*International Journal of Thermophysics, Vol. 24, No. 3, May 2003 (© 2003)*

# $CO_2 + R23$ Binary System: Virial Coefficients Derived from Burnett Measurements[1]

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Burnett *PVT* measurements were performed on trifluoromethane (R23) and mixtures of R23 with carbon dioxide ($CO_2$). The Burnett apparatus was calibrated using helium. Fourteen expansions were performed for 5 isotherms and in a pressure range from 130 kPa to 6 MPa for R23. Second and third virial coefficients were derived from the collected data and compared with literature values; good agreement was found between them. *PVTx* measurements for the binary $CO_2 + R23$ system were carried out for five isotherms (303, 313, 323, 333, and 343 K). In all, 18 runs were performed in a pressure range from 150 kPa to 5.9 MPa. The composition of the mixtures was measured with a gas chromatograph after it had been calibrated using samples prepared gravimetrically. Second and third virial coefficients for the system were derived, together with the second and third cross virial coefficients, from experimental results using virial coefficients for $CO_2$ from previous measurements (for the same sample as used in the present study). Samples for composition measurements were collected during the first Burnett expansion. Second virial coefficients for the system showed positive deviations from ideal values, while the third virials were negative. No previous experimental results were found for the *PVTx* properties of this binary system.

**KEY WORDS:** Burnett apparatus; $CO_2$; $CO_2 + R23$; experimental *PVTx*; R23; virial coefficients.

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[1] Paper presented at the Sixteenth European Conference on Thermophysical Properties, September 1–4, 2002, London, United Kingdom.

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## 1. INTRODUCTION

Both carbon dioxide ($CO_2$) and trifluoromethane (R23) are widely used as low-temperature refrigerants. The thermodynamic properties of $CO_2$ are well known from the literature [1]. The main disadvantage of $CO_2$ is its high pressure at the melting point. Trifluoromethane (R23) has several favorable thermodynamic characteristics, e.g., low normal boiling and low melting point temperatures. The combination of $CO_2$ and R23 may thus offer some advantages over either component alone and the study of such a mixture may offer insight for future applications. In addition, the results obtained can provide important information on the molecular interaction of $CO_2$ and R23 as a strong proton donor.

Data on $CO_2$ + HFCs systems are very scarce. Isothermal vapor-liquid equilibrium (VLE) data for $CO_2$ + R23 and for $CO_2$ + R32 were measured by Roth and Lucas [2] and by Adams and Stein [3], respectively. Recently, VLE data for $CO_2$ + R134a were measured by Silva-Oliver and Galicia-Luna [4]. We had already measured *PVTx* according to the Burnett method for the $CO_2$ + R125 [5] and $CO_2$ + R32 [6] systems. We also measured *PVTx* in both the superheated vapor phase and in the two-phase region by the isochoric method for these two systems [7].

Continuing the extensive research work done by our laboratory on the thermophysical properties of hydrofluorocarbon + $CO_2$ systems, *PVTx* measurements were obtained by the Burnett method on the $CO_2$ + R23 system. These results are supplemented by isochoric measurements for the superheated vapor phase and two-phase region [8]. No other experimental results have been published so far on the *PVTx* properties of this specific binary system, and only VLE data are available [3].

To obtain consistent results, *PVT* measurements were carried out for R23 in the present work while we used our previous results on $CO_2$.

## 2. EXPERIMENTAL APPARATUS AND PROCEDURES

$CO_2$ and R23 were supplied by Sol SpA and ICI, respectively; their purities were checked by gas chromatography using a thermal conductivity detector and found to be 99.99% for the $CO_2$ and 99.6% for the R23 on an area-response basis.

A diagram of the apparatus is shown in Fig. 1. It is the same as the one described elsewhere [5, 6], consisting of two pressure vessels, a measurement chamber, $V_A$, and an expansion chamber, $V_B$, with volumes of approximately 70 and 35 $cm^3$, respectively, and several auxiliary systems for filling and mixing the compounds in the Burnett vessels and for controlling and measuring the pressure and temperature. The measurement

