J. Chem. Eng. Data **2002,** *47,* 876−881

Burnett Measurements for the Difluoromethane + Carbon Dioxide System

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As part of our ongoing research program on *PVTx* measurements using the isochoric and Burnett methods for hydrofluorocarbon + hydrocarbon and/or inorganic compound systems, this work reports on the experimental results for the difluoromethane (R32) + carbon dioxide (CO_2) system obtained by the Burnett method. The apparatus was calibrated using helium, and its performance was confirmed by measurements for pure R32. The second and third virial coefficients were derived, and a good consistency was found after comparison with data in the literature. A new experimental procedure for mixture measurements was developed, on the basis of the gas chromatographic analysis of the sample collected during expansions. The gas chromatograph was calibrated precisely using samples prepared by the gravimetric method. *PVTx* measurements were performed for the binary R32 + CO_2 system at T = (303, 313, 323, 333, and 343) K. The second and third cross virial coefficients were derived from the experimental results. No experimental data could be found in accessible literature sources on the *PVTx* for the R32 + CO_2 system. Results were compared with the prediction obtained using REFPROP 6.01.

Introduction

Carbon dioxide has received much attention for industrial applications. It is also an attractive compound for research because of its convenient critical temperature and thermal stability, which explains the fairly abundant and accurate literature providing thermophysical data for CO_2.[1] It is neither flammable nor toxic, is inexpensive and is widely available. One of the main disadvantages of this natural fluid is that the plant components need to be designed for much higher pressures; typically 150 bar is the maximum operating pressure.

Difluoromethane is a hydrofluorocarbon used in the refrigeration industry. In particular, it is an important alternative refrigerant as a constituent in several binary or ternary mixtures intended as a substitute for difluorochloromethane (R22), and its thermophysical properties have been studied extensively in the past decade. The main limit of this refrigerant fluid lies in its flammability. This alternative refrigerant has a zero ODP but a far from negligible GWP, so its combination with a low-GWP and nonflammable compound such as CO_2 is particularly promising.

Nevertheless, publications on the *PVTx* properties of systems containing carbon dioxide as one of their components and a hydrofluorocarbon as the other are rare. Studying the combination of carbon dioxide and difluoromethane thus provides important information for future applications. Moreover, no experimental results have been published to our knowledge on the *PVTx* properties of this specific binary system.

This work presents and discusses the *PVTx* resulting from Burnett measurements.

Experimental Section

Reagents. CO_2 and R32 were supplied by Sol SpA and Ausimont SpA, respectively; the purity was checked by gas chromatographic analysis, using a thermal conductivity detector. It was found to be 99.99% for the CO_2 and 99.98% for the R32 on an area-response basis.

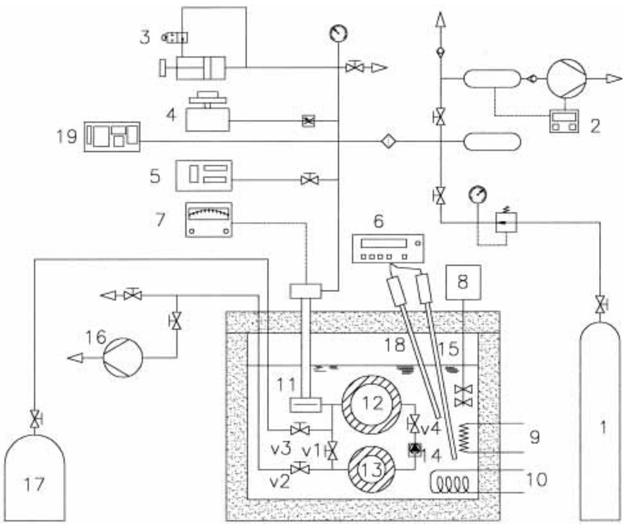

Figure 1. Schematic view of the experimental apparatus: 1, nitrogen reservoir; 2, vacuum pump (Vacuubrand, mod. RZ2); 3, precision pressure controller (Ruska, mod. 3981); 4, gas lubricated dead weight gauge (Ruska, mod. 2465); 5, vibr. cylinder pressure gauge (Ruska, mod. 6220); 6, digital temperature indicator (Corradi, RP 7000); 7, electronic null indicator (Ruska, mod. 2416); 8, stirrer; 9, heater; 10, cooling coil connected with an auxiliary bath; 11, differential pressure transducer (Ruska, mod. 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, mod. RZ2); 17, charging fluid reservoir; 18, Pt resistance thermometer (Hart Scientific, Pt 25); 19, digital pressure indicator (Ruska, mod. 7000); V_1, V_2, V_3, V_4, constant volume valves.

