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Virial Coefficients from Burnett Measurements for the R116 + CO_2 System[1]

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PVTx measurements for the R116 + CO_2 system for four isotherms (283, 304, 325 and 346 K) were performed. In total, 16 runs were performed in a pressure range from 5100 to 140 kPa. Seven runs along four isotherms in a pressure range from 3400 to 280 kPa were performed for pure hexafluoroethane (R116), and the second and third virial coefficients were derived. The values of the virial coefficients for CO_2 were adopted from our previous measurements. The second and third virial coefficients along with the second and third cross-virial coefficients were derived from the mixture results. The Burnett apparatus was calibrated using helium. The experimental uncertainty in second and third virial coefficients was estimated to be within ±2 $cm^3 \cdot mol^{-1}$ and ±500 $cm^6 \cdot mol^{-2}$, respectively.

KEY WORDS: Burnett apparatus; CO_2; CO_2 + R116; experimental *PVTx*; R116; virial coefficients.

1. INTRODUCTION

This work continues the research project that has been carried out by our laboratories on the thermophysical properties of hydrofluorocarbon + hydrocarbon and/or inorganic compound systems and follows previous measurements on the binary (R125, R32, R23, and R41) + CO_2 systems.

Both carbon dioxide (CO_2) and hexafluoroethane (R116) are widely used as low-temperature refrigerants. The thermodynamic properties of

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CO_2 are well known from the literature [1]. R116 has been studied as a constituent of the trifluoromethane (R23) + R116 azeotropic binary system [2,3]. In the past, its thermophysical properties in the gas phase have also been the object of extensive study [4–9]. The combination of CO_2 and R116 may offer some advantages over either component alone, and the study of such a mixture may offer insight for future low temperature applications.

PVTx measurements for the CO_2 + pentafluoroethane (R125), CO_2 + difluoromethane (R32), CO_2 + R23, and CO_2 + fluoromethane (R41) systems [10–13] have already been carried out by our laboratory using the Burnett method. Continuing this research work on the thermophysical properties of hydrofluorocarbon + CO_2 systems, we have performed *PVTx* measurements on the CO_2 + R116 system with the Burnett method. No other experimental results have been published so far for the *PVTx* and VLE properties of this binary system. To obtain consistent results, *PVT* measurements were carried out for R116 in the present work while we used our previous results on CO_2 [10].

2. EXPERIMENTAL APPARATUS AND PROCEDURES

CO_2 and R116 were supplied by Sol SpA and Lancaster Synthesis Inc., respectively; their purity was checked by gas chromatography using a thermal conductivity detector and found to be 99.99 % for CO_2 and 99.7 % for R116 on an area-response basis.

A diagram of the apparatus, since it is the same as described elsewhere, [10–13] is not reported here. It consists 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 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 L of silicon oil. The temperature of the bath is kept constant by means of a system with a PID device, controlled 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 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 and its 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. 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 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 [10]. 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.

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 R116 AND CO_2

For R116, 62 experimental points were collected along 4 isotherms (7 sets in all) in a temperature range from 283 to 345 K and for pressures from 3.4 MPa down to 280 kPa. For CO_2, 234 experimental points were 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 R116 are shown in Table I while the experimental data for CO_2 are reported elsewhere [10].

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.

Table I. Experimental Pressures Measured during Burnett Expansions of R116

283.55 K	304.10 K	304.10 K	324.86 K P (kPa)	324.86 K	345.58 K	345.58 K
2305.0	3124.5	2998.7	3390.8	3073.0	3471.0	3349.5
1869.3	2512.4	2371.1	2563.3	2285.5	2528.3	2428.7
1411.7	1901.6	1772.8	1864.2	1642.9	1793.8	1717.5
1020.2	1379.3	1276.0	1318.6	1153.0	1248.4	1192.7
717.6	973.1	895.5	914.9	796.0	857.2	817.9
496.0	674.1	618.2	627.0	543.3	583.1	556.1
339.1	461.3	422.2	426.7	368.0	394.4	375.9
230.9	313.2	286.2	289.3	248.4	265.8	253.2
	211.5	193.2	195.5	166.9	178.7	170.1

Defining the average absolute deviation in pressure as

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

we found AAD = 0.18 kPa for R116 and AAD = 0.16 kPa for CO_2 [10], well within the estimated experimental uncertainty. The second and third virial coefficients for R116 are shown in Table II, together with the pressure deviations from the fit, which were observed to be randomly distributed.

