the two pure gases certified by Air Liquide, the supplier, was 99.995% for both gases. The binary mixtures were prepared by Gaz de France from gases with a purity of 99.995% (carbon dioxide) and 99.95% (ethane). The exact composition of each of the three binary systems containing approximately 25, 50, and 75% (molar) carbon dioxide was determined by weighing during the mixing process.

To determine the second and third refraction virial coefficients B_n and C_n, additional measurements were made with the optical system and the data were compared with those obtained using the Burnett apparatus. The maximum pressure was 260 bar for the 46.88°C (320.03 K) isothermal line (for carbon dioxide) and for the 75°C isothermal line (for ethane).

5.1. Pure Gases

The first refraction virial coefficients for the pure gases (carbon dioxide and ethane) were obtained directly from the measured refractive index and are very accurate. The maximum uncertainty is 0.06%. Within the uncertainty limitations, the coefficients are independent of the gas temperature. The second and third refraction virial coefficients have hardly any influence on specific refraction and are therefore more uncertain. Nevertheless, the influence of temperature on these coefficients appears to be negligible.

The experimental refractive index data were processed further using the refraction virial coefficients from Table I to obtain experimental density

Table I. Refraction Virial Coefficients for Carbon Dioxide and Ethane Between 0 and 80°C

Component	Purity	A_n ($cm^3 \cdot mol^{-1}$)	B_n ($cm^6 \cdot mol^{-2}$)	C_n ($cm^9 \cdot mol^{-3}$)
Carbon dioxide	99.995	6.641 ± 0.003	0.0 ± 2	-224 ± 80
Ethane	99.995	11.229 ± 0.006	22.9 ± 3	-1560 ± 400

and compressibility factor data using Eqs. (6) and (7). The second and third virial coefficients for the two pure gases were calculated from these density and compressibility factor data. For the latter work,

$$Z = 1 + B(T)\,\rho + C(T)\,\rho^2 \tag{9}$$

was not determined for each isothermal line but for all isothermal lines together for each gas. In this process, the virial coefficient and temperature were correlated by third-degree polynomials:

$$B(T) = b_0 + b_1 T + b_2 T^2 + b_3 T^3 \tag{10}$$

$$C(T) = c_0 + c_1 T + c_2 T^2 + c_3 T^3 \tag{11}$$

Experimental data for eight isothermal lines were available for carbon dioxide and ethane for the 0 to 80°C temperature range. The root mean square error of the densities predicted by the virial equations is better than 2×10^{-4} for the two pure gases.

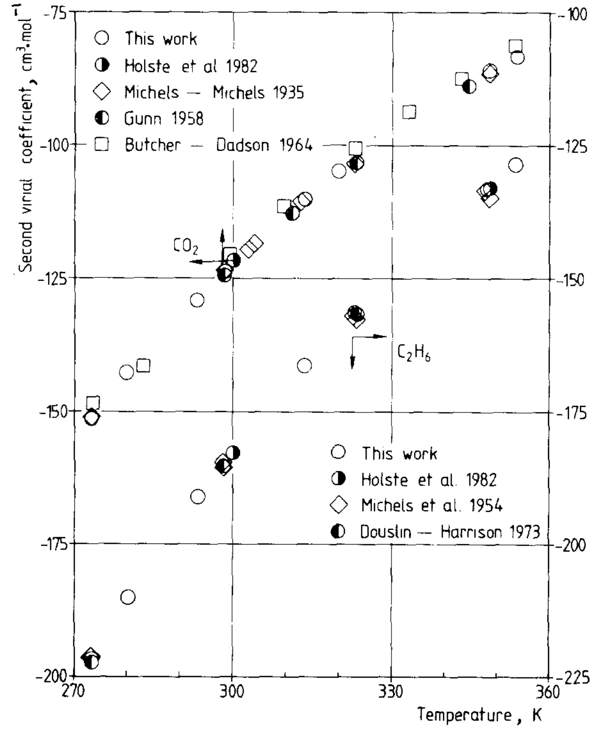

Fig. 2. Comparison of second virial coefficients for CO_2 and C_2H_6 from this work with other values for the 270 to 360 K temperature range.