Apparatus. A diagram of the apparatus is shown in Figure 1. It is the same as the one described elsewhere[2−4] and used with only minimal modifications. It consists of

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10.1021/je015537m CCC: $22.00

Table 1. Experimental Pressures Measured during Burnett Expansions of R32

P/kPa								
series 1 T/K = 303.15	series 2 T/K = 303.16	series 3 T/K = 313.15	series 4 T/K = 313.16	series 5 T/K = 323.16	series 6[a] T/K = 323.16	series 7[a] T/K = 333.16	series 8 T/K = 343.16	series 9 T/K = 343.16
1548.2	1783.7	1730.8	2363.1	2291.1	3110.5	2123.3	4198.0	4365.7
1119.8	1313.8	1249.4	1786.3	1685.3	2444.3	1526.7	3335.6	3520.5
788.6	935.6	878.4	1293.4	1200.0	1816.3	1071.3	2503.2	2667.7
545.5	652.0	607.3	911.2	835.9	1301.9	739.7	1807.8	1940.4
373.0	448.1	415.1	630.8	574.4	911.3	504.9	1273.4	1372.7
253.3	305.2	281.6	431.5	390.9	628.0	342.1	881.3	953.2
171.1	206.7	190.1	292.9	264.2	428.4	230.6	603.4	653.3
115.2	139.4	128.0	197.9	177.9	290.1	155.1	409.5	444.2
			133.3		195.8		276.7	300.5
					131.6		186.4	202.5
							125.2	136.2

[a] Data obtained with N = 1.495 70.

Table 2. Second and Third Virial Coefficients for R32[a]

series	T/K	B/cm^3·mol^{-1}	C/cm^6·mol^{-2}	$\rho(1)^a$/mol·dm^{-3}	abs(dP)/kPa	$100(P - P_{calc})P^{-1}$/%
1	303.15	−284.3	24 420	0.772 70	0.1	−0.01
2	303.16	−283.5	23 940	0.936 77	0.0	0.01
3	313.15	−257.5	20 650	1.294 02	0.1	−0.01
4	313.16	−257.4	19 890	0.831 16	0.1	−0.02
5	323.16	−238.7	19 570	1.852 09	0.2	−0.06
6[b]	323.16	−238.3	18 980	1.129 25	0.2	−0.04
7[b]	333.16	−220.8	17 380	0.951 37	0.2	−0.05
8	343.16	−203.2	16 070	2.465 54	0.4	0.04
9	343.16	−202.3	15 760	2.680 47	0.6	0.06

[a] $\rho(1)$ denotes regressed initial density. [b] Data obtained with N = 1.495 70.

Table 3. Second and Third Virial Coefficients for CO_2[a]

series	T/K	B/cm^3·mol^{-1}	C/cm^6·mol^{-2}	$\rho(1)$/mol·dm^{-3}	abs(dP)/kPa	$100(P - P_{calc})P^{-1}$/%
1	283.14	−136.2	4390	2.246 27	0.3	−0.30
2	283.14	−136.6	4580	2.534 39	0.2	−0.07
3	283.14	−136.4	4890	2.570 16	0.1	−0.03
4	303.15	−118.9	4870	3.280 11	0.1	−0.09
5	303.15	−118.1	4690	3.118 60	0.2	−0.04
6	303.15	−119.2	4980	3.274 10	0.0	−0.02
7	303.15	−118.9	4860	3.301 30	0.0	−0.02
8	313.15	−109.8	4600	2.808 84	0.1	−0.01
9	323.16	−103.6	4660	2.812 53	0.2	−0.03
10	323.16	−103.7	4680	2.878 13	0.2	−0.09
11	333.63	−95.0	4040	2.495 94	0.2	−0.09
12	333.63	−94.5	4000	2.541 26	0.2	−0.25
13	343.15	−88.7	3920	2.344 21	0.1	0.02
14	343.15	−90.2	4250	2.475 49	0.1	0.03
15	363.15	−79.6	4130	2.164 73	0.1	0.00
16	363.15	−78.4	3670	2.099 60	0.2	0.01
17	363.15	−75.9	3210	2.147 79	0.4	−0.03

[a] $\rho(1)$ denotes regressed initial density.

two pressure vessels, the measurement chamber, V_A, and the expansion chamber, V_B, with a volume of approximately (70 and 35) cm^3, respectively, and some auxiliary systems for filling and mixing the compounds in the Burnett vessels and for controlling and measuring the pressure and temperature. The spherical shape of the vessels simplifies the evaluation of the distortion coefficients as a function of temperature and pressure. Moreover, the ratio of outer and inner diameters of both spheres is the same. The relative volume change with pressure is consequently identical for the two vessels. The vessels are made of Invar, because of its excellent corrosion resistance and low thermal expansion coefficient. The constant volume valves have been redesigned to ensure thermal compensation of the packing and valve body. The four-valve arrangement enables the vessels V_A and V_B to be filled or emptied separately and, in addition to the expansion experiment, allows for the compounds in the Burnett vessels to be mixed using a magnetic recirculating pump.