In Figs 1 and 2, the second and third virial coefficients for R116 are plotted and compared with values in the literature [5–9]. The second virial coefficients, also compared with the Tsonopoulos correlating method [14], showed good consistency with the different sources, while the literature data for the third virial coefficients revealed larger differences with literature sources, where data were obtained with speed-of-sound measurements [9] and with the Orbey and Vera correlation method [15]. Comparing with literature [9], differences, being less than 750 $\mathrm{cm^6 \cdot mol^{-2}}$, are well within the experimental uncertainties of the two sources in the reduced temperature range from 1.1 to 1.2, while a clear discrepancy appears at reduced temperatures less than 1.05 (with deviations from 2700 to 1500 $\mathrm{cm^6 \cdot mol^{-2}}$).

Uncertainties in the second and third virial coefficients are about 2 $\mathrm{cm^3 \cdot mol^{-1}}$ and 500 $\mathrm{cm^6 \cdot mol^{-2}}$, respectively. 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 R116. It is probably responsible for the differences observed with respect to data on the third virial coefficients reported in the literature.

Table II. Second and Third Virial Coefficients for R116

T (K)	B ($\mathrm{cm^3 \cdot mol^{-1}}$)	C ($\mathrm{cm^6 \cdot mol^{-2}}$)	ρ (1) ($\mathrm{mol \cdot dm^{-3}}$)	abs (dP) (kPa)	bias (dP) (%)
283.55	−292.8	25690	1.69039	0.3	0.06
304.10	−249.3	23880	2.15336	0.1	0.01
304.10	−248.1	23730	1.96144	0.1	0.02
324.86	−210.4	20630	1.83828	0.5	0.12
324.86	−209.6	20460	1.58035	0.2	−0.03
345.58	−177.9	17730	1.58399	0.1	0.00
345.58	−177.8	18220	1.50715	0.0	0.01

ρ(1) Denotes Regressed Initial Density.

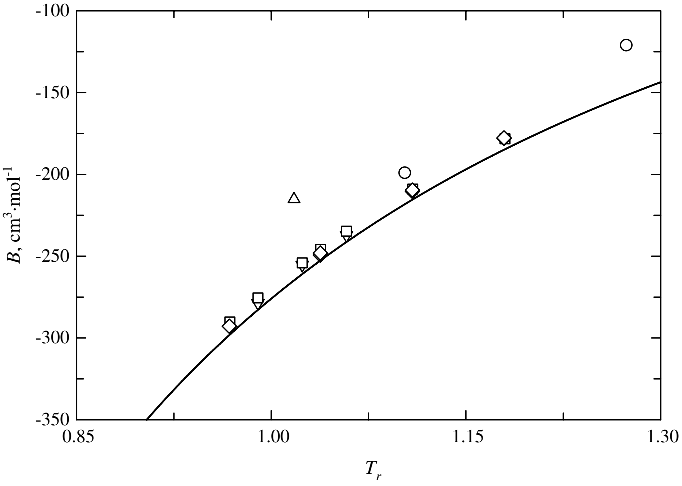

Fig. 1. Experimental second virial coefficients for R116 vs. reduced temperature, T/T_c, where $T_c = 293.02$ K is the critical temperature [16]. (◇) Present work; (○) Dantzler and Knobler [5]; (△) Wickland et al. [7]; (▽) Bell et al. [8]; (□) Hurly [9]. The solid line represents the second virial coefficients calculated by the Tsonopoulos correlating method [14].

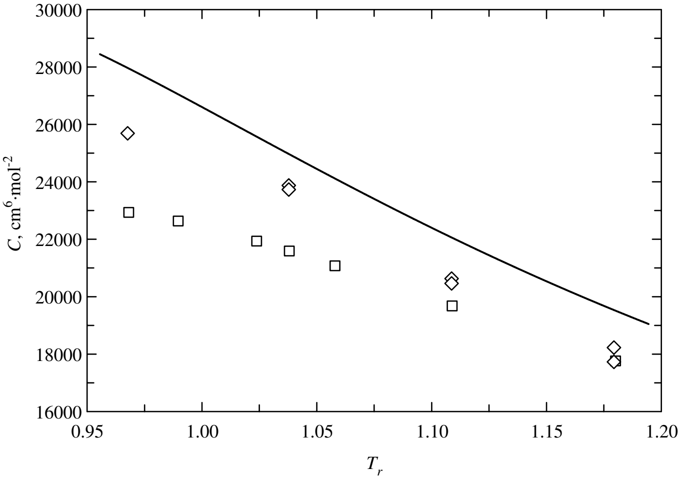

Fig. 2. Experimental third virial coefficients for R116 vs. reduced temperature, T/T_c. (◇) Present work; (□) Hurly [9]. Solid line represents the third virial coefficients calculated by the Orbey and Vera correlating method [15].