Figures 2 and 3 present the second and third virial coefficients measured for the various isothermal lines and compare these data with the data of other investigators. The accuracy of the measured second virial coefficient data was estimated at $\pm 0.5\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$.

The results are in excellent agreement with the data reported by others. For the third virial coefficient, the scatter is somewhat wider, mainly for carbon dioxide. The temperature dependence is somewhat greater than reported by Michels and Michels [17] (Table II). For ethane, the experimental data are in good agreement with the data of Michels [18].

5.2. Binary Carbon Dioxide–Ethane Mixtures

The refraction virial coefficients must be known for the prediction of the density or the compressibility factor from the refractive index measured by the optical system.

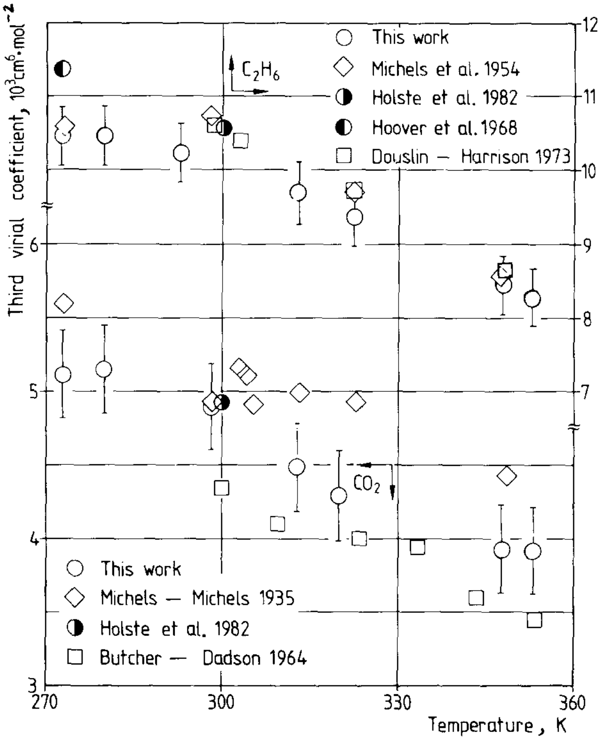

Fig. 3. Comparison of the third virial coefficients for CO_2 and C_2H_6 from this work with other values for the 270 to 360 K temperature range.

Table II. Temperature Dependence of Virial Coefficients for Carbon Dioxide and Ethane

	b_0 ($cm^3 \cdot mol^{-1}$)	b_1 ($cm^3 \cdot mol^{-1} \cdot K^{-1}$)	b_2 ($cm^3 \cdot mol^{-1} \cdot K^{-2}$)	b_3 ($cm^3 \cdot mol^{-1} \cdot K^{-3}$)
Carbon dioxide	-1.22383	7.66671×10^{-3}	-1.75020×10^{-5}	1.39859×10^{-8}
Ethane	-2.02508	1.38719×10^{-2}	-3.52689×10^{-5}	3.16954×10^{-8}
	c_0 ($cm^6 \cdot mol^{-2}$)	c_1 ($cm^6 \cdot mol^{-2} \cdot K^{-1}$)	c_2 ($cm^6 \cdot mol^{-2} \cdot K^{-2}$)	c_3 ($cm^6 \cdot mol^{-2} \cdot K^{-3}$)
Carbon dioxide	-2.57396×10^{-1}	2.57595×10^{-3}	-8.34982×10^{-6}	8.92371×10^{-9}
Ethane	-8.17533×10^{-2}	8.71390×10^{-4}	-2.66632×10^{-6}	2.60730×10^{-9}