The packing surfaces of valves V_1 and V_4 are exposed to the expansion volume V_B, and those of valves V_2 and V_3 are exposed in the opposite direction of the volumes V_A and V_B. Thus, the principal volume V_A and its fixtures are all-metal, to prevent contact between the sample gas in vessel V_A and the Teflon packing throughout the lengthy Burnett experiment, except for the time it takes to reach thermal equilibrium after expansion.

The measurement vessel is connected to a diaphragm-type differential pressure transducer (Ruska Model 2413), which is 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 pressures. Nitrogen is used to balance the sample gas pressure, and the nitrogen circuit consists of a reservoir, expansion vessels, and pressure regulating systems.

The vessels are immersed in a thermostatic bath filled with about 45 L of an ethylene glycol and water mixture.

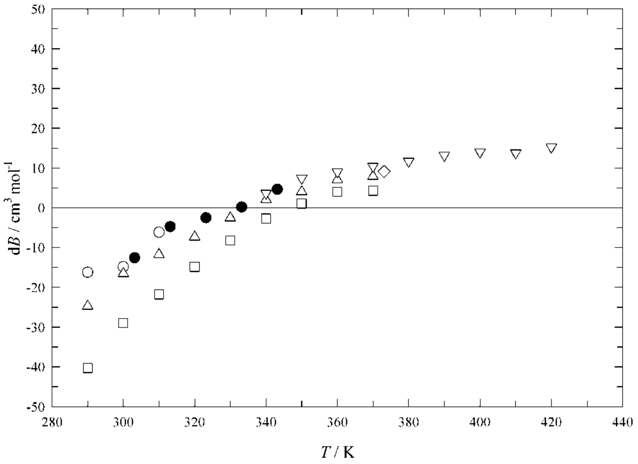

Figure 2. Deviations between the second virial coefficients calculated according to the Tsonopoulos method[12] and the experimental second virial coefficients for R32 against temperature: ●, present work; ○, ref 7; ◇, ref 8; □, ref 9; ▽, ref 10; △, ref 11.

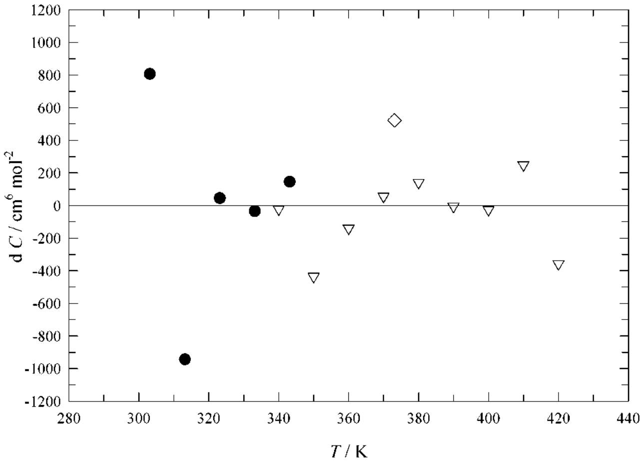

Figure 3. Deviations between the third virial coefficients calculated according to eq 3 and the experimental third virial coefficients for R32 against temperature: ■, present work; ◇, ref 8; ▽, ref 10.

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 temperature 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 temperature measurements, a Hart Scientific Pt 25 Ω resistance thermometer (mod. Hart 5680) is used, while for control purposes a Tersid Pt 100 Ω resistance thermometer is used. Both the thermometers are connected to a digital temperature indicator (Corradi, RP 7000).

The Burnett constant, N, defined as the ratio of the volume of cell A and the sum of the volumes of cells A and B at zero pressure, was determined by means of gaseous helium measurements (since its thermodynamic properties are well established). After taking measurements at several isotherms, the constant was found to be $N = 1.494\,85 \pm 0.0001$; after servicing the setup, we found the Burnett constant to be $N = 1.495\,70 \pm 0.0001$ and $N = 1.496\,91 \pm 0.0001$. These results are marked with a footnote in Tables 1, 2, and 4. The Burnett constant found reproduces the pressures of helium with absolute average deviations, AAD = 0.418 kPa or AAD = 0.142, in percent.