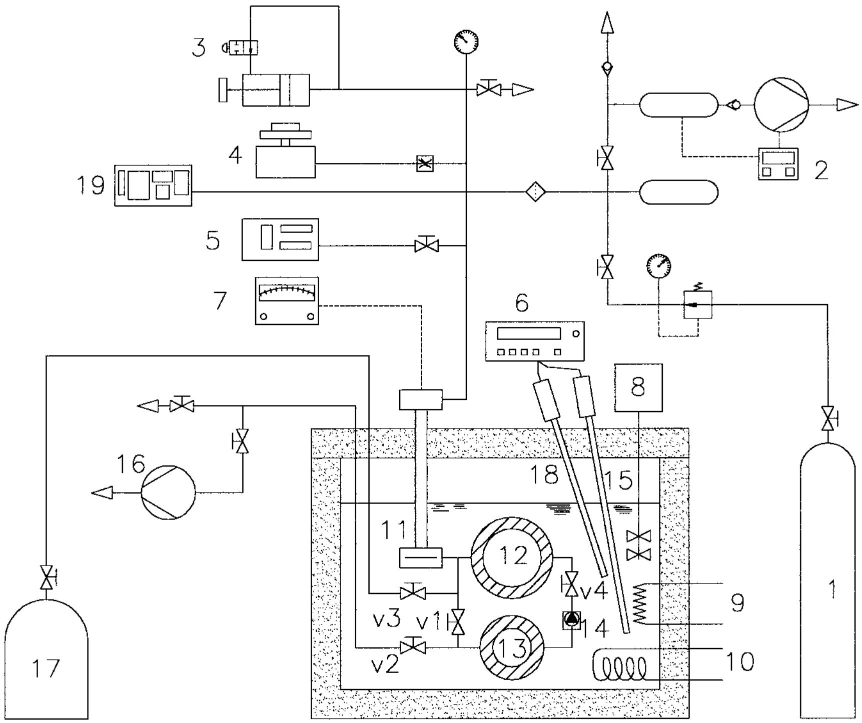

**Fig. 1.** Schematic diagram of the experimental apparatus. Key: (1) Nitrogen reservoir; (2) Vacuum pump (Vacuubrand Model RZ2); (3) Precision pressure controller (Ruska Model 3981); (4) Gas lubricated dead weight gage (Ruska Model 2465); (5) Vibr. cylinder pressure gage (Ruska Model 6220); (6) Digital temperature indicator (Corradi, RP 7000); (7) Electronic null indicator (Ruska Model 2416); (8) Stirrer; (9) Heater; (10) Cooling coil connected to an auxiliary bath; (11) Differential press. transducer (Ruska Model 2413); (12) Measurement chamber ($V_A$); (13) Expansion chamber ($V_B$); (14) Magnetic recirculating pump; (15) Pt resistance thermometer (Tersid, Pt 100); (16) Vacuum pump for $V_B$ (Vacuubrand Model RZ2); (17) Charging fluid reservoir; (18) Pt resistance thermometer (Hart Scientific, Pt 25); (19) Digital pressure indicator (Ruska Model 7000); v1, v2, v3, v4: Constant volume valves.

vessel is connected to a diaphragm-type differential pressure transducer (Ruska Model 2413) coupled to an electronic null indicator (Ruska Model 2416).

The pressure is regulated by a precision pressure controller (Ruska Model 3981), while a digital pressure indicator (Ruska Model 7000) is used to measure pressure. Nitrogen is used as the pressure-transmitting fluid, and the nitrogen system consists of a reservoir, expansion vessels, and pressure regulating systems.

The vessels are immersed in a thermostatic bath filled with about 45 liters of an ethylene glycol and water mixture. The temperature of the bath is kept constant by means of a system with a PID device, piloted by a computer to which the temperature measurement system is also connected. The control and acquisition system relies on two platinum resistance thermometers calibrated according to ITS 90 at the Istituto di Metrologico G. Colonnetti (IMGC) of Turin. In particular, for data acquisition and control measurements, a Hart Scientific Pt 25 resistance thermometer (Hart 5680) and a Tersid Pt 100 resistance thermometer are used, both connected to a digital temperature indicator (Corradi, RP 7000).

The Burnett constant, $N$, defined as the ratio of the volumes of cell A and the sum of the volumes of cells A and B at zero pressure, was determined from gaseous helium measurements (since its thermodynamic properties are well established) and it's validity was continuously verified during measurements. After taking measurements for several isotherms, the constant was found to be $N = 1.49691 \pm 0.0001$ for all measurements of the mixtures, apart from some results for R23 where $N = 1.49485$ and $N = 1.49570 \pm 0.0001$, after small modifications on valve volumes. These values are given in Table I. The Burnett constant reproduces the pressures of helium with the following absolute average deviations: AAD = 0.42 kPa or AAD = 0.14%.

Measurements were performed using the classical Burnett experimental procedure. Initially, the first vessel was filled with the sample and its temperature and pressure were measured. Then, after evacuating the second vessel, the expansion valve was opened. Once the pressures between the vessels had equalized, the second vessel was isolated and evacuated again. This procedure were repeated until low pressures were achieved.

In the mixture-charging procedure, the two vessels were separately filled with different compounds. Then the fluids were mixed together with the aid of a magnetic pump while the expansion valve was kept open. During the first expansion, a sample of the mixture was collected and used for gas chromatographic analysis of the mixture composition. In order to check the sample composition, an analysis of the composition was repeated several times for each run.

The gas chromatograph was calibrated using a series of samples of exactly known composition (different amounts by mass of the two fluids were charged in small stainless steel bottles and weighed with an analytical balance) and analyzing them until a statistically adequate data set was obtained. Details of the method are given elsewhere [6]. A third-degree polynomial expression, obtained by fitting the expression to the points corresponding to pure compounds, provides the unknown composition when its peak area ratio is measured.

**Table I.** Experimental Pressures Measured during Burnett Expansions of R23

$T = 303.16$ K
$N = 1.49485$

| | | | |
|---|---|---|---|
| $P$ (kPa) | 4355.6 | 4473.4 | 4634.2 |
| | 3495.5 | 3632.3 | 3822.9 |
| | 2641.4 | 2768.2 | 2948.6 |
| | 1911.7 | 2020.1 | 2166.0 |
| | 1347.3 | 1431.0 | 1540.8 |
| | 933.8 | 993.8 | 1074.3 |
| | 639.2 | 681.8 | 738.1 |
| | 434.2 | 463.1 | 501.9 |
| | 293.5 | 313.3 | 337.8 |
| | 197.7 | 211.1 | 227.7 |
| | 132.9 | 141.9 | 153.2 |

$T = 313.15$ K
$N = 1.49485$

| | | | |
|---|---|---|---|
| $P$ (kPa) | 4888.8 | 5015.9 | 5040.6 |
| | 3869.3 | 4005.6 | 4026.5 |
| | 2906.4 | 3029.2 | 3045.1 |
| | 2102.5 | 2200.1 | 2213.2 |
| | 1482.1 | 1554.8 | 1565.1 |
| | 1026.3 | 1079.3 | 1086.5 |
| | 702.8 | 739.6 | 745.2 |
| | 477.5 | 503.1 | 506.5 |
| | 322.7 | 340.3 | 342.5 |
| | 217.9 | 229.4 | 230.7 |
| | 147.0 | 154.2 | 154.9 |

