

# Isochoric Measurements for CO<sub>2</sub> + R125 and CO<sub>2</sub> + R32 Binary Systems

Giovanni Di Nicola,\* Marco Pacetti, and Fabio Polonara

Dipartimento di Energetica, Università di Ancona, Via Breccia Bianche, 60100 Ancona, Italy

Roman Stryjek

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

---

*P*–*V*–*T*–*x* measurements, both in the two-phase and in the superheated vapor regions, were carried out for the CO<sub>2</sub> + R125 and CO<sub>2</sub> + R32 systems. The isochoric experiment covered a temperature range from 254 K to 363 K and a pressure range from 680 kPa to 4920 kPa. The number of moles charged into the isochoric cell was calculated by means of the virial equation of state using the second and third virial coefficients derived from our *P*–*V*–*T*–*x* measurements taken with the Burnett method. After the number of moles was determined, the VLE parameters were derived from experimental data in the two-phase region, applying the flash method and the Carnahan–Starling–DeSantis equation of state (CSD EOS). The dew point parameters were found by interpolating the *P*–*T* isochoric sequences, again applying the CSD EOS. Because of the lack of data, the *P*–*V*–*T*–*x* data for the superheated region were compared with estimates of the REFPROP software 6.01.

---

## Introduction

In our search for fluids that are potentially suitable for low-temperature refrigerant applications, we have turned our attention to systems composed of hydrofluorocarbons (HFCs) in mixtures with CO<sub>2</sub>. In previous studies,<sup>1,2</sup> the *P*–*V*–*T*–*x* properties of the CO<sub>2</sub> + R125 and CO<sub>2</sub> + R32 systems were measured by the Burnett method in a temperature range from 303 K to 363 K. The second and third virials for the system constituents and their respective cross virial coefficients were derived from the experimental results for both systems.

The present study applied the isochoric setup<sup>3,4</sup> and measurements were taken for both the two-phase and the superheated vapor regions, covering a wider temperature range (from 254 K to 363 K). The data in the two-phase region enable VLE parameters to be derived using a flash method with the Carnahan–Starling–De Santis<sup>5</sup> equation of state (CSD EOS); in addition, the dew point for each isochore was found from the intersection of *P*–*T* sequences. These dew point values were also used to derive the VLE parameters. The methods adopted have been described previously.<sup>6</sup> The two derived parameters were compared with each other and a good consistency was found. The VLE data for the CO<sub>2</sub> + R32 system were compared with the literature,<sup>7</sup> but no data were available in the literature for the CO<sub>2</sub> + R125 system. The *P*–*V*–*T*–*x* data in the superheated region were compared, for a wider temperature range than was previously measured by the Burnett method, with the REFPROP 6.01<sup>8</sup> estimate.

## Experimental Section

**Chemicals.** Carbon dioxide was supplied by Sol SpA, while R32 and R125 were supplied by Ausimont SpA; their

purity was checked by gas chromatography, using a thermal conductivity detector, and was found to be 99.99% on an area response basis for the CO<sub>2</sub> and 99.98% and 99.96% for the R32 and R125, respectively.

**Experimental Apparatus.** The experimental setup was as described previously,<sup>3,4</sup> so it is only briefly outlined here. An AISI 304 stainless steel spherical cell contains the refrigerant sample and is connected to a differential diaphragm pressure transducer coupled to an electronic null indicator. The spherical cell and pressure transducer are immersed in the main thermostatic bath containing a mixture of water and glycol and controlled by a PID device. An auxiliary bath, also controlled by a PID device, helps the system to keep the temperature constant. Temperatures were measured with a calibrated resistance thermometer and the total uncertainty in temperature was found to be lower than ±0.02 K. The uncertainty in the pressure measurements is due to the uncertainty of the transducer and null indicator system and of 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; it was found to be less than ±1 kPa.

**Experimental Procedure.** A substantial modification was introduced in the charging and composition measuring procedures. The isochoric cell was originally charged<sup>9</sup> from special bottles and the mass of the charge was determined as the difference in the mass in the bottle before and after charging. Calculating the mass charged for each component gave us the composition of the mixtures. This procedure was accurate, but rather tedious. It was easy to implement, however, and provided a proper molecular weight and saturated pressure for the compounds likely to be involved in most HFCs. In some cases, however, a special bottle with a different capacity, size, and/or wall thickness, and

\* To whom correspondence should be addressed. Tel.: +39-0712204432. Fax: +39-0712804239. E-mail: anfreddo@unian.it.

**Table 1. Compositions of the Investigated Systems<sup>a</sup>**

$z_1$	$T$ range K	$P$ range kPa	$n$ mol	no. expl. points			dew point	
				2ph	Vap	tot	$T$ K	$P$ kPa
CO <sub>2</sub> + R125								
0.3007	260–354	733–2184	0.22218	7	13	20	292.63	1614.9
0.5189	263–362	1125–2701	0.26358	7	14	21	287.84	1899.6
0.6301	258–363	1328–4600	0.48481	11	12	23	304.99	3327.9
0.6884	259–358	1497–4718	0.50659	10	12	22	297.19	3322.4
0.8240	253–348	1514–4059	0.42660	11	14	25	284.48	2904.9
CO <sub>2</sub> + R32								
0.1010	264–358	682–1911	0.18509	6	14	20	287.97	1380.0
0.3895	266–357	1116–2678	0.26385	7	14	21	289.60	1950.6
0.6071	254–356	1219–4084	0.42087	9	13	22	294.07	2970.2
0.7343	256–348	1479–3622	0.37006	11	13	24	283.55	2639.0
0.8023	255–343	1659–4923	0.54119	8	11	19	288.67	3598.6

<sup>a</sup> 2ph and Vap denote data within the VLE boundary and superheated region, respectively.