Table 4. Experimental Pressures Measured during Burnett Expansions and Regressed Compressibility Factors of the R32 (1) + CO$_2$ (2) System

T/K = 303.15

Series 1[a] $x_1 = 0.1667$		Series 2 $x_1 = 0.3192$		Series 3 $x_1 = 0.4576$		Series 4 $x_1 = 0.6462$	
P/kPa	z	P/kPa	z	P/kPa	z	P/kPa	z
4639.0	0.6841	4077.7	0.6786	3004.2	0.7486	2353.4	0.7697
3532.1	0.7797	3120.0	0.7762	2220.2	0.8270	1722.4	0.8420
2568.4	0.8487	2275.8	0.8463	1584.8	0.8824	1221.6	0.8927
1813.5	0.8970	1611.5	0.8958	1105.5	0.9202	849.0	0.9274
1256.8	0.9305	1118.7	0.9295	760.2	0.9459	582.7	0.9515
860.2	0.9534	766.9	0.9526	518.3	0.9639	396.5	0.9678
583.9	0.9687	520.4	0.9663	351.1	0.9762	267.4	0.9758
394.0	0.9784	351.8	0.9766	236.7	0.9836	180.2	0.9832
265.0	0.9851	237.2	0.9841	159.1	0.9883		
		159.4	0.9888				

T/K = 313.15

Series 5 $x_1 = 0.3220$		Series 6 $x_1 = 0.4628$		Series 7 $x_1 = 0.6312$		Series 8 $x_1 = 0.8029$	
P/kPa	z	P/kPa	z	P/kPa	z	P/kPa	z
4222.1	0.7154	3251.3	0.7618	2367.6	0.8042	2294.3	0.7708
3163.9	0.8013	2387.2	0.8361	1705.9	0.8662	1676.8	0.8421
2280.5	0.8634	1696.6	0.8883	1197.7	0.9091	1187.9	0.8918
1602.3	0.9068	1181.5	0.9247	827.5	0.9390	825.8	0.9268
1107.7	0.9371	811.0	0.9488	565.2	0.9587	566.8	0.9508
757.4	0.9577	552.2	0.9657	383.4	0.9720	385.7	0.9673
513.9	0.9714	373.6	0.9767	259.0	0.9816	261.0	0.9784
347.1	0.9808	251.9	0.9843	174.1	0.9866	175.9	0.9859
233.7	0.9872	169.3	0.9890				
157.0	0.9914						

T/K = 323.15

Series 9 $x_1 = 0.3108$		Series 10 $x_1 = 0.3487$		Series 11 $x_1 = 0.5709$		Series 12 $x_1 = 0.5866$	
P/kPa	z	P/kPa	z	P/kPa	z	P/kPa	z
5124.0	0.6908	3833.7	0.7764	3270.9	0.7641	3409.1	0.7473
3880.7	0.7820	2791.2	0.8450	2394.7	0.8363	2514.8	0.8241
2818.6	0.8491	1975.1	0.8938	1700.5	0.8877	1794.7	0.8791
1991.5	0.8968	1371.6	0.9278	1183.7	0.9237	1253.3	0.9177
1381.6	0.9299	940.7	0.9513	813.1	0.9484	862.8	0.9444
947.0	0.9529	639.9	0.9673	553.6	0.9654	588.3	0.9626
643.9	0.9685	432.9	0.9781	374.8	0.9769	398.7	0.9751
435.5	0.9791	291.8	0.9855	252.7	0.9846	269.0	0.9834
293.5	0.9864	196.1	0.9904	169.9	0.9898	180.9	0.9888
197.3	0.9915	131.6	0.9935			121.5	0.9928
132.3	0.9934						

T/K = 333.15

Series 13 $x_1 = 0.3222$		Series 14 $x_1 = 0.4489$		Series 15 $x_1 = 0.5791$		Series 16 $x_1 = 0.7372$	
P/kPa	z	P/kPa	z	P/kPa	z	P/kPa	z
2456.6	0.8842	4388.0	0.7457	3522.3	0.7739	2877.4	0.7889
1711.9	0.9210	3235.9	0.8220	2566.3	0.8429	2082.6	0.8535
1177.0	0.9466	2310.2	0.8772	1817.2	0.8922	1468.4	0.8996
801.8	0.9640	1614.2	0.9162	1262.6	0.9266	1017.3	0.9317
543.0	0.9759	1111.7	0.9433	866.3	0.9504	696.8	0.9539
366.0	0.9834	758.4	0.9619	589.5	0.9667	473.6	0.9691
246.2	0.9889	514.1	0.9747	398.8	0.9777	320.2	0.9795
165.3	0.9925	346.9	0.9833	268.9	0.9854	215.7	0.9864
		233.5	0.9891	180.8	0.9906	145.0	0.9912
		156.8	0.9930	121.4	0.9942		