$T = 323.15$ K
$N = 1.49485$

| | | | | |
|---|---|---|---|---|
| $P$ (kPa) | 5755.4 | 5543.2 | 5615.3 | 5400.6 |
| | 4563.1 | 4354.2 | 4424.8 | 4209.8 |
| | 3441.9 | 3259.4 | 3319.2 | 3133.5 |
| | 2499.7 | 2354.4 | 2402.1 | 2255.4 |
| | 1767.9 | 1654.4 | 1691.2 | 1585.2 |
| | 1226.8 | 1145.0 | 1170.8 | 1095.8 |
| | 841.6 | 782.2 | 801.5 | 749.6 |
| | 572.6 | 531.1 | 544.5 | 508.6 |
| | 387.4 | 358.8 | 368.0 | 343.5 |
| | 261.0 | 241.6 | 247.8 | |
| | 175.5 | 162.3 | 166.4 | |

$T = 333.16$ K
$N = 1.49570$

| | | |
|---|---|---|
| $P$ (kPa) | 5848.6 | 5839.3 |
| | 4488.4 | 4478.2 |
| | 3306.4 | 3299.6 |
| | 2363.5 | 2358.4 |
| | 1652.4 | 1650.3 |
| | 1138.7 | 1137.8 |
| | 776.6 | 776.0 |
| | 526.2 | 525.8 |
| | 354.7 | 354.7 |
| | 238.6 | 238.3 |
| | 160.2 | 160.1 |

$T = 333.16$ K
$N = 1.49691$

| | | |
|---|---|---|
| $P$ (kPa) | 6050.7 | 5420.1 |
| | 4670.6 | 4100.8 |
| | 3456.2 | 2987.1 |
| | 2476.4 | 2116.3 |
| | 1735.4 | 1471.0 |
| | 1197.6 | 1009.7 |
| | 817.1 | 686.7 |
| | 553.6 | 464.1 |
| | 373.2 | 312.6 |
| | 250.8 | 210.0 |
| | 168.2 | |

$T = 343.15$ K
$N = 1.49691$

| | | |
|---|---|---|
| $P$ (kPa) | 3156.0 | 4652.0 |
| | 2225.8 | 3385.8 |
| | 1543.3 | 2399.4 |
| | 1056.9 | 1668.9 |
| | 717.8 | 1144.8 |
| | 484.6 | 778.4 |
| | 326.0 | 526.1 |
| | 218.7 | 354.1 |
| | 146.6 | 237.9 |
| | | 159.4 |

The uncertainty in the temperature measurements is due to the thermometer and any instability of the bath. The stability of the bath was found to be better than ±0.015 K, and the uncertainty of the thermometer was found to be better than ±0.010 K in our temperature range. The total uncertainty in the temperature measurements was thus less than ±0.02 K.

The uncertainty in the pressure measurements is due to the transducer and null indicator system, and to the pressure gages. The digital pressure indicator (Ruska Model 7000) has an uncertainty of ±0.003% of full scale. The total uncertainty in the pressure measurement is also influenced by temperature fluctuations due to bath instability and was found to be less than ±1 kPa.

The uncertainty of the mixture composition was found to be about 0.1% in mole fraction, based on calibration with samples prepared gravimetrically and on the reproducibility of the gas chromatograph (Carlo Erba Mega Series 5380 with a thermal conductivity detector).

## 3. RESULTS FOR R23 AND $CO_2$

For R23, 170 experimental points were collected along 5 isotherms (16 sets in all) in a temperature range from 303 to 343 K and for pressures from 6 MPa down to 130 kPa. For $CO_2$, 234 experimental points were

**Table II.** Second and Third Virial Coefficients for R23; $\rho(1)$ Denotes Regressed Initial Density

| $N$ | $T$ (K) | $B$ ($cm^3 \cdot mol^{-1}$) | $C$ ($cm^6 \cdot mol^{-2}$) | $\rho(1)$ ($mol \cdot dm^{-3}$) | abs ($dP$) (kPa) | bias ($dP$) (%) |
|---|---|---|---|---|---|---|
| 1.49485 | 303.16 | −173.3 | 11010 | 2.96395 | 0.4 | −0.01 |
| 1.49485 | 303.16 | −176.6 | 11870 | 3.17492 | 0.4 | −0.07 |
| 1.49485 | 303.16 | −174.9 | 11450 | 3.45052 | 1.0 | −0.23 |
| 1.49485 | 313.15 | −164.3 | 11400 | 3.15486 | 0.3 | 0.08 |
| 1.49485 | 313.15 | −163.6 | 11140 | 3.32875 | 0.2 | 0.03 |
| 1.49485 | 313.15 | −163.6 | 11210 | 3.35224 | 0.3 | 0.00 |
| 1.49485 | 323.15 | −150.2 | 10030 | 3.66957 | 0.6 | 0.06 |
| 1.49485 | 323.15 | −148.6 | 9660 | 3.40566 | 0.9 | −0.10 |
| 1.49485 | 323.15 | −148.9 | 9720 | 3.48952 | 0.5 | −0.05 |
| 1.49485 | 323.15 | −151.2 | 10410 | 3.25058 | 0.5 | 0.02 |
| 1.49570 | 333.16 | −138.5 | 9240 | 3.26751 | 0.3 | −0.01 |
| 1.49570 | 333.16 | −139.9 | 9600 | 3.26542 | 0.4 | 0.00 |
| 1.49691 | 333.16 | −138.3 | 9180 | 3.45949 | 0.6 | 0.03 |
| 1.49691 | 333.16 | −138.8 | 9380 | 2.88802 | 0.3 | 0.03 |
| 1.49691 | 343.15 | −129.2 | 9180 | 1.30604 | 0.3 | −0.05 |
| 1.49691 | 343.15 | −128.4 | 8780 | 2.12675 | 0.3 | −0.04 |