**Table 2. Experimental Data within the VLE Boundary for the CO<sub>2</sub> + R125 System**

$z_1$	$T$	$P$	$V$	$z_1$	$T$	$P$	$V$	
	K	kPa	dm <sup>3</sup> ·mol <sup>-1</sup>		K	kPa	dm <sup>3</sup> ·mol <sup>-1</sup>	
0.3007	260.11	732.8	1.145	0.6884	258.90	1496.9	0.502	
	262.78	786.1	1.145		262.92	1650.4	0.502	
	267.34	878.6	1.145		267.56	1843.7	0.502	
	273.46	1019.6	1.146		273.31	2097.6	0.502	
	278.45	1163.8	1.146		278.46	2338.1	0.502	
	283.35	1306.7	1.146		283.48	2583.7	0.503	
0.5189	288.43	1469.5	1.146	287.46	2752.7	0.503		
	263.11	1125.5	0.965	0.8240	291.38	2999.3	0.503	
		267.46	1239.4		0.965	293.50	3115.5	0.503
		270.89	1337.1		0.966	298.59	3356.2	0.503
		273.42	1410.3		0.966	253.48	1514.4	0.596
		278.51	1576.9		0.966	256.32	1627.9	0.596
283.45		1741.6	0.966		258.34	1710.3	0.596	
0.6301	285.93	1829.1	0.966	261.17	1831.6	0.596		
	257.61	1328.3	0.525	263.21	1923.2	0.596		
		260.83	1438.5	0.525	265.91	2039.6	0.596	
		263.27	1523.5	0.525	268.25	2159.3	0.597	
		267.84	1694.8	0.525	271.05	2274.7	0.597	
		273.32	1906.5	0.525	273.47	2378.4	0.597	
		278.53	2116.9	0.525	275.90	2485.4	0.597	
		283.46	2328.5	0.525	278.31	2653.9	0.597	
		288.30	2546.6	0.525				
		293.38	2774.9	0.526				
		298.45	3007.8	0.526				
		303.58	3293.4	0.526				

consequently with a different tare, would have to be designed or a nongravimetric method developed. As an alternative better suited to systems with CO<sub>2</sub>, we developed a procedure based on the virial equation of state for the system under study, using the virial EOS with coefficients found from our independent Burnett measurements. To be more precise, the mass charged was calculated by applying virial coefficients for individual components and cross virial coefficients (all found from the data reduction), providing the mixtures' composition was known from independent measurements. The composition was found by analyzing the sample withdrawn from the isochoric cell after collecting data for the  $P$ ,  $T$  sequence. This was done with a thermal conductivity detector and gas chromatography. The gas chromatograph was calibrated using a set of samples of exactly known composition (different amounts by mass of the two fluids were charged in a small bottle and weighed with an analytical balance) and analyzing them until a statistically adequate data set was obtained. A third-degree polynomial expression, obtained by forcing it to the points corresponding to pure compounds, enabled

the unknown composition to be established when its peak area ratio was measured. The uncertainty in composition measurements was estimated from the reproducibility of the gas chromatography and the uncertainty in sample preparation and amounted to 0.1% of the mole fraction. Considering the uncertainty in the composition measurements and the uncertainty in the virial coefficient values, we estimated that the overall uncertainty for the mass charged amounted to 0.001 mol on average and 0.005 mol in the worst case.

## Results and Discussion

The temperature and pressure ranges are shown in Table 1, along with the mixture's composition and the number of moles charged. The experimental VLE data are given in Tables 2 and 3, while Tables 4 and 5 show the  $P$ - $V$ - $T$ - $x$  measurements for CO<sub>2</sub> + R125 and CO<sub>2</sub> + R32, respectively. The  $T$ - $P$  data are also presented graphically in Figures 1 and 2. Analyzing the slope of each  $T$ - $P$  sequence, each experimental point was described in rela-

**Table 3. Experimental Data within the VLE Boundary for the CO<sub>2</sub> + R32 System**

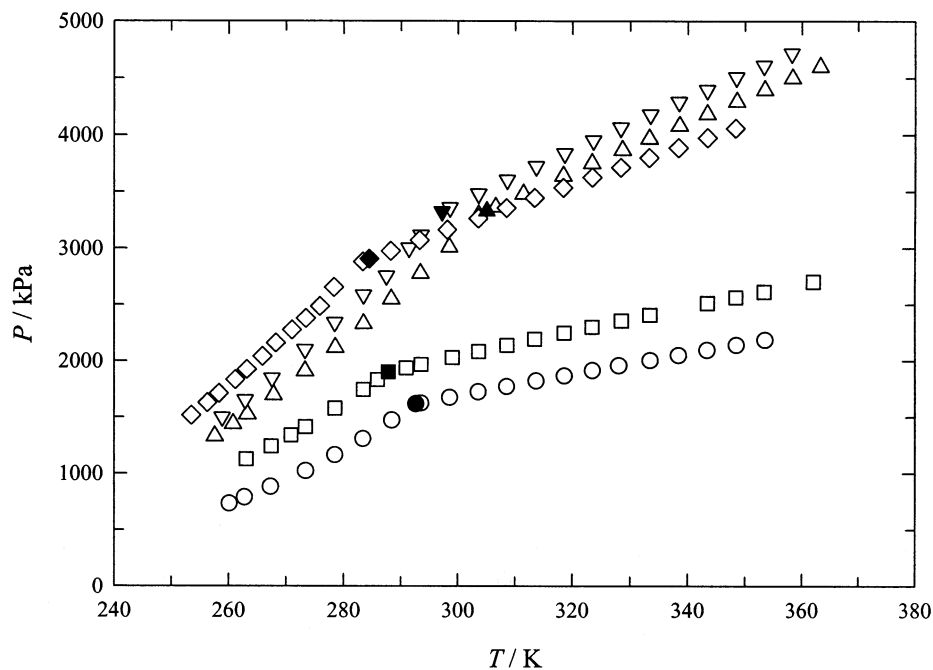
$z_1$	$T$ K	$P$ kPa	$V$ dm <sup>3</sup> ·mol <sup>-1</sup>	$z_1$	$T$ K	$P$ kPa	$V$ dm <sup>3</sup> ·mol <sup>-1</sup>
0.1010	263.82	681.7	1.375	0.7343	255.83	1478.7	0.687
	268.82	794.1	1.375		258.40	1575.2	0.687
	273.79	925.4	1.375		261.03	1677.6	0.687
	278.47	1061.6	1.376		263.39	1774.3	0.688
	283.37	1217.1	1.376		265.96	1878.6	0.688
	288.37	1381.3	1.376		268.45	1983.4	0.688
0.3895					270.88	2086.1	0.688
	265.69	1116.0	0.964		273.30	2188.2	0.688
	274.48	1389.0	0.965		275.89	2310.9	0.688
	270.29	1252.3	0.965		278.38	2428.7	0.688
	277.31	1482.7	0.965		283.28	2619.0	0.688
	280.33	1592.8	0.965	0.8023			
	283.42	1707.1	0.965		255.45	1659.0	0.470
	288.34	1898.7	0.965		258.50	1804.8	0.470
0.6071					263.51	2059.4	0.470
	254.35	1218.6	0.604		268.38	2325.3	0.470
	258.33	1353.8	0.604		273.43	2616.0	0.470
	263.32	1536.9	0.605		278.43	2923.2	0.470
	268.39	1741.6	0.605		283.40	3241.9	0.471
	273.35	1947.5	0.605		289.36	3614.3	0.471
	278.49	2178.2	0.605				
	283.40	2410.6	0.605				
	288.46	2687.6	0.605				
	293.34	2932.7	0.605				