All results and comparisons with the literature for CO_2 are reported elsewhere [10]. The obtained second and third virial coefficients for CO_2 showed a good agreement with the literature.

4. RESULTS FOR THE MIXTURES

For the CO_2 + R116 system, 154 experimental points were collected for 16 sets and 4 isotherms at temperatures ranging from 284 to 344 K and pressures ranging from 5.1 MPa down to 140 kPa. The experimental results are presented in Table III. The virial coefficients for the mixtures were determined by applying the same procedure as for pure compounds. The values of the second and third virial coefficients (Table IV), along

Table III. Experimental Pressures Measured during Burnett Expansions for the R116 (1) + CO_2 (2) System

x_1, $T = 283.55$ K				x_1, $T = 304.10$ K			
0.2397	0.4139	0.5970	0.7583	0.2364	0.4415	0.5970	0.7462
	P (kPa)				P (kPa)		
3515.6	2978.9	3057.0	2604.2	4173.4	4273.6	4092.6	4327.1
2655.2	2226.1	2375.7	2013.4	3089.9	3236.2	3148.4	3541.0
1921.1	1600.3	1751.1	1476.7	2209.6	2351.8	2313.1	2727.3
1352.5	1122.3	1248.1	1049.6	1545.1	1661.0	1644.5	2004.8
935.5	774.4	870.4	730.8	1063.9	1152.3	1145.9	1425.9
639.9	528.8	597.4	501.8	724.9	789.5	787.3	994.1
435.0	358.7	407.0	341.7	490.8	536.6	536.2	683.5
294.3	242.1	275.3	231.6	330.8	363.0	363.9	465.7
198.6	163.1	185.7	156.6	222.3	244.8	246.4	315.3
							201.0
x_1, $T = 324.84$ K				x_1, $T = 343.69$ K			
0.2476	0.4347	0.6098	0.7872	0.2412	0.4397	0.6153	0.7924
	P (kPa)				P (kPa)		
4427.7	3681.5	3571.7	3498.3	5104.6	4149.1	3494.1	2895.2
3196.2	2641.2	2588.3	2573.4	3650.0	2942.2	2472.8	2046.4
2249.7	1852.7	1827.8	1836.3	2553.1	2048.6	1719.5	1420.3
1556.2	1279.1	1266.7	1282.2	1759.9	1407.5	1180.3	974.1
1063.9	873.7	867.9	882.4	1201.0	958.0	803.3	662.4
722.4	592.7	589.4	601.3	814.0	648.4	543.5	447.9
487.8	400.0	398.5	407.0	549.2	436.9	366.3	301.7
328.5	269.1	268.4	274.4	369.4	293.7	246.2	202.7
220.7	180.7	180.5	184.6	248.1	197.1	165.2	136.0

Table IV. Experimental and Calculated Second and Third Virial Coefficients for the R116 (1) + CO_2 (2) System

Series	T(K)	x_1	$B_m$exp	$B_m$calc	dB_m	C_m exp	C_m calc	C'_mcalc	dC_m	dC'_m
1	283.55	0.2397	−161.0	−158.0	−3.0	9200	9240	9240	−40	−40
2		0.4139	−181.7	−180.1	−1.6	12300	12080	12080	220	220
3		0.5970	−206.9	−209.0	2.1	14880	15270	15270	−390	−390
4		0.7583	−236.6	−239.2	2.6	18970	18720	18720	250	250
5	304.10	0.2364	−134.1	−130.7	−3.4	7260	7190	7210	70	50
6		0.4415	−151.4	−151.0	−0.4	9650	9560	9710	90	−60
7		0.5970	−168.6	−171.9	3.3	11640	12000	12230	−360	−590
8		0.7462	−195.3	−196.6	1.3	15490	15210	15460	280	30
9	324.84	0.2476	−114.0	−114.2	0.2	6220	6990	6290	−770	−70
10		0.4347	−133.4	−130.0	−3.4	10010	9000	8330	1010	1680
11		0.6098	−149.0	−149.6	0.6	11200	11440	11030	−240	170
12		0.7872	−172.6	−174.2	1.6	14600	14880	14760	−280	−160
13	345.69	0.2412	−98.0	−99.1	1.1	5410	5530	5510	−120	−100
14		0.4397	−112.1	−113.3	1.2	8200	8290	8070	−90	120
15		0.6153	−131.1	−129.6	−1.5	11870	11360	10990	510	890
16		0.7924	−150.4	−149.6	0.8	14130	14570	14200	−440	−70

B in $cm^3 \cdot mol^{-1}$ and C in $cm^6 \cdot mol^{-2}$

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,

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

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 cal-

Table V. Smoothed Second and Third Virial Coefficents for R116 (1) + CO_2 (2) System