For the binary mixtures, the measured first refraction virial coefficients A_n in Table III are in good agreement with the virial coefficients calculated by the following mixing rule:

$$A_n = x_1 A_{n,1} + x_2 A_{n,2} \tag{12}$$

where

x_1 = molar fraction of carbon dioxide

x_2 = molar fraction of ethane

The following mixing rules were used for the second and third refraction virial coefficients:

$$B_{n,\text{mix}} = x_1^2 B_{n,1} + x_2^2 B_{n,2} + 2x_1 x_2 (B_{n,1} B_{n,2})^{\frac{1}{2}} \tag{13}$$

$$C_{n,\text{mix}} = x_1^3 C_{n,1} + x_2^3 C_{n,2} + 3x_1^2 x_2 (C_{n,1}^2 C_{n,2})^{\frac{1}{3}} + 3x_1 x_2^2 (C_{n,1} C_{n,2}^2)^{\frac{1}{3}} \tag{14}$$

Table III. First Refraction Virial Coefficients for the Binary Carbon Dioxide–Ethane System

	A_n ($cm^3 \cdot mol^{-1}$)	
Carbon dioxide fraction (mol %)	Measured	Calculated
77.33	7.687 ± 0.004	7.684
54.32	8.744 ± 0.005	8.739
28.45	9.927 ± 0.005	9.926

The densities and the compressibility factors of the binary mixtures were predicted from the experimental refractive index data, using the second and third refraction virial coefficients calculated. No attempt was made to obtain these virial coefficients directly from the Burnett data, since the maximum pressure of the Burnett apparatus experiments was 40 bar and the effect of the coefficients on density or the compressibility factor at this pressure is less than 0.05%.

Figures 4 to 6 present the compressibility factors measured for four isothermal lines as a function of pressure. The figures show the difference ΔZ between the compressibility factors predicted by the GRI Super Z method [6] and the experimental data,

$$\Delta Z = \frac{Z_{\text{Super Z}} - Z_{\text{exp}}}{Z_{\text{exp}}} 100 \tag{15}$$

The agreement between the predicted compressibility factors and the experimental data is better than ±0.4% for the three binary mixtures containing some 75, 50, and 25 mol % carbon dioxide. The difference between

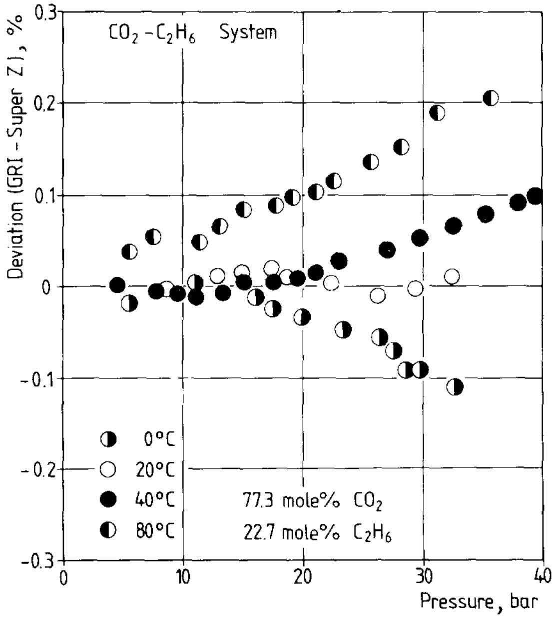

Fig. 4. Difference between calculated Z values (GRI Super Z) and measured Z values for a binary CO_2–C_2H_6 mixture containing 77.3 mol % CO_2.