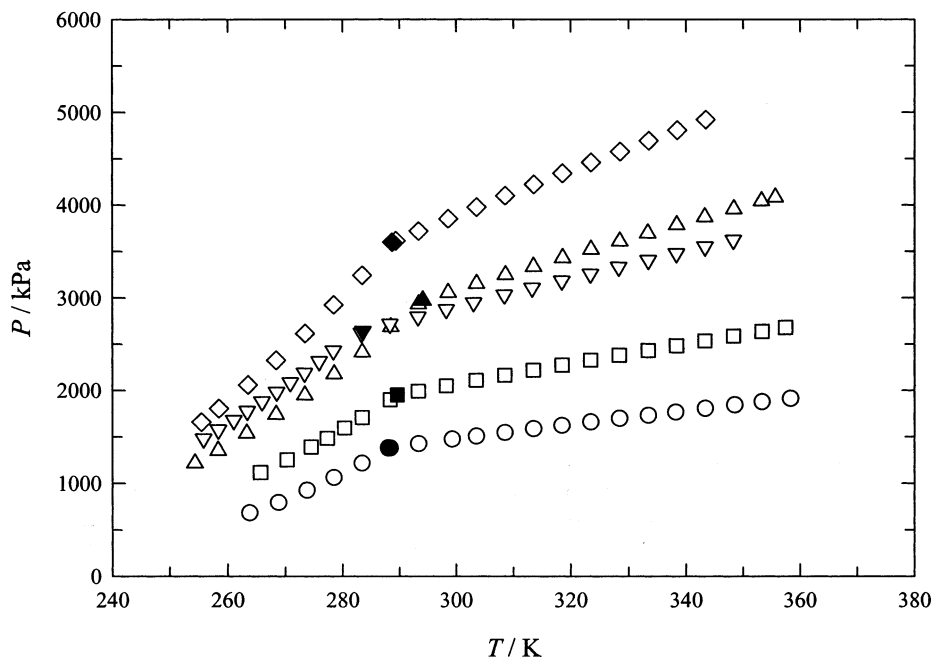
**Table 4. Experimental Data in the Superheated Vapor Region for the CO<sub>2</sub> + R125 System**

$z_1$	$T$ K	$P$ kPa	$V$ dm <sup>3</sup> ·mol <sup>-1</sup>	$z_1$	$T$ K	$P$ kPa	$V$ dm <sup>3</sup> ·mol <sup>-1</sup>
0.3007				0.6884			
	293.50	1623.1	1.147		303.55	3478.2	0.503
	298.55	1673.2	1.147		308.61	3600.3	0.503
	303.53	1722.2	1.147		313.68	3720.3	0.504
	308.53	1770.6	1.147		318.63	3835.6	0.504
	313.71	1820.0	1.148		323.62	3950.4	0.504
	318.61	1866.4	1.148		328.39	4063.6	0.504
	323.50	1912.2	1.148		333.50	4178.9	0.504
	328.09	1954.6	1.148		338.49	4290.8	0.504
	333.47	2004.0	1.149		343.37	4394.7	0.504
	338.39	2048.9	1.149		348.46	4506.3	0.504
	343.37	2093.8	1.149		353.31	4611.3	0.504
	348.49	2139.5	1.150		358.24	4718.1	0.505
	353.53	2184.4	1.150	0.8240			
0.5189					283.36	2880.6	0.597
	290.95	1935.1	0.966		288.21	2975.1	0.597
	293.53	1965.1	0.967		293.23	3071.0	0.597
	299.00	2028.5	0.967		298.09	3162.9	0.597
	303.61	2080.9	0.967		303.53	3264.0	0.598
	308.59	2136.7	0.967		308.48	3354.6	0.598
	313.45	2192.0	0.967		313.41	3444.9	0.598
	318.58	2246.8	0.968		318.39	3534.2	0.598
	323.44	2299.7	0.968		323.46	3624.8	0.598
	328.52	2354.4	0.968		328.42	3712.7	0.598
	333.45	2406.0	0.968		333.32	3799.1	0.598
	343.44	2511.7	0.969		338.37	3887.1	0.598
	348.40	2563.2	0.969		343.42	3974.7	0.599
	353.37	2612.8	0.969		348.32	4059.3	0.599
	362.00	2701.5	0.970				
0.6301							
	306.53	3362.6	0.526				
	311.43	3478.1	0.526				
	318.42	3637.5	0.526				
	323.41	3749.0	0.526				
	328.70	3866.0	0.526				
	333.35	3966.9	0.526				
	338.56	4079.7	0.527				
	343.39	4182.2	0.527				
	348.53	4291.5	0.527				
	353.47	4395.6	0.527				
	358.35	4497.9	0.527				
	363.27	4599.8	0.527				