collected along 7 isotherms (17 sets altogether) in a temperature range from 283 to 363 K and in a pressure range from 5.7 MPa down to 11 kPa. The experimental data for R23 are shown in Table I while the experimental data for $CO_2$ are reported elsewhere [5].

The experimental *PVT* measurements were used to derive the second, *B*, and third, *C*, virial coefficients of the virial equation,

$$P = \frac{RT}{V}\left(1 + \frac{B}{V} + \frac{C}{V^2}\right) \tag{1}$$

In the regression, each run was treated separately and $(dP)^2$ was used as an objective function applying the Burnett constant from the helium calibration.

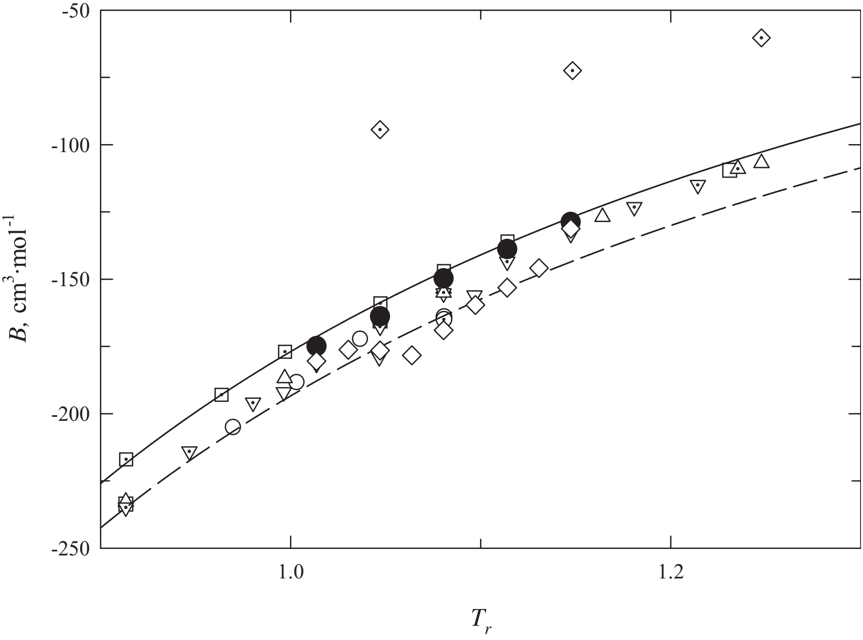

**Fig. 2.** Experimental second virial coefficients for R23 versus reduced temperature, $T/T_c$, where $T_c = 299.29$ K is the critical temperature. The lines represent the second virial coefficients calculated by the Tsonopoulos [19] correlating method, with (solid line) and without (dashed line) the polar contribution. ●, Present work; ⊡, Dymond and Smith [9]; ⊙, Sutter and Cole [10]; ◬, Sutter and Cole [11]; ⟐, Hajjar and MacWood [12]; ▽, Haworth and Sutton [13]; ⩢, Timoshenko et al. [14]; □, Lange and Stein [15]; △, Belzile et al. [16]; ○, Bignell and Dunlop [17]; ◇, Lee et al. [18].

Defining the average absolute deviation in pressure as

$$\mathrm{AAD} = \sum_{i=1}^{N} \mathrm{abs}(dP)/N \tag{2}$$

we found AAD = 0.45 kPa for R23 and AAD = 0.16 kPa for $CO_2$ [5], well within the estimated experimental uncertainty.

The second and third virial coefficients for R23 are shown in Table II, together with the pressure deviations from the fit, which were observed to be randomly distributed. This analysis enables us to say that the adsorption does not affect the results.

In Figs. 2 and 3, the second and third virial coefficients for R23 are plotted and compared with values in the literature. Part of the data was taken from the Dymond and Smith [9–14] compilation, and supplemented by other results [15–18]. The second virial coefficients, also compared with the Tsonopoulos correlating method [19], showed good consistency, while the literature data for the third virial coefficients revealed differences