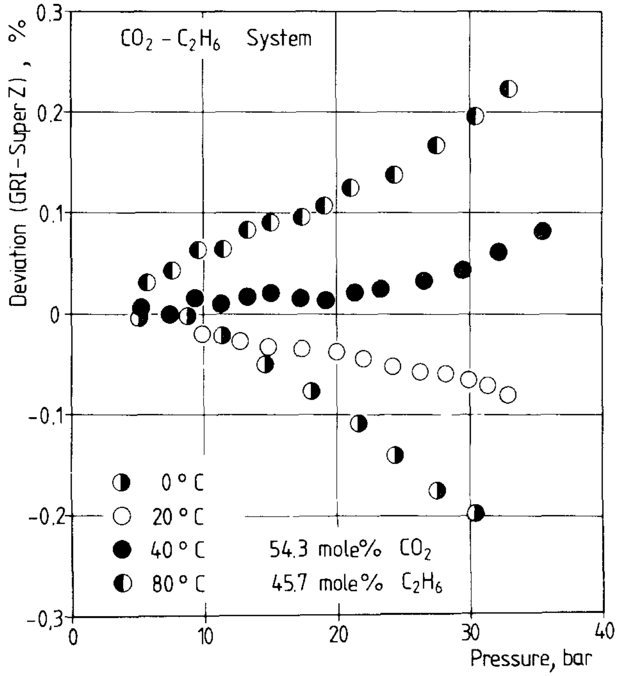

Fig. 5. Difference between calculated Z values (GRI Super Z) and measured Z values for a binary CO_2–C_2H_6 mixture containing 54.3 mol % CO_2.

the GRI Super data and the experimental data is greatest for 0 and 80°C. The differences are greatest for the high-ethane mixtures.

Figure 7 presents experimental compressibility factors determined in this work and Reinsema's experimental data [7] for a binary mixture containing some 75 mol carbon dioxide. The figure shows again the differences between the experimental data and the compressibility factors predicted by the GRI Super Z method. Both experiments overlap for pressures of about 35 bar. The isothermal lines for which comparable data are available are 20°C and 36 to 38°C. The experimental data differ by some 0.3% in this pressure and temperature region.

Interaction virial coefficients were calculated from the measured density and compressibility factor data. To begin with, the virial coefficients B and C for each mixture were calculated by means of Eqs. (10) and (11). The second interaction virial coefficients B_{12} were computed directly

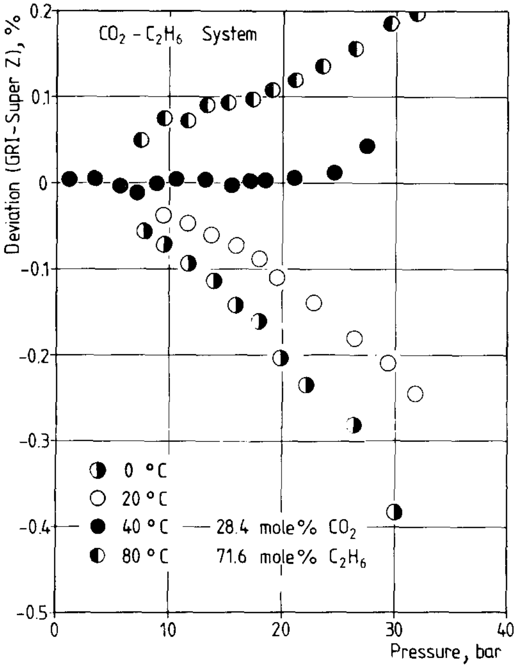

Fig. 6. Difference between calculated Z values (GRI Super Z) and measured Z values for a binary CO_2–C_2H_6 mixture containing 28.4 mol % CO_2.