**Table 5. Experimental Data in the Superheated Vapor Region for the CO<sub>2</sub> + R32 System**

$z_1$	$T$ K	$P$ kPa	$V$ dm <sup>3</sup> ·mol <sup>-1</sup>	$z_1$	$T$ K	$P$ kPa	$V$ dm <sup>3</sup> ·mol <sup>-1</sup>		
0.1010	293.38	1425.6	1.376	0.7343	288.30	2714.0	0.688		
	299.29	1472.7	1.377		293.28	2793.8	0.688		
	303.54	1503.9	1.377		298.23	2872.5	0.689		
	308.54	1546.0	1.377		303.08	2947.9	0.689		
	313.53	1584.5	1.378		308.42	3030.2	0.689		
	318.46	1621.8	1.378		313.30	3104.6	0.689		
	323.46	1659.3	1.378		318.44	3182.3	0.689		
	328.47	1696.5	1.379		323.41	3256.7	0.689		
	333.46	1733.1	1.379		328.31	3329.6	0.690		
	338.21	1767.1	1.379		333.43	3405.2	0.690		
	343.38	1804.5	1.380		338.33	3477.2	0.690		
	348.53	1841.3	1.380		343.31	3549.5	0.690		
	353.34	1875.6	1.380		348.29	3621.7	0.690		
	358.33	1910.7	1.381						
	0.3895	293.32	1992.0		0.966	0.8023	293.36	3719.2	0.471
		298.25	2048.5		0.966		298.56	3852.8	0.471
303.49		2107.8	0.966	303.56	3977.9		0.471		
308.49		2163.2	0.966	308.56	4101.0		0.471		
313.48		2218.0	0.966	313.56	4222.3		0.471		
318.49		2272.5	0.967	318.55	4342.4		0.471		
323.46		2325.0	0.967	323.52	4460.5		0.471		
328.41		2377.8	0.967	328.52	4578.1		0.472		
333.41		2430.5	0.967	333.51	4694.3		0.472		
338.35		2482.2	0.968	338.47	4809.1		0.472		
343.34		2534.0	0.968	343.44	4923.3		0.472		
348.32		2585.2	0.968						
353.33		2636.5	0.968						
357.45		2678.2	0.968						
0.6071		298.55	3055.6	0.606					
		303.55	3151.0	0.606					
	308.58	3245.6	0.606						
	313.52	3336.7	0.606						
	318.58	3431.3	0.606						
	323.49	3520.3	0.606						
	328.47	3609.7	0.606						
	333.35	3696.7	0.606						
	338.38	3785.2	0.607						
	343.29	3871.1	0.607						
	348.34	3958.9	0.607						
	353.22	4042.8	0.607						
	355.62	4084.0	0.607						

**Figure 1.**  $P, V, T, x$  experimental data for the CO<sub>2</sub> + R125 binary system (open symbols) and dew points found by interpolation (closed symbols): (○)  $z_1 = 0.3007$ ; (□)  $z_1 = 0.5189$ ; (△)  $z_1 = 0.6301$ ; (▽)  $z_1 = 0.6884$ ; (◇)  $z_1 = 0.8240$ .

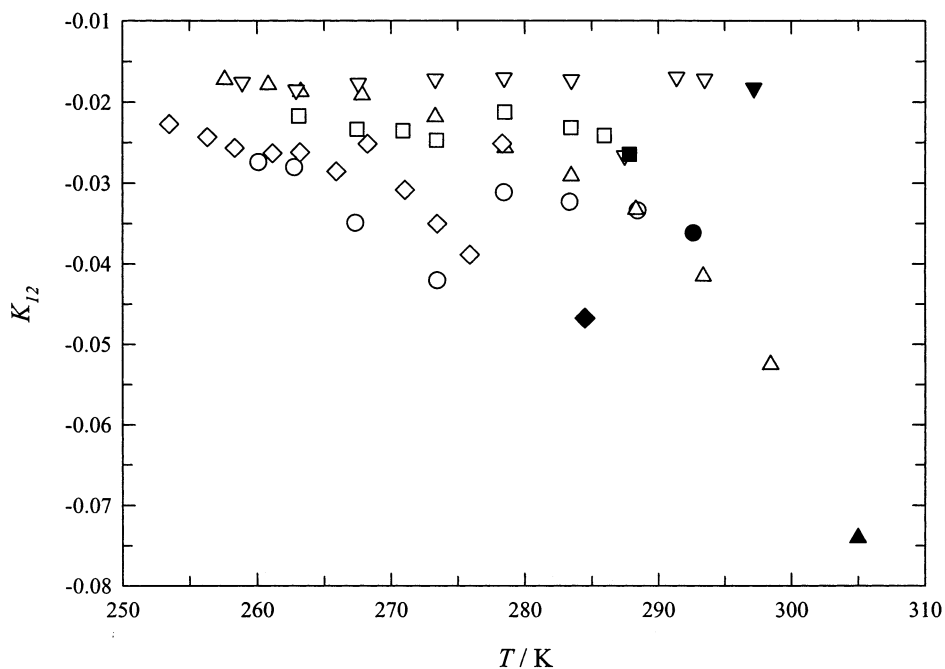


**Figure 2.**  $P, V, T, x$  experimental data for the  $\text{CO}_2 + \text{R32}$  binary system (open symbols) and dew points found by interpolation (closed symbols): ( $\circ$ )  $z_1 = 0.1010$ ; ( $\square$ )  $z_1 = 0.3895$ ; ( $\triangle$ )  $z_1 = 0.6071$ ; ( $\nabla$ )  $z_1 = 0.7343$ ; ( $\diamond$ )  $z_1 = 0.8023$ .