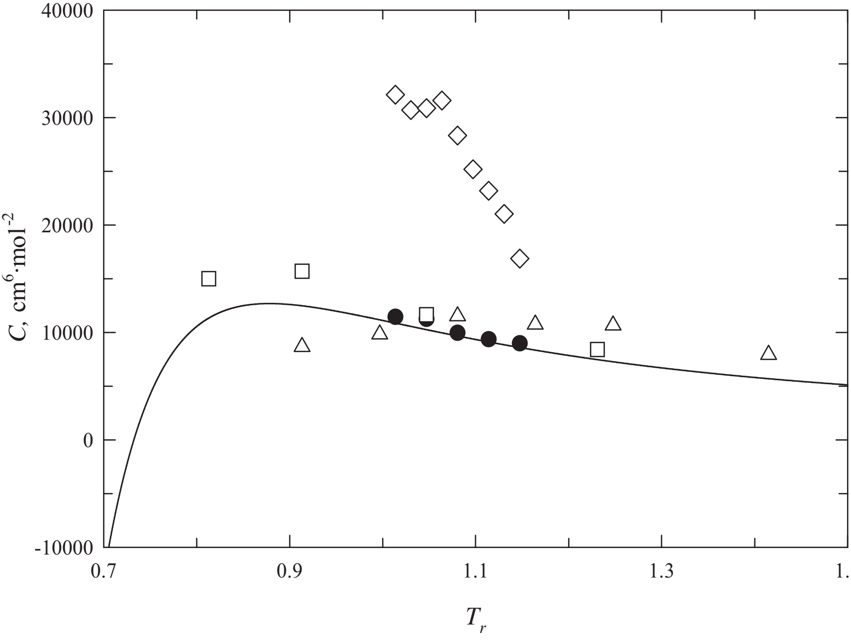

**Fig. 3.** Experimental third virial coefficients for R23 versus reduced temperature, $T/T_c$. The line represents the third virial coefficients calculated by the Orbey and Vera [20] correlating method. ●, Present work; □, Lange and Stein [15]; △, Belzile et al. [16]; ◇, Lee et al. [18].

**Table III.** Experimental Pressures Measured during Burnett Expansions for the $CO_2$ (1) + R23 (2) System. (Data Obtained with $N = 1.49691$)

| | $T = 303.15$ K | | | | $T = 313.15$ K | | |
|---|---|---|---|---|---|---|---|
| | $x_1 = 0.3119$ | $x_1 = 0.6444$ | $x_1 = 0.8526$ | | $x_1 = 0.359$ | $x_1 = 0.5149$ | $x_1 = 0.8412$ |
| $P$ (kPa) | 5396.4 | 5450.3 | 5416.8 | $P$ (kPa) | 3581.1 | 3552.3 | 4033.8 |
| | 4502.8 | 4326.2 | 4201.7 | | 2602.1 | 2562.2 | 2910.0 |
| | 3494.0 | 3238.9 | 3095.6 | | 1837.5 | 1799.4 | 2044.7 |
| | 2575.7 | 2330.2 | 2205.7 | | 1273.5 | 1243.0 | 1412.3 |
| | 1835.9 | 1634.4 | 1537.7 | | 871.7 | 848.9 | 965.7 |
| | 1280.4 | 1127.9 | 1056.2 | | 591.9 | 575.4 | 654.8 |
| | 879.5 | 769.9 | 719.1 | | 399.7 | 387.8 | 441.1 |
| | 598.6 | 521.6 | 486.6 | | 268.2 | 260.5 | 296.5 |
| | 404.7 | 351.5 | 327.8 | | 179.6 | 174.7 | 198.8 |
| | 272.6 | 236.0 | 220.3 | | | | |
| | 183.1 | 158.1 | 147.7 | | | | |

| | $T = 323.15$ K | | | | | $T = 333.15$ K | |
|---|---|---|---|---|---|---|---|
| | $x_1 = 0.1413$ | $x_1 = 0.3344$ | $x_1 = 0.5884$ | $x_1 = 0.7910$ | | $x_1 = 0.3129$ | $x_1 = 0.3882$ |
| $P$ (kPa) | 5153.5 | 5113.6 | 5168.6 | 5192.5 | $P$ (kPa) | 5864.6 | 5056.1 |
| | 3920.0 | 3834.9 | 3820.4 | 3812.2 | | 4398.7 | 3704.3 |
| | 2862.6 | 2767.5 | 2738.4 | 2712.2 | | 3182.2 | 2631.3 |
| | 2029.8 | 1948.1 | 1915.2 | 1889.7 | | 2243.0 | 1832.0 |
| | 1411.9 | 1346.5 | 1319.0 | 1297.2 | | 1554.3 | 1258.2 |
| | 968.3 | 920.2 | 898.3 | 882.5 | | 1063.6 | 856.5 |
| | 658.2 | 624.2 | 608.1 | 596.2 | | 722.2 | 579.0 |
| | 444.9 | 421.3 | 409.8 | 401.4 | | 487.5 | 389.9 |
| | 299.3 | 283.1 | 275.3 | 269.7 | | 327.9 | 261.6 |
| | 201.0 | 189.7 | 184.4 | | | 220.0 | 175.4 |
| | | | | | | 147.3 | |

| | $T = 333.15$ K | | | $T = 343.15$ K | | | |
|---|---|---|---|---|---|---|---|
| | $x_1 = 0.6292$ | $x_1 = 0.7856$ | | $x_1 = 0.2003$ | $x_1 = 0.4251$ | $x_1 = 0.6263$ | $x_1 = 0.7745$ |
| $P$ (kPa) | 3731.2 | 5117.3 | $P$ (kPa) | 5468.7 | 5254.6 | 5384.0 | 5110.8 |
| | 2638.1 | 3694.1 | | 4016.9 | 3806.7 | 3882.8 | 3655.0 |
| | 1830.8 | 2603.0 | | 2862.7 | 2687.3 | 2730.2 | 2554.5 |
| | 1254.5 | 1801.2 | | 1997.5 | 1862.4 | 1887.1 | 1759.5 |
| | 852.5 | 1231.4 | | 1374.7 | 1275.6 | 1290.3 | 1199.3 |
| | 575.7 | 834.6 | | 936.9 | 865.6 | 875.3 | 811.9 |
| | 387.4 | 563.2 | | 634.3 | 584.4 | 590.6 | 547.1 |
| | 259.9 | 378.6 | | 427.3 | 392.9 | 397.2 | 367.5 |
| | 174.1 | 254.0 | | 287.0 | 263.6 | 266.4 | 246.4 |
| | | 170.2 | | 192.4 | 176.5 | 178.3 | 165.0 |