T(K)	B_{11}	B_{12}	B_{22}	C_{111}	C_{112}	C'_{112}	C_{122}	C'_{122}	C_{222}
283.55	−292.9	−171.5	−136.1	25880	13830	13830	12020	12020	4720
304.10	−248.6	−133.5	−117.6	23510	9750	10380	8560	8410	4700
324.84	−210.1	−117.6	−101.7	20840	9600	9750	8160	6440	4490
345.69	−177.7	−104.3	−87.9	17860	13360	12330	4140	4420	4080

B in $cm^3 \cdot mol^{-1}$ and C in $cm^6 \cdot mol^{-2}$

culate 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 1.7 cm^3·mol^{-1}, while the AAD for C_m was 324 cm^6·mol^{-2}.

In order to improve the results, the third cross virial coefficients were refitted disregarding series 7, 10 and 15. New regressed values, C'_{112} and C'_{122}, are reported in Table V. According to the new third cross virial coefficients, the third virial coefficients for the mixture C'_m *calc* and dC'_m, were recalculated and reported in Table IV.

The second and third virial coefficients for the CO$_2$ + R116 system plotted against the mole fraction in Figs. 3 and 4, respectively, show positive and negative deviations from the ideal second and third virial coefficients, which are defined as

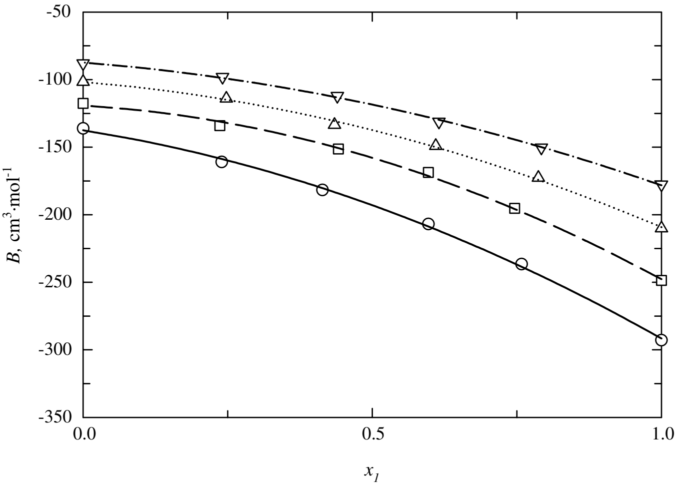

Fig. 3. Experimental second virial coefficients for the R116 (1) + CO$_2$ (2) system vs mole fraction at temperatures, T: (○) 283.55 K; (□) 304.10 K; (△) 324.84 K; (∇) 345.69 K. Lines represent the correlated values.

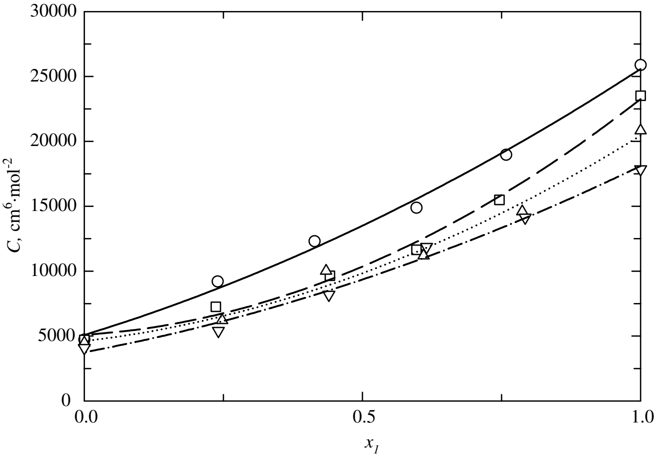

Fig. 4. Experimental third virial coefficients for the R116 (1) + CO_2 (2) system vs mole fraction at temperatures, T: (○) 283.55 K; (□) 304.10 K; (△) 324.84 K; (▽) 345.69 K. The lines represent the correlated values.

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

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

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

5. CONCLUSIONS

PVTx properties were measured by the Burnett method for the CO_2 + R116 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 for CO_2 were taken from our previous measurements, while, for R116, they were determined as part of the present study. Overall measurements cover a pressure range from about 5 MPa down to about 100 kPa and a temperature range from 284 to 344 K. Satisfactory agreement with data in the literature was found for the second virial coefficients of R116, while the comparison between the third virial coefficients revealed considerable differences between sources. For the CO_2 + R116 system, the second virial coefficients showed positive deviations, while the third virials showed negative deviations from ideality.

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