T/K = 343.15

Series 17 $x_1 = 0.3210$		Series 18 $x_1 = 0.4956$		Series 19 $x_1 = 0.6856$		Series 20 $x_1 = 0.7132$	
P/kPa	z	P/kPa	z	P/kPa	z	P/kPa	z
4093.8	0.8229	3340.7	0.8293	2253.8	0.8664	3160.6	0.7994
2922.3	0.8781	2377.3	0.8822	1580.8	0.9084	2276.6	0.8607
2041.3	0.9169	1657.7	0.9195	1091.6	0.9377	1600.4	0.9045
1405.5	0.9437	1140.2	0.9454	745.9	0.9579	1106.7	0.9350
958.4	0.9619	777.0	0.9631	506.2	0.9716	757.0	0.9560
649.6	0.9746	526.4	0.9753	341.9	0.9810	514.1	0.9705
438.1	0.9827	355.1	0.9835	230.2	0.9873	347.5	0.9805
295.0	0.9889	238.9	0.9892	154.7	0.9917	234.1	0.9874
198.2	0.9931	160.4	0.9930			157.3	0.9922
132.9	0.9959	107.6	0.9952				

[a] Data obtained with $N = 1.496\,91$.

Table 5. Experimental and Calculated Second and Third Virial Coefficients for the R32 (1) + CO_2 (2) System

T/K	x_1	$B_\mathrm{m}^\mathrm{exp}$ / $\mathrm{cm^3 \cdot mol^{-1}}$	$B_\mathrm{m}^\mathrm{calc}$ / $\mathrm{cm^3 \cdot mol^{-1}}$	$\mathrm{d}B_\mathrm{m}$ / $\mathrm{cm^3 \cdot mol^{-1}}$	$C_\mathrm{m}^\mathrm{exp}$ / $\mathrm{cm^6 \cdot mol^{-2}}$	$C_\mathrm{m}^\mathrm{calc}$ / $\mathrm{cm^6 \cdot mol^{-2}}$	$\mathrm{d}C_\mathrm{m}$ / $\mathrm{cm^6 \cdot mol^{-2}}$
303.15	0.1667	−133.0	−133.3	0.3	5790	5850	−60
	0.3192	−151.5	−151.1	−0.3	6990	6940	50
	0.4576	−171.3	−171.1	−0.2	8430	8420	10
	0.6462	−204.0	−204.1	0.0	11680	11710	−30
313.15	0.3220	−142.1	−141.6	−0.5	7280	6370	910
	0.4628	−157.8	−160.1	2.3	7620	8210	−590
	0.6312	−184.5	−186.2	1.6	10060	11190	−1130
	0.8029	−219.1	−216.9	−2.2	16350	15010	1340
323.15	0.3108	−130.3	−131.2	0.9	6620	6710	−90
	0.3487	−135.0	−135.5	0.4	7280	7180	100
	0.5709	−165.0	−164.2	−0.8	10640	10620	20
	0.5866	−167.3	−166.5	−0.8	10870	10900	−30
333.15	0.3222	−122.0	−123.2	1.2	6520	6170	350
	0.4489	−136.6	−137.5	0.9	7940	8110	−170
	0.5791	−153.9	−154.0	0.2	9900	10420	−520
	0.7362	−178.5	−176.6	−1.9	13790	13320	470
343.15	0.3210	−110.5	−110.8	0.3	5130	5500	−370
	0.4956	−132.5	−128.4	−4.2	8250	8010	240
	0.6856	−157.6	−152.3	−5.3	12160	11260	900
	0.7927	−161.4	−168.0	6.5	12020	13070	−1050

Table 6. Smoothed Second and Third Virial Coefficents for the R32 (1) + CO_2 (2) System

T/K	B_{11} / $\mathrm{cm^3 \cdot mol^{-1}}$	B_{12} / $\mathrm{cm^3 \cdot mol^{-1}}$	B_{22} / $\mathrm{cm^3 \cdot mol^{-1}}$	C_{111} / $\mathrm{cm^6 \cdot mol^{-2}}$	C_{112} / $\mathrm{cm^6 \cdot mol^{-2}}$	C_{122} / $\mathrm{cm^6 \cdot mol^{-2}}$	C_{222} / $\mathrm{cm^6 \cdot mol^{-2}}$
303.15	−283.9	−154.5	−118.8	24180	7415	6930	4860
313.15	−257.5	−147.4	−109.8	20270	10640	4550	4600
323.15	−238.5	−137.6	−103.7	19280	12220	4890	4670
333.15	−220.8	−129.6	−95.1	17380	13510	3340	4020
343.15	−202.8	−111.7	−89.4	15920	12420	2460	4090

Experimental Procedure, Gas Chromatographic Calibration and Experimental Uncertainties

Experimental Procedure. To measure the system components, the classical Burnett experimental procedure was followed. 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 was 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 the 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's composition.