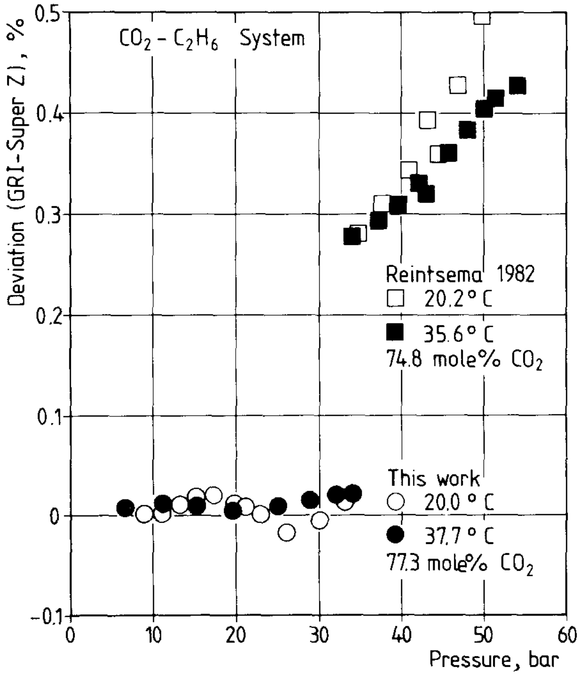

Fig. 7. Comparison of experimental compressibility factors from this work with values of Reintsema et al. [7] for a binary CO_2–C_2H_6 mixture containing some 75 mol % CO_2.

from the second virial coefficients for the three binary mixtures using the following formula:

$$B = x_1^2 B_1 + x_2^2 B_2 + 2x_1 x_2 B_{12} \tag{16}$$

The coefficients in Table II were used for the second virial coefficients of the pure gas B_1 and B_2 (subscript 1 relates to carbon dioxide, and subscript 2 to ethane).

The analysis of the data resulted finally in the following temperature dependence of the interaction second virial coefficient B_{12} for the carbon dioxide–ethane system in the temperature range between 0 and 80°C:

$$B_{12} = -0.703973 + 2.83266 \times 10^{-3} T - 2.52381 \times 10^{-6} T^2 - 1.57545 \times 10^{-9} T^3 \tag{17}$$

where B_{12} is in $\mathrm{cm^3 \cdot mol^{-1}}$.

Figure 8 compares the experimental result for B_{12} from this work with data published by Mason and Eakin [23] and Holste et al. [11].

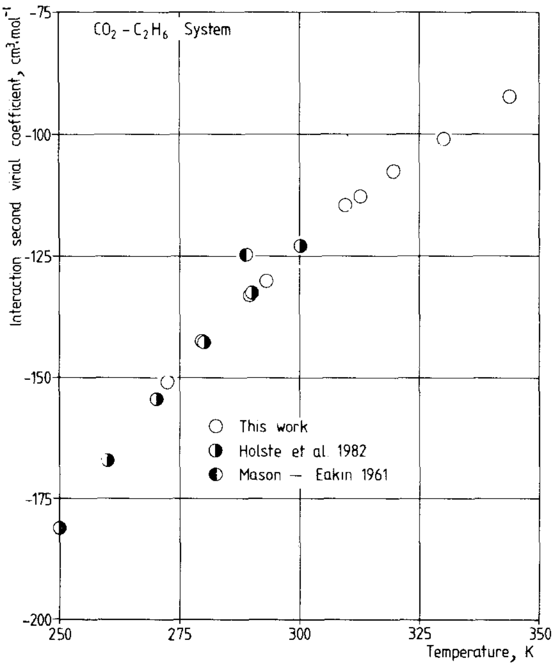

Fig. 8. Comparison of interaction second virial coefficients from this work with values of other investigators for the CO_2–C_2H_6 system.

Assuming the accuracy of $\pm 1.2\ \mathrm{cm^3 \cdot mol^{-1}}$ specified by Holste et al., the low-temperature Holste data and the data from this project do agree. The uncertainty estimated for the work covered by this paper is $\pm 1.5\ \mathrm{cm^3 \cdot mol^{-1}}$.

The effect of temperature on B_{12} is substantial for predictions by equations of state and, in particular, compressibility factors calculated by such equations. For the same reason the third interaction virial coefficients are of major importance. Hardly any reliable data are reported in the literature. Therefore, the experimental data will be further processed to obtain these third interaction virial coefficients and to investigate the effect of higher virial coefficients on B_{12} (T). For this purpose, new binary mixture experiments will be made, mainly at low temperatures, somewhat below 273 K.

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