**Table IV.** Experimental and Calculated Second and Third Virial Coefficients for the $CO_2$ (1) + R23 (2) System. ($B$ in $cm^3 \cdot mol^{-1}$ and $C$ in $cm^6 \cdot mol^{-2}$)

| $T$ (K) | $x_1$ | $B_m$ exp | $B_m$ calc | $dB_m$ | $C_m$ exp | $C_m$ calc | $dC_m$ |
|---|---|---|---|---|---|---|---|
| 303.15 | 0.3119 | −152.0 | −153.1 | 1.1 | 8500 | 8460 | 40 |
| | 0.6444 | −133.7 | −134.1 | 0.4 | 6410 | 6500 | −90 |
| | 0.8526 | −125.3 | −124.5 | −0.8 | 5640 | 5540 | 100 |
| 313.15 | 0.3590 | −137.1 | −136.8 | −0.3 | 6900 | 6650 | 250 |
| | 0.5149 | −127.0 | −127.7 | 0.7 | 5260 | 5600 | −340 |
| | 0.8412 | −114.1 | −113.9 | −0.2 | 4860 | 4660 | 200 |
| 323.15 | 0.1413 | −140.4 | −140.1 | −0.3 | 8860 | 8700 | 160 |
| | 0.3344 | −127.4 | −128.6 | 1.1 | 6840 | 7280 | −440 |
| | 0.5884 | −118.8 | −116.3 | −2.5 | 6540 | 5880 | 660 |
| | 0.7910 | −107.8 | −109.0 | 1.2 | 4640 | 5130 | −490 |
| 333.15 | 0.3129 | −120.5 | −120.2 | −0.3 | 6960 | 6530 | 430 |
| | 0.3882 | −114.3 | −116.4 | 2.1 | 5680 | 6120 | −440 |
| | 0.6292 | −106.5 | −105.9 | −0.6 | 5120 | 5190 | −70 |
| | 0.7856 | −101.4 | −100.6 | −0.8 | 4890 | 4730 | 160 |
| 343.16 | 0.2003 | −115.8 | −115.8 | 0.0 | 6680 | 6900 | −220 |
| | 0.4251 | −105.3 | −104.2 | −1.1 | 5310 | 5120 | 190 |
| | 0.6263 | −96.7 | −96.6 | −0.1 | 4220 | 4110 | 110 |
| | 0.7745 | −91.9 | −92.7 | 0.8 | 3570 | 3790 | −220 |

between sources; our data follow the trend of Orbey and Vera's correlation method [20].

The overall uncertainty in the derived virial coefficients stems mainly from the small pressure range and consequently small number of expansions, limited by the saturation pressures of R23. It is probably responsible for the differences observed with respect to data on the third virial coefficients reported in the literature, although our results are consistent with some sources [15, 16].

**Table V.** The Smoothed Second and Third Virial Coefficents for the $CO_2$ (1) + R23 (2) System. ($B$ in $cm^3 \cdot mol^{-1}$ and $C$ in $cm^6 \cdot mol^{-2}$)

| $T$ (K) | $B_{11}$ | $B_{12}$ | $B_{22}$ | $C_{111}$ | $C_{112}$ | $C_{122}$ | $C_{222}$ |
|---|---|---|---|---|---|---|---|
| 303.15 | −118.8 | −136.7 | −174.9 | 4860 | 6480 | 7420 | 11440 |
| 313.15 | −109.8 | −124.8 | −163.8 | 4600 | 4560 | 5300 | 11250 |
| 323.15 | −103.6 | −113.7 | −149.7 | 4670 | 5160 | 6790 | 9950 |
| 333.15 | −95.1 | −105.4 | −138.9 | 4020 | 5370 | 5170 | 9350 |
| 343.15 | −89.5 | −93.1 | −128.8 | 4090 | 2890 | 5210 | 8980 |

All results and comparisons with the literature for $CO_2$ are reported elsewhere [5].

## 4. RESULTS FOR MIXTURES

For the $CO_2$ + R23 system, 186 experimental points were collected for 18 sets and 5 isotherms at temperatures ranging from 303 to 343 K and pressures ranging from 5.9 MPa down to 150 kPa. The experimental results are presented in Table III. The virial coefficients for the mixtures were found by applying the same procedure as for pure compounds. The values of the second and third virial coefficients (Table IV), along with the virial coefficients for the pure compounds (smoothed as a function of reduced temperature) were used to derive cross virial coefficients. The results are shown in Table V. The second cross virial coefficients were calculated from the expression,