Gas Chromatographic Calibration. The mixtures for the calibration were prepared in stainless steel bottles of about 250 cm^3 capacity; the mass of charged components, depending on the composition, was varied from 8 to 15 g and was weighed with an analytical balance to ±0.1 mg. On that basis, the molar fraction of the sample was found. Next, the prepared samples were connected on-line to the gas chromatograph, and after the sample was preheated to about 323 K (for the sample homogenization), a series of gas chromatographic analyses was performed. The reproducibility of the gas chromatograph for each sample was within 0.1%. The results of the analysis for the series of samples covering a wide range of composition were next regressed to find the relation between ratio of area and composition in molar fraction. A third-degree polynomial expression, obtained by forcing it also to the points corresponding to pure compounds, gives us the unknown composition when its peak area ratio is measured. The composition of the mixtures was found from the gas chromatographic analysis performed for the same gas chromatograph parameters and applying the expression found. For the analysis, the samples collected from the first Burnett expansions were used. Further details of the method are given in ref 5.

Experimental Uncertainties. 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 lower than ±0.03 K.

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

The uncertainty of the mixture's composition was found to be always lower than 0.5% in mole fraction, based on the calibration with samples prepared gravimetrically and on the reproducibility of the gas chromatograph (Carlo Erba Mega Series 5380 with a thermal conductivity detector).

Results for R32 and CO_2

For R32, 81 experimental points along 5 isotherms (9 sets in all) were collected in the temperature range from 303 K to 343 K and for pressures from 125 kPa up to 4370 kPa. For CO_2, 234 experimental points along 7 isotherms (17 sets altogether) were collected in the temperature range from 283 K to 363 K and in the pressure range from 11 kPa to 5700 kPa. The experimental data for R32 are shown in Table 1 while the experimental data for CO_2 are reported elsewhere.[6]

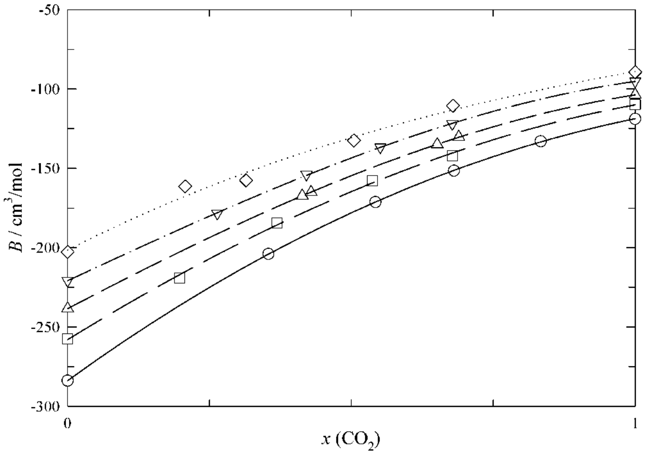

Figure 4. Second virial coefficients for the R32 (1) + CO$_2$ (2) system against the mole fraction at the following temperatures, T: ○, 303.15; □, 313.15; △, 323.15; ▽, 333.15; ◇, 343.15 K. The lines represent the correlated values.

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

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

In the regression, each run was treated separately and $(\mathrm{d}P)^2$ was used as an objective function applying the Burnett constant from the helium calibration. The pressure distortion of the Burnett cells was considered, as explained elsewhere.[2−4]

Defining the average absolute deviation in pressure as

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

the AAD = 0.239 kPa for R32 and AAD = 0.163 kPa for CO$_2$[6] were found, well within the estimated experimental uncertainty.

The second and third virial coefficients for R32 and for CO$_2$ are shown in Tables 2 and 3, together with the pressure deviations from the fit that proved to be randomly distributed. A systematic deviation in pressure is not evident for both compounds, enabling us to say that the adsorption does not affect the results.

In Figures 2 and 3, the second and third virial coefficients for R32 are plotted and compared with values in the literature.[7−11] In Figure 2, the derived second virial coefficients were compared with the values calculated by means of the Tsonopoulos correlating method,[12] while, in Figure 3, the third virial coefficients were compared with the ones calculated with the empirical expression

$$C = A_1 + A_2(T_r - 1) + A_3(T_r - 1)^2 \qquad (3)$$

where A_1 = 14 565.3408; A_2 = −49 881.8850; and A_3 = 105 331.4976.

For R32, there is a good consistency with most of the literature data for the second virial coefficient (refs 7, 8, 10, and 11), while the data in ref 9 are systematically lower. For the third virial coefficients, the results (obtained in a different temperature region) clearly follow a common temperature trend with data in the literature,[8,10] even if quite big deviations from the trend are evident while comparing data from various sources. For comparison, we only considered literature sources in which original data were reported.