**Table 6. Binary Interaction Parameters and Bubble Point Composition ( $x_2$ ) Found from the Dew Point Applying the CSD EOS**

$\text{CO}_2 + \text{R125}$				$\text{CO}_2 + \text{R32}$			
series	$K_{12\text{dew}}$	$K_{12\text{flash}}$	$x_2$	series	$K_{12\text{dew}}$	$K_{12\text{flash}}$	$x_2$
1	-0.03616	-0.03280	0.1367	1	-0.02902 <sup>a</sup>	-0.02070 <sup>a</sup>	0.0426
2	-0.02648	-0.02315	0.2754	2	0.00084	0.00417	0.1856
3	-0.07403	-0.02770	0.4503	3	0.00894	0.01244	0.3791
4	-0.01830	-0.01847	0.4895	4	-0.00438	0.01556	0.5059
5	-0.04677	-0.02808	0.6346	5	0.01688	0.01829	0.6326
avg	-0.04035	-0.02600		avg	0.00557	0.00835	

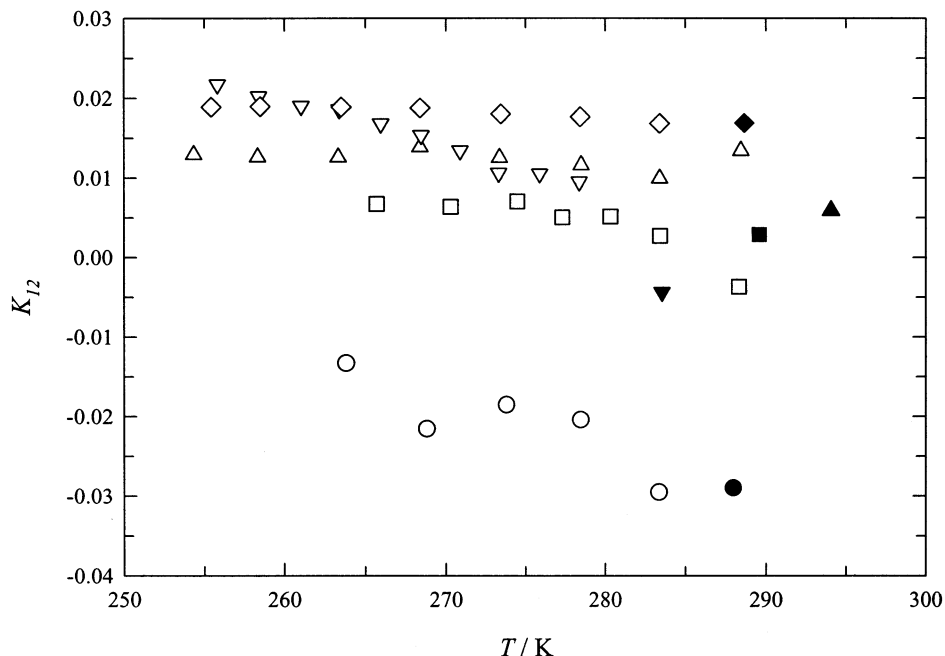
<sup>a</sup> Not used in further regression.



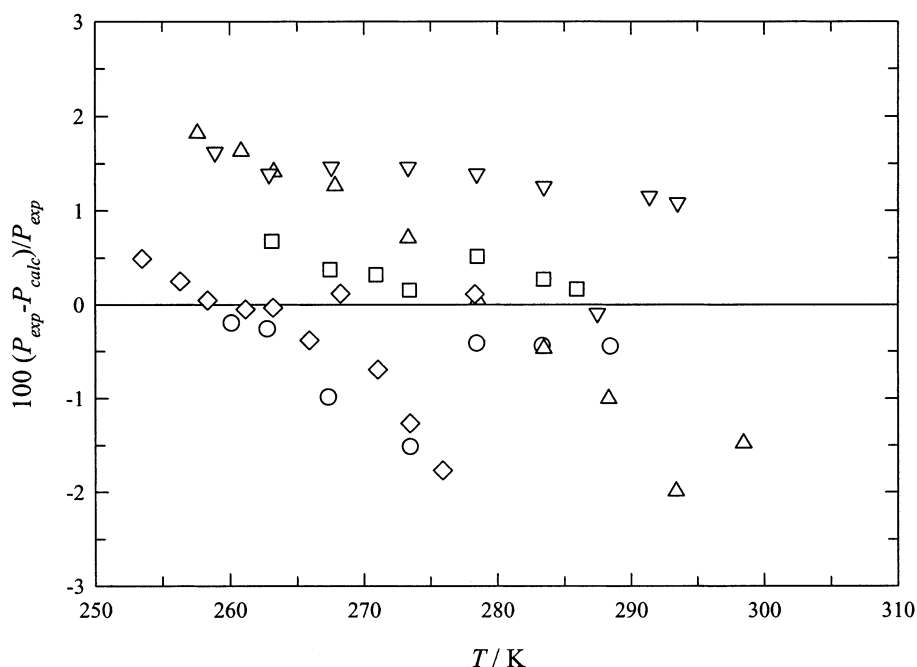
**Figure 3.**  $K_{12}$  values found by the flash method for the  $\text{CO}_2 + \text{R125}$  system: Closed symbols.  $K_{12}$  values found by the dew point method: symbols denoted as in Figure 1.

tion either to the superheated or to the two-phase region. The number of data belonging to each region is also

included in Table 1. The data belonging to the two-phase region were fitted by the Antoine equation, while the data



**Figure 4.**  $K_{12}$  values found by the flash method for the  $\text{CO}_2 + \text{R32}$  system: Closed symbols.  $K_{12}$  values found by the dew point method: symbols denoted as in Figure 2.



**Figure 5.** Deviations in pressure between experimental values and those calculated with the  $K_{12}$  coefficients for the  $\text{CO}_2 + \text{R125}$  system; symbols denoted as in Figure 1.