$$B_m = \sum_{i=1}^{n} \sum_{j=1}^{n} B_{ij} x_i x_j \tag{3}$$

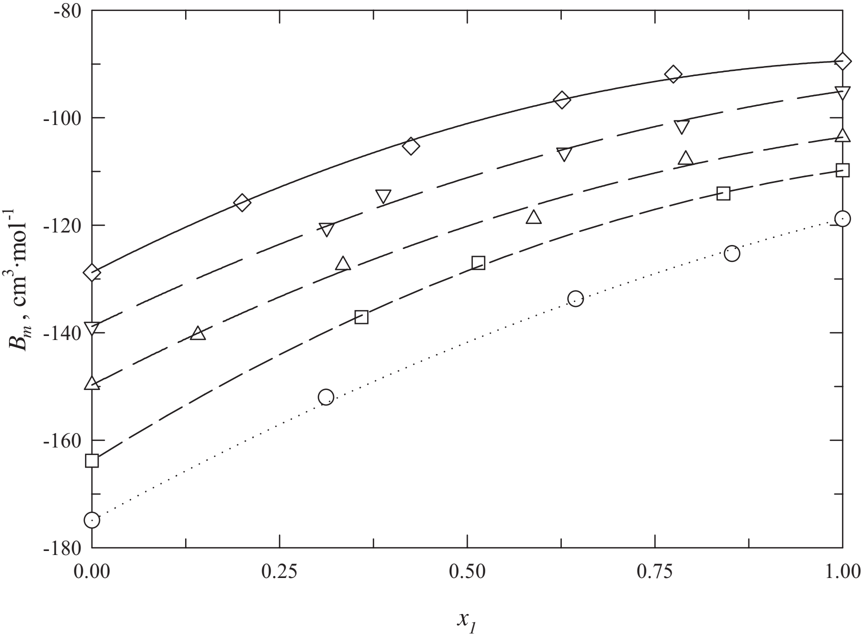

**Fig. 4.** Experimental second virial coefficients for the $CO_2$ (1) + R23 (2) system versus mole fraction at temperatures: ○, $T = 303.15$ K; □, $T = 313.15$ K; △, $T = 323.15$ K; ▽, $T = 333.15$ K; ◇, $T = 343.15$ K. The lines represent the correlated values.

for each experimental datum point. Then the $B_{12}$ values for each temperature were averaged; the averaged $B_{12}$ values (Table V) were used to calculate the deviations from the experimental values shown in Table IV. The third cross virial coefficients were calculated as average values by combining the data for each temperature from the defining equation,

$$C_m = \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} C_{ijk} x_i x_j x_k \tag{4}$$

The averaged values of the third cross virial coefficients are given in Table V. Using these values, the third virial coefficients for the mixtures were recalculated for each point. The results, together with the deviations, are also given in Table IV. The AAD for $B_m$ was 0.8 $\text{cm}^3 \cdot \text{mol}^{-1}$, while the AAD for $C_m$ was 260 $\text{cm}^6 \cdot \text{mol}^{-2}$. The second and third virial coefficients for the $CO_2 + R23$ system plotted against the mole fraction in Figs. 4 and 5,

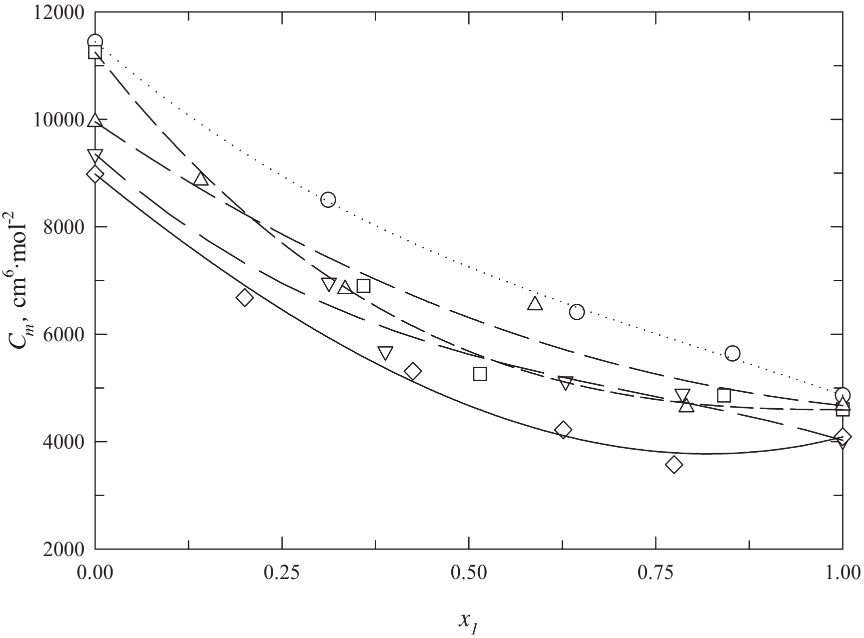

**Fig. 5.** Experimental third virial coefficients for the $CO_2$ (1) + R23 (2) system versus the mole fraction at temperatures: ○, $T = 303.15$ K; □, $T = 313.15$ K; △, $T = 323.15$ K; ▽, $T = 333.15$ K; ◇, $T = 343.15$ K. The lines represent the correlated values.

respectively, show slightly positive and negative deviations from, respectively, the ideal second and third virial coefficients, which are defined as

$$B_{12} = (B_{11} + B_{22})/2 \tag{5}$$

$$C_{112} = (2C_{111} + C_{222})/3 \tag{6}$$

$$C_{122} = (C_{111} + 2C_{222})/3 \tag{7}$$

The averaged values of $B_{11}$, $B_{12}$, and $B_{22}$ are plotted against temperature in Fig. 6.

The uncertainty in the Burnett constant estimated to be $\pm 0.0001$ produces average deviations of $\pm 0.25\ \mathrm{cm^3 \cdot mol^{-1}}$ in $B$, $\pm 70\ \mathrm{cm^6 \cdot mol^{-2}}$ in $C$, and $\pm 0.039\%$ in $\rho(1)$. These deviations are of a systematic nature as follows: for greater N a decrease of $B$, $C$, and $\rho(1)$ was obtained whereas, for lower $N$, an increase of $B$, $C$, and $\rho(1)$ is observed. It should be also noted that deviations in $\rho(1)$ are almost constant for all series of measurements.