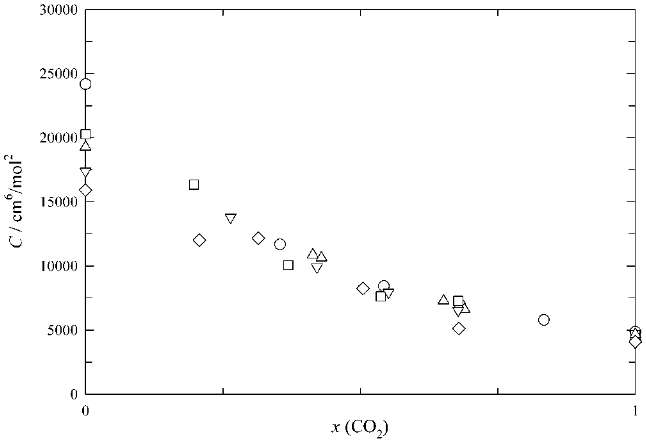

Figure 5. Third virial coefficients for the R32 (1) + CO$_2$ (2) system against the mole fraction at the following temperatures, T: ○, 303.15; □, 313.15; △, 323.15; ▽, 333.15; ◇, 343.15 K.

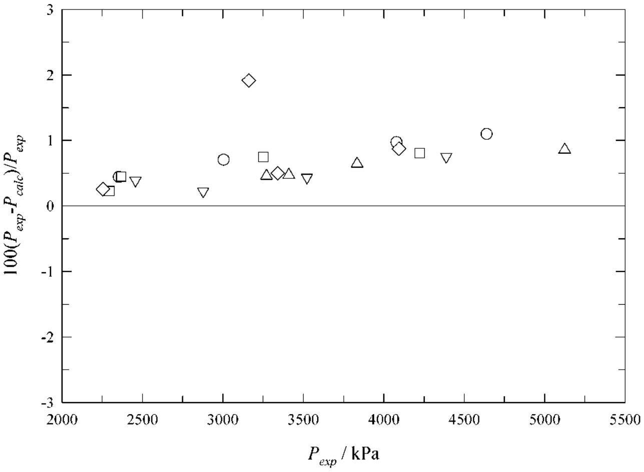

Figure 6. Deviations in pressure produced by the REFPROP 6.01[15] at the following temperatures, T: ○, 303.15; □, 313.15; △, 323.15; ▽, 333.15; ◇, 343.15 K.

For CO$_2$, all the comparisons with the literature are reported elsewhere;[6] hence, we only report a brief summary of the results here. For the second virial coefficient, the present experimental results are consistent with the literature sources.[1] Also, the Tsonopoulos correlating method[13] represents the experimental data well. For the third virial coefficients, the experimental data in the literature are randomly scattered within 25% around values resulting from the Orbey and Vera correlation;[14] our results lay well within that limit.

Results for the Mixtures

For the R32 + CO$_2$ system, 185 experimental points along 20 sets and 5 isotherms were collected within the temperature range from 303 to 343 K and the pressure range from 110 kPa to 5100 kPa. The experimental findings, together with the compressibility factor values, are given in Table 4. The virial coefficients for the mixtures were found by applying the same procedure as that for the pure compounds. The values of the second and third virial coefficients (Table 5), 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 6. The second cross virial coefficients were calculated from the expression

$$B_m = \sum_{i=1}^{n}\sum_{j=1}^{n} B_{ij}x_ix_j \qquad (4)$$

for each experimental datum point. Next, the B_{12} values found for each temperature were averaged; the averaged B_{12} values, given in Table 6, were used to calculate the deviations of B_m from the experimental values shown in Table 5. The third cross virial coefficients were calculated from the defining equation

$$C_m = \sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n} C_{ijk}x_ix_jx_k \qquad (5)$$

Bearing in mind that two-third cross virial coefficients (namely C_{112} and C_{122}) represent third virial coefficients for each mixture's composition, their values could not be calculated directly for each datum point, so they were calculated as average values by combining data for each temperature. The averaged values of the third cross virial coefficients are included in Table 6. Using these values, the third virial coefficients for the mixtures were recalculated for each point. The results, together with the deviations, are also included in Table 5. The greatest random error in B_m was found at T = 343.15 K with AAD = 4.08 $cm^3 \cdot mol^{-1}$, while at T = (303.15, 313.15, 323.15, and 333.15) K the average absolute deviation was found to be AAD = 0.91 $cm^3 \cdot mol^{-1}$. This is presumably due to a possible slightly poorer thermal stability at higher temperatures while a (water + ethylene glycol) mixture is used as the bath fluid. The overall AAD for B_m was evaluated at 2.5 $cm^3 \cdot mol^{-1}$, while the AAD for C_m was 399 $cm^6 \cdot mol^{-2}$, corresponding to an average deviation of around 10%. These values are acceptable if compared with numerous experimental data, obtained in reduced temperature ranges below or close to 1, reported in the compilation.[14] The second and third virial coefficients for the system being plotted against the mole fraction in Figures 4 and 5, respectively, show positive and negative deviations from ideality, defined here as

$$B_{12} = (B_{11} + B_{22})/2 \qquad (6)$$

$$C_{112} = (2C_{111} + C_{222})/3 \qquad (7)$$

$$C_{122} = (C_{111} + 2C_{222})/3 \qquad (8)$$

Because of the total lack of data in the literature on the superheated vapor region for this system, the experimental findings were compared with the prediction obtained with the REFPROP 6.01[15] software. The calculations were performed at the highest experimental pressures of each run, adopting regressed values for $\rho(1)$, B_m, and C_m. The differences in pressure are given in Figure 6, showing a consistency within 1%; the figures were systematically below those resulting from our experiment.