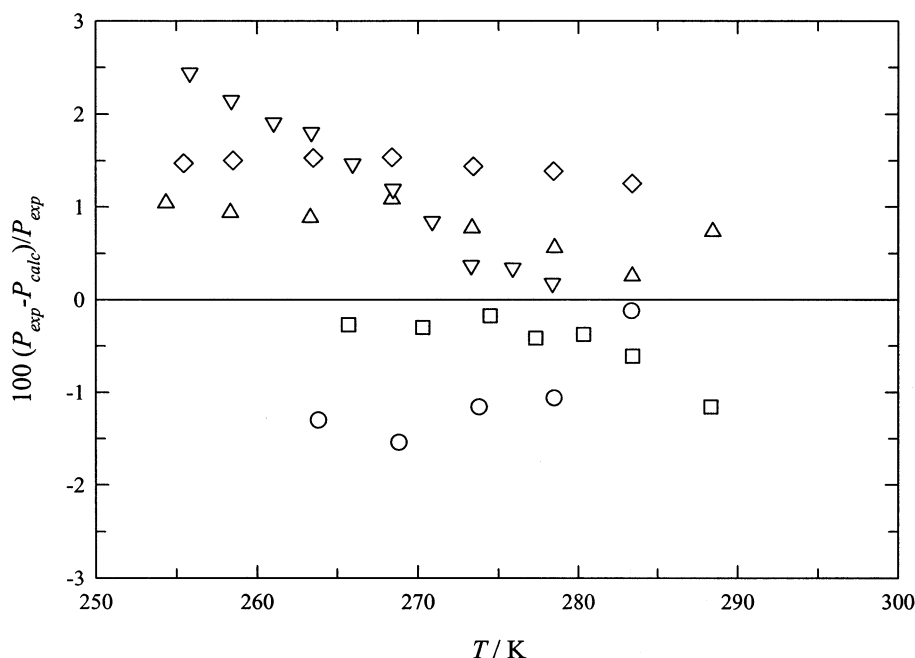
in the superheated region were fitted by a polynomial of second degree, taking the temperature as the independent variable. Then, from the solution of the two equations representing the behavior of the system in the two-phase and superheated regions, the temperature and pressure corresponding to the dew point were found algebraically for each isochore. The solutions are given in Table 1.

**VLE Derivation.** Two methods were used to derive VLE data from the isochoric measurements, as reported previously.<sup>6</sup>

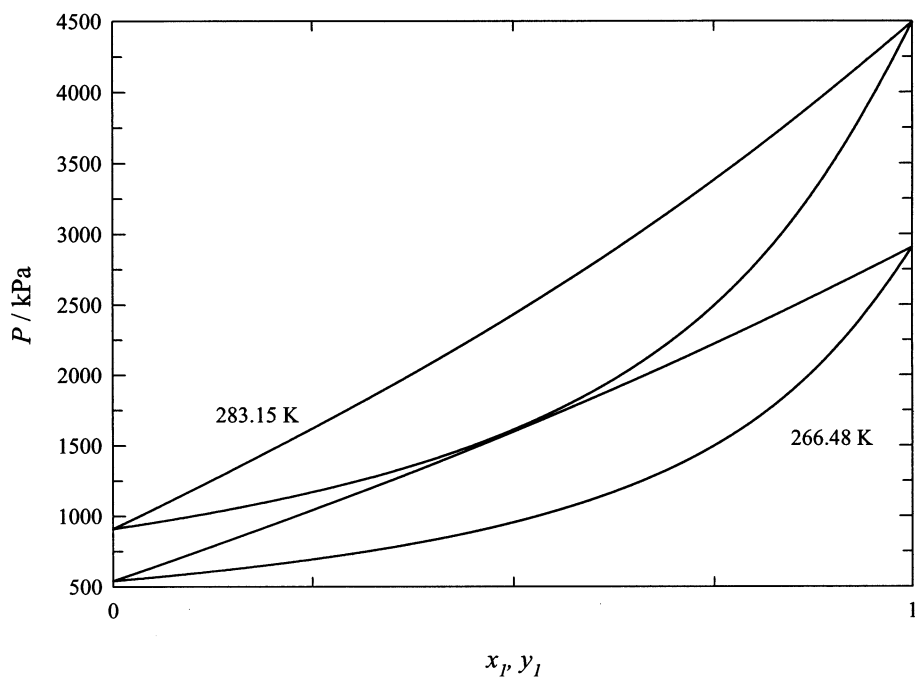
In the first method, the VLE parameters were derived using the “dew point” method with the CSD EOS. The necessary dew point parameters (Table 1) were used as independent variables, while the interaction binary pa-

rameter  $K_{12}$ , and the corresponding pressure and liquid-phase composition at the bubble point, considered as dependent variables, were adjusted until the phase equilibrium condition was reached. The resulting  $K_{12}$  values and bubble point parameters are shown in Table 6.

In the second method, the VLE parameters were derived for each data point in the two-phase region by means of the “flash method” with the CSD EOS. To apply the flash method to the isochoric data, the volumetric properties of both phases are also needed and were calculated from the CSD EOS. During the fitting procedure,  $T$ ,  $P$ ,  $z_i$ , and  $n$  (number of moles charged) were kept constant for each experimental point. Because the isochoric cell volume was known from the gravimetric calibration, the binary interac-



**Figure 6.** Deviations in pressure between experimental values and those calculated with the  $K_{12}$  coefficients for the  $\text{CO}_2 + \text{R32}$  system; symbols denoted as in Figure 2.



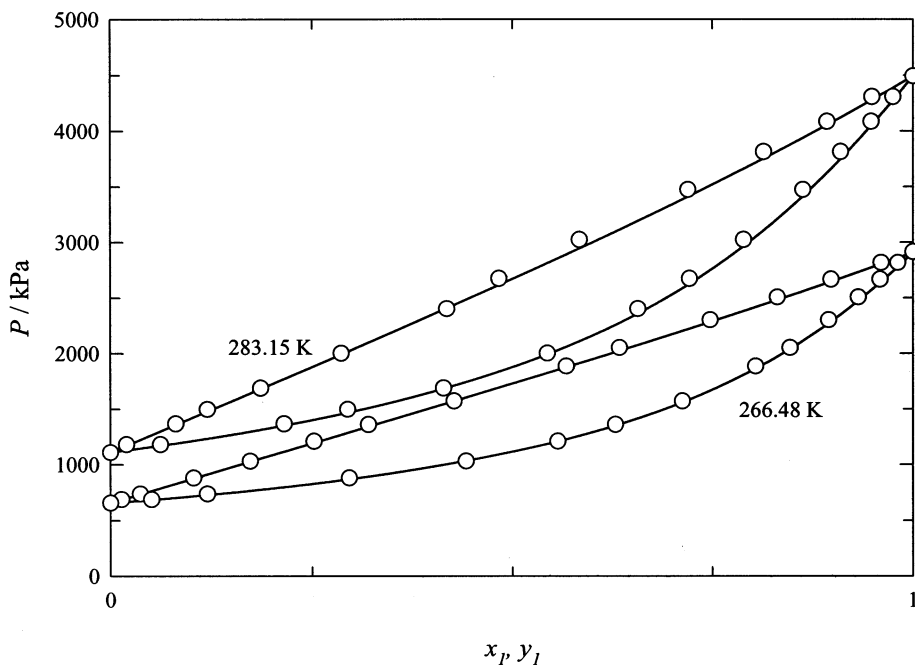
**Figure 7.** VLE data for the  $\text{CO}_2 + \text{R125}$  system at two temperatures: solid lines, present results, correlated.