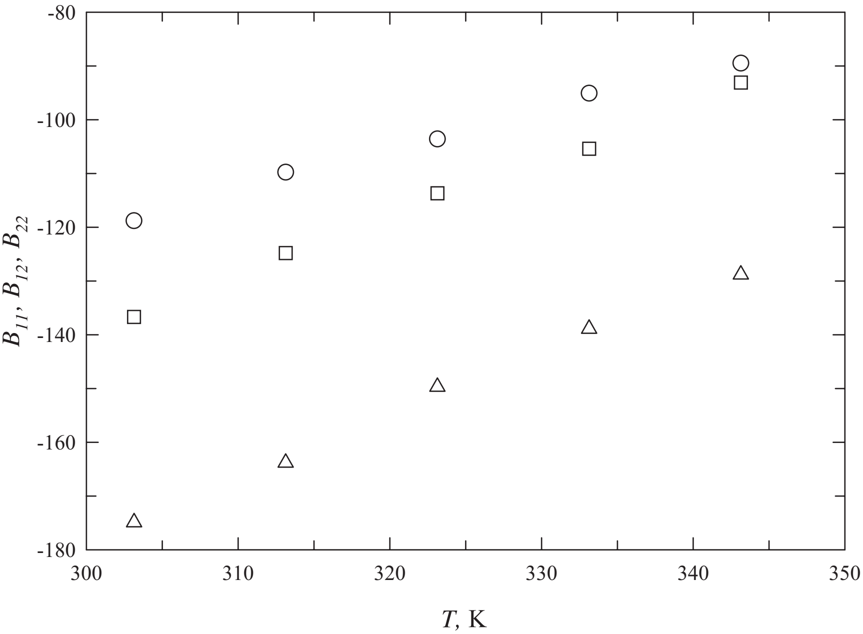

**Fig. 6.** Averaged values of $B_{11}$, $B_{12}$, and $B_{22}$ for the $CO_2$ (1) + R23 (2) system against temperature. ○, $B_{11}$; □, $B_{12}$; △, $B_{22}$.

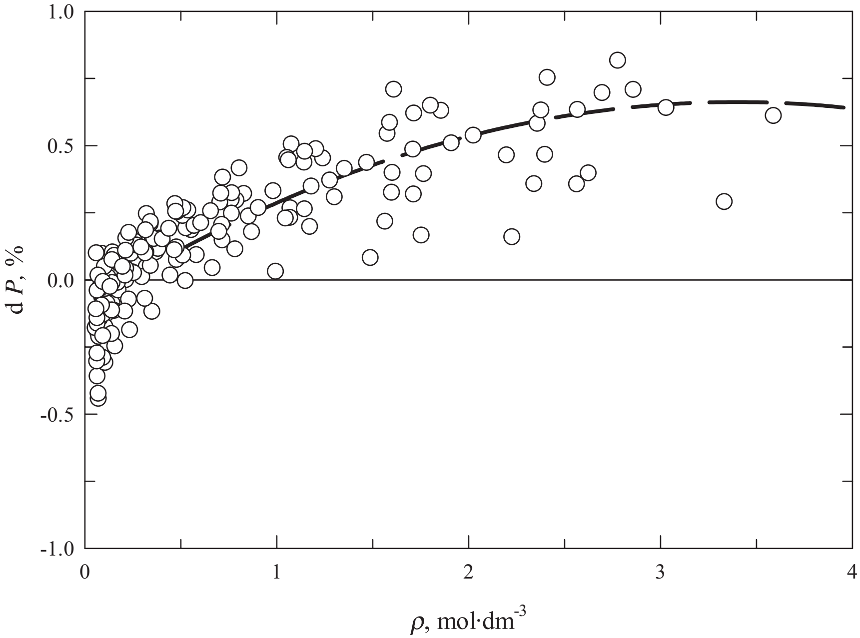

**Fig. 7.** Deviations in pressure produced by REFPROP 6.01 [21] versus density. The line represents the overall trend.

Due to the total lack of data in the literature on the superheated vapor region for this system, the experimental results were compared with predictions obtained from REFPROP 6.01 [21]. The calculations were performed at the highest experimental pressures of each run, adopting regressed values for $\rho(1)$, $B_m$, and $C_m$. The pressure differences are given in Fig. 7, showing consistencies to within 1%, with some systematic trend.

## 5. CONCLUSIONS

*PVTx* properties were measured by the Burnett method for the $CO_2 + R23$ binary system, and second and third virial coefficients of the virial equation of state were derived from the collected data. The second and third virial coefficients of $CO_2$ were taken from our previous measurements, while, for R23, they were measured as part of the present study. Overall measurements cover a pressure range from about 6 MPa down to about 120 kPa and a temperature range from 303 to 343 K. Satisfactory agreement with data in the literature was found for the second virial coefficients of R23, while the comparison between the third virial coefficients revealed considerable differences between sources. Uncertainties in the second and third virial coefficients are about 2 $cm^3 \cdot mol^{-1}$ and 500 $cm^6 \cdot mol^{-2}$, respectively. Due to the lack of other experimental data on the $PVTx$ properties of the system, our experimental results were compared with predictions from REFPROP 6.01. The predicted values are, on average, about 1% different in terms of pressure, which can be considered quite satisfactory bearing in mind that, for this system, REFPROP 6.01 is based on a semi-empirical method. The second virial coefficients showed positive deviations, while the third virials showed negative deviations from ideality.

## ACKNOWLEDGMENT

This work was supported by Fondazione CARIVERONA, Verona, Italy.

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