Conclusions

This work reports on experimental results for the R32 + CO_2 system obtained with the Burnett method. The performance of the apparatus was checked by means of measurements for R32 and CO_2, and a good consistency was observed between the virial coefficients obtained and those reported in the literature. The R32 + CO_2 system was studied over five isotherms, and second and third cross virial coefficients were derived. Over the entire temperature range, the second virial coefficients showed positive (while the third virial coefficients showed negative) deviations from ideality. Our results proved consistent with the prediction obtained using REFPROP 6.01.

Acknowledgment

The authors are grateful to Filippo Giorgi for his kind help.

Literature Cited

(1) Angus, S.; Armstrong, B.; de Reuck, K. M. *International Thermodynamic Tables of the Fluid State, vol. 3, Carbon Dioxide*; Pergamon Press: Oxford, 1976.
(2) Glowka, S. A Burnett Apparatus for Accurate Determination of the Volumetric Properties of Gases. *Naucznaja apparatura* **1988**, *3*, 79−84.
(3) Glowka, S. Determination of Volumetric Properties of Ammonia Between 298 and 473 K and Carbon Dioxide Between 304 and 423 K Using the Burnett Method. *Polym. J. Chem.* **1990**, *64*, 699−709.
(4) Glowka, S. Volumetric Properties of Ammonia + Argon, + Helium, + Methane, and + Nitrogen Mixtures Between 298 and 423 by the Burnett- Isochoric Method. *Fluid Phase Equilib.* **1992**, *78*, 285−296.
(5) Bobbo, S.; Stryjek, R.; Elvassore, N.; Bertucco, A. A Recirculation Apparatus for Vapor-Liquid Equilibrium Measurements of Refrigerants Binary Mixtures of R600a, R134a and R236fa. *Fluid Phase Equilib.* **1998**, *150−151*, 343−352.
(6) Di Nicola, G.; Giuliani, G.; Polonara, F.; Stryjek, R. *PVTx* Measurements for the R125+CO_2 System by the Burnett Method. *Fluid Phase Equilib.* **2002**, *199*, 163−176.
(7) Bignell, C. M.; Dunlop, P. J. Second Virial Coefficients for Fluoromethanes and their Binary Mixtures with Helium and Argon. *J. Chem. Eng. Data* **1993**, *38*, 139−140.
(8) Defibaugh, D. R.; Morrison, G.; Weber, L. A. Thermodynamic Properties of Difluoromethane. *J. Chem. Eng. Data* **1994**, *39*, 333−340.
(9) Quian, Z. Y.; Nishimura, A.; Sato, H.; Watanabe, K. Compressibility Factors and Virial Coefficients of Difluoromethane (HFC-32) Determined by Burnett Method. *JSME Int. J.* **1993**, *36*, 665−670.
(10) Sato, T.; Sato, H.; Watanabe, K. PVT Property Measurements for Difluoromethane (HFC-32). *J. Chem. Eng. Data* **1994**, *39*, 851−854.
(11) Zhang, H. L.; Sato, H.; Watanabe, K. Second Virial Coefficients for R-32, R-125, R-134a, R-143a, R-152a and their Binary Mixtures. *Proceedings of the 19th International Congress of Refrigeration*, The Hague, The Netherlands, 1995; Vol. IVa, pp 622−629.
(12) Tsonopoulos, C. An empirical correlation of second virial coefficients. *AICHE J.* **1974**, *20*, 263−272.
(13) Orbey, H.; Vera, J. H. Correlation for the third virial coefficient using T_c, P_c and ω as parameters. *AICHE J.* **1983**, *29*, 107−113.
(14) Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Gases*; Clarendon Press: Oxford, 1969.
(15) McLinden, M. O.; Klein, S. A.; Lemmon, E. W.; Peskin, A. P. *NIST Thermodynamic and transport properties of refrigerants and refrigerant mixtures (REFPROP)*, version 6.01; Boulder, CO, 1998.

Received for review November 19, 2001. Accepted April 21, 2002. This work was supported by the Italian *Ministero dell'Università e della Ricerca Scientifica e Tecnologica*.

JE015537M