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Virial Coefficients from Burnett Measurements for the R23 + N_2O System[1]

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This paper presents experimental results for the trifluoromethane (R23) + nitrous oxide (N_2O) system, which has been chosen as a working fluid for low-temperature applications since it might be a valid option for the low-temperature stage in a cascade cycle. The thermodynamic properties of the binary mixture's constituents are well known from the literature, but no experimental results have been published to date on the $PVTx$ properties of this binary system. $PVTx$ measurements were obtained for the binary R23 + N_2O system for three isotherms (303, 323, and 343 K), performing 15 Burnett expansions in a range of pressures from about 4400 to 80 kPa. The second and third virial coefficients were derived from experimental results together with the second and third cross virial coefficients. The experimental uncertainties in the second and third virial coefficients were estimated to be within $\pm 1\,\text{cm}^3\cdot\text{mol}^{-1}$ and $\pm 500\,\text{cm}^6\cdot\text{mol}^{-2}$, respectively.

KEY WORDS: Burnett measurements; N_2O; $PVTx$; R23; virial coefficients.

1. INTRODUCTION

Nitrous oxide (N_2O) is a gas that is cheap and readily available. It is often used as a weak anesthetic in surgical procedures, and as a mixing and foaming agent in the making of cheese because it is non-flammable, bacteriostatic and tasteless and odorless. It is also used to improve the

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acceleration of racing motorcars and to prepare scuba divers for nitrous-like effects. In such expendable uses, nitrous oxide is considered one of the main offenders contributing to global warming. Used as a working fluid for refrigeration, its global warming potential (GWP) of 310 for 100 years is low by comparison with hydrofluorocarbons (HFCs). Among the HFCs suggested as working fluids in low-temperature Rankine cycle systems, trifluoromethane (R23) has several thermodynamic properties of interest, such as its low normal boiling point, critical temperature, and solidification point. In the past few years, attention has focused on its thermophysical properties, given its potential as an alternative refrigerant, both as a pure fluid and in mixtures, and combined with R13, in particular, to create the binary azeotropic mixture known as R503. Given these promising features, the system considered here might be a valid option for the low-temperature side of a cascade cycle, but no reports of experiments to determine its *PVTx* properties have been made available so far.

In recent papers [1, 2], virial coefficients for the two pure compounds were obtained from experimental measurements. We described 14 Burnett runs along 7 isotherms from 283 to 363 K in a range of pressures from 4500 to 150 kPa for nitrous oxide in [1], while [2] concerns 9 series collected for trifluoromethane along 5 isotherms at temperatures ranging between 303 and 343 K and pressures from 130 to 6000 kPa. The second and third virial coefficients were derived, revealing good consistency when compared with data in the literature for the two pure compounds. Now we report on our measurements of the *PVTx* properties of the binary system along four different isotherms (21 runs in all), while deriving the virial coefficients of the mixture, together with the cross virial coefficients.

The experimental uncertainty in the second and third virial coefficients was estimated to be no more than $\pm 1.5\,\mathrm{cm^3 \cdot mol^{-1}}$ and $\pm 500\,\mathrm{cm^6 \cdot mol^{-2}}$, respectively.

2. EXPERIMENTAL

N$_2$O and R23 were supplied by Sol SpA and ICI, respectively. A check on their purity using gas chromatography with a thermal conductivity detector established a purity of 99.99% in mass for the N$_2$O and 99.6% in mass for the R23 on an area-response basis. The experimental apparatus that was used is illustrated in Fig. 1. It is much the same as the one already described [3], apart from a few minimal modifications discussed elsewhere [4]. The setup comprises two spherical pressure vessels, a measurement chamber, V_A, and an expansion chamber, V_B, the volumes of which are, respectively, approximately 70 and 35 cm^3; some auxiliary systems are used to fill them, to mix the compounds in the vessels,