tion parameter,  $K_{12}$ , and the composition at bubble and dew point were found, considering them as dependent variables. The  $K_{12}$  values found for each data point in the two-phase region are shown in Figures 3 and 4. The  $K_{12}$  values found from the dew point are included for comparison in the same figures, revealing good consistency. The values calculated with the dew point method  $K_{12}$  clearly follow the trend of the values calculated for each point with the flash method. A small temperature dependence is evident for the  $K_{12}$  of both systems. In another attempt to assess the quality of the derived VLE parameters, the system pressure was reproduced using the averaged  $K_{12}$  values, disregarding the small temperature dependence of the  $K_{12}$  values. The absolute average deviation in the system pressure was 0.79% and 1.02% for the  $\text{CO}_2 + \text{R125}$  and  $\text{CO}_2 + \text{R32}$

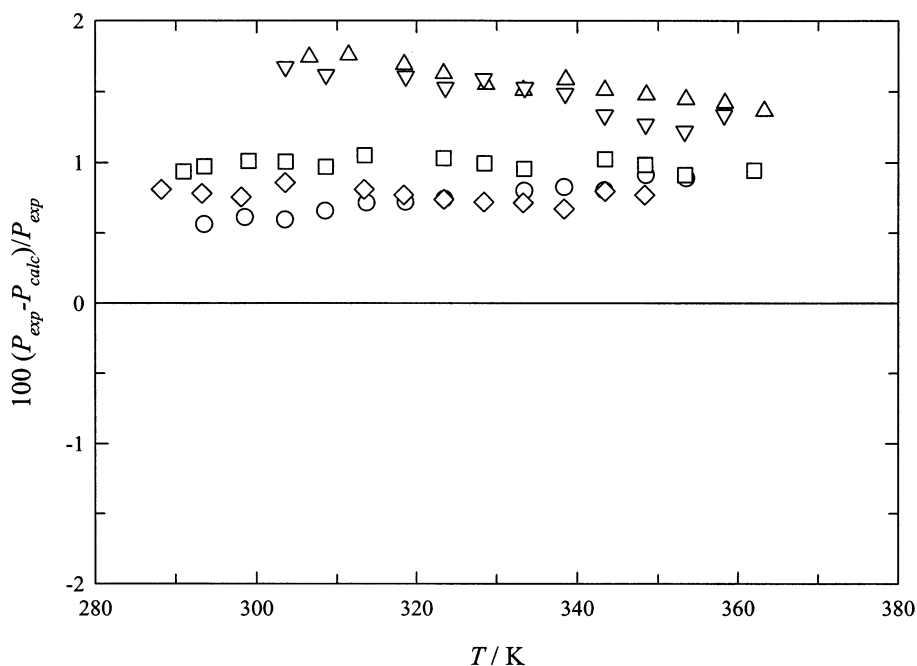
mixtures, respectively. The deviations in pressure are plotted in Figures 5 and 6.

The actual values of  $K_{12}$  were also used to calculate the VLE at 266.48 and 283.15 K for the  $\text{CO}_2 + \text{R32}$  system. The chosen temperature corresponds exactly to the experimental data in the literature,<sup>7</sup> which were also correlated using the CSD EOS. The comparison showed that ref 7 pressures are about 2% higher than the present results, a figure within or close to the uncertainty for the data from both sources.

Comparing  $K_{12}$  from the dew point and flash methods revealed good consistency. It is also worth noting that, in some cases, the CSD EOS was used outside of the temperature range for which its parameters were established, that is, above the critical temperature of  $\text{CO}_2$ .



**Figure 8.** VLE data for the CO<sub>2</sub> + R32 system at two temperatures: solid lines, present results, correlated. (○) Experimental data from Adams and Stein.<sup>7</sup>



**Figure 9.** Deviations in pressure for the CO<sub>2</sub> + R125 system between experimental values and those calculated with the prediction of REFPROP 6.01; symbols denoted as in Figure 1.

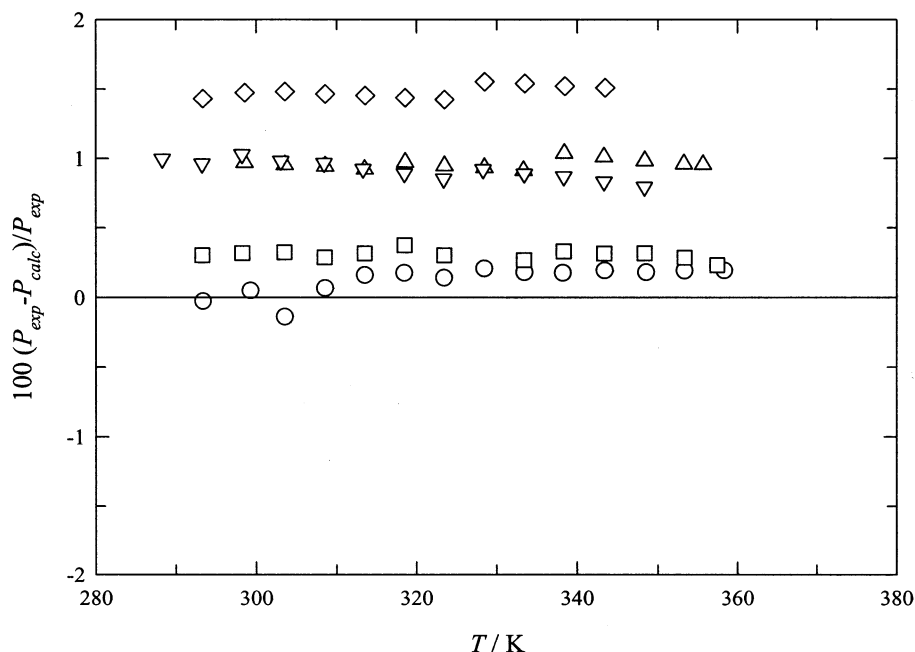
With  $K_{12}$  values from our measurements in the two-phase region, the VLE data calculated at two temperatures are shown in Figures 7 and 8 to illustrate the behavior of the CO<sub>2</sub> + R125 and CO<sub>2</sub> + R32 systems. Figure 8 also shows data from the literature<sup>7</sup> compared with our experimental data interpolated to the literature isotherms.

The VLE behavior of both systems can be considered to be ideal, in terms of Raoult's law, as shown in Figures 7 and 8. This could presumably be interpreted as a compensation of two opposing effects of repulsive forces of -CF groups in HFCs with CO<sub>2</sub> and attractive forces between the hydrogen in HFCs and CO<sub>2</sub>. Qualitatively, it is consistent with the results of a study<sup>10</sup> on hydrogen bonding in HFC + dimethyl ether systems.

**P-V-T-x.** Because of the total absence of published data for the superheated vapor region for the binary systems considered, our experimental  $P-V-T-x$  data were compared with the REFPROP 6.01 estimate. The comparison is reported in Figures 9 and 10. The consistency averaged 1.1% and 0.73% of the pressures for CO<sub>2</sub> + R125 and CO<sub>2</sub> + R32, respectively. Though the values calculated by the REFPROP 6.01 are not based on direct experiment for the systems and temperature range considered, said consistency was considered satisfactory.

The experimental  $PVTx$  data from the isochoric experiment and the calculated ones applying the virial EOS with coefficients found from the Burnett experiment were also compared. For the CO<sub>2</sub> + R32 system over the whole





**Figure 10.** Deviations in pressure for the CO<sub>2</sub> + R32 system between experimental values and those calculated with the prediction of REFPROP 6.01; symbols denoted as in Figure 2.

temperature range and for CO<sub>2</sub> + R125 for temperature  $T > 315$  K deviations are well within  $\pm 1\%$ . For the CO<sub>2</sub> + R125 system we observed systematic deviations for temperatures  $T < 315$  K increasing up to  $-3\%$  at the lowest temperature. Presumably, the increase of deviation with lowering temperature are resulting (i) from the extrapolation of the virial coefficients to lower temperatures using purely empirical expression for their temperature dependence and (ii) from the relatively short temperature range covered by the Burnett experiment. Finally, a comparison of the  $PVT_x$  data with prediction by the CSD was performed using  $K_{12}$  values found from the two-phase region data reduction. For the CO<sub>2</sub> + R125 and CO<sub>2</sub> + R32 systems, AAD values equal to 0.27% and 1.08% were found, respectively.

### Conclusions

Both measured systems showed a very small deviation from Raoult's law. The comparison of our findings with the literature for the CO<sub>2</sub> + R32 system showed good consistency. Independent experiments using both the Burnett and the isochoric setups enabled us to check the internal consistency of all results. The values found from our experimental density data in the superheated region were also compared with data calculated using the REFPROP 6.01 program and consistency to within 1% was recorded. This also validates the cross virial coefficients derived using the Burnett method. Moreover, the VLE data were consistent to within 1% when analyzed as a function of temperature or liquid-phase composition. Generally speaking, the global validity of the methods and results can be claimed to within 1% of the density and/or pressure values.

### Literature Cited

- (1) Di Nicola, G.; Giuliani, G.; Polonara, F.; Stryjek, R.  $PVT_x$  Measurements for the R125+CO<sub>2</sub> System by the Burnett Method. *Fluid Phase Equilib.* **2002**, *199*, 163–176.
- (2) Di Nicola, G.; Polonara, F.; Stryjek, R. Burnett Measurements for the R32 + CO<sub>2</sub> System. *J. Chem. Eng. Data* **2002**, *47*, in press.
- (3) Giuliani, G.; Kumar, S.; Zazzini, P.; Polonara, F. Vapor Pressure and Gas-Phase PVT Data and Correlation for 1,1,1,-Trifluoroethane (R143a). *J. Chem. Eng. Data* **1995**, *40*, 903–908.
- (4) Giuliani, G.; Kumar, S.; Polonara, F. A Constant Volume Apparatus for Vapour Pressure and Gas Phase  $P$ - $v$ - $T$  Measurements: Validation with Data for R22 and R134a. *Fluid Phase Equilib.* **1995**, *109*, 265–279.
- (5) De Santis, R.; Gironi, F.; Marrelli, L. Vapor-Liquid Equilibrium from a Hard-Sphere Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 183–189.
- (6) Di Nicola, G.; Giuliani, G.; Passerini, G.; Polonara, F.; Stryjek, R. Vapor-Liquid Equilibria (VLE) Properties of R-32 + R-134a System Derived from Isochoric Measurements. *Fluid Phase Equilib.* **1998**, *153*, 143–165.
- (7) Adams, R. A.; Stein, F. P.; Vapor-Liquid Equilibria for Carbon Dioxide-Difluoromethane System. *J. Chem. Eng. Data* **1971**, *16*, 146–149.
- (8) 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.
- (9) Di Nicola, G.; Giuliani, G.; Polonara, F.; Stryjek, R. Saturated Pressure and  $P$ - $V$ - $T$  Measurements for 1,1,1,3,3,3-Hexafluoropropane (R-236fa). *J. Chem. Eng. Data*, **1999**, *44*, 696–700.
- (10) Bobbo, S.; Fedele, L.; Camporese, R.; Stryjek, R. Hydrogen-bonding of HFCs with dimethyl ether: evaluation by isothermal VLE measurements. *Fluid Phase Equilib.* **2002**, *199*, 155–162.

Received for review December 11, 2001. Accepted May 27, 2002. This work was supported by the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica.

JE015541Y