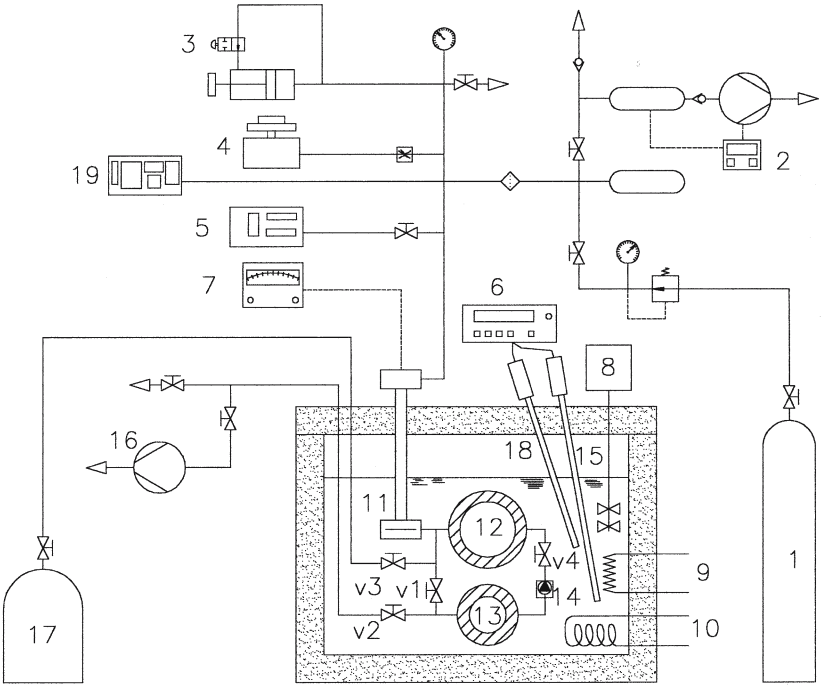

Fig. 1. Diagram of the experimental equipment. 1 Nitrogen reservoir; 2 Vacuum pump (Vacuubrand Mod. RZ2); 3 Precision pressure controller (Ruska Mod. 3981); 4 Gas lubric. dead weight gage (Ruska Mod. 2465); 5 Vibr. cylinder pressure gage (Ruska Mod. 6220); 6 Digital temperature indicator (Corradi, RP 7000); 7 Electronic null indicator (Ruska Mod. 2416); 8 Stirrer; 9 Heater; 10 Cooling coil connected to an auxiliary bath; 11 Differential press. 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

and to control and measure the pressure and temperature. The vessels are made of Invar because it has excellent corrosion resistance and a low thermal expansion coefficient. 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 on either side of the diaphragm is balanced with nitrogen using a precision pressure controller (Ruska Model 3981), and the pressure is read by a digital pressure gauge (Ruska Model 7000).

The vessels are immersed, completely with the magnetic pump and pressure transducer, in a thermostatic bath containing about 45 L of silicon oil. The bath is kept at a constant temperature by a PID device, controlled by a computer. The temperature measuring system is connected to the same computer and relies on two platinum resistance thermometers calibrated according to ITS 90 at the Istituto di Metrologia "G. Colonnetti" (IMGC) of Turin. A Hart Scientific Pt 25 Ω resistance thermometer (Hart Model 5680) and a Tersid Pt 100 Ω resistance thermometer are used for temperature measurement and control, respectively. Both 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 using helium gas. Measurements were taken at several isotherms, and the resulting constant was found to be $N = 1.4986 \pm 0.0001$. This Burnett constant reproduces the helium pressures with absolute average deviations, $AAD = 0.547$ kPa or $AAD = 0.194\%$.

The uncertainty in the recorded temperatures is due to the thermometer and any instability of the bath. The stability of the bath proved to be better than ±0.015 K, and the uncertainty of the thermometer was less than ±0.010 K in the range of temperatures we considered; so the total uncertainty in the temperature measurements was less than ±0.04 K.

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

The gravimetric method was used to prepare the mixtures. First of all, pure samples were placed in different bottles, degassed to eliminate the non-condensable gases and air, and then weighed with an analytical balance (uncertainty of ±0.3 mg). The cell was evacuated and then the content of the bottles was transferred to the cell, which was immersed in the bath. Then, the bottles were weighed again, and the difference between the two weights gave us the mass of the charge. The dispersion of the mass within the connection duct was estimated and subtracted from the total mass of the charge. The uncertainty of these composition measurements was estimated to be consistently less than 0.1% in mole fraction.

3. RESULTS AND DISCUSSION

For the binary system, we measured 142 experimental points for 15 sets and 3 isotherms in a range of temperatures from 303.25 to 343.95 K and pressures between 80 and 4359 kPa. The values are given in Table I along with the regressed compressibility factors of the mixtures.

Table I. Experimental Pressures during Burnett Expansions and Regressed Compressibility Factors (z) for the N_2O (1) + R23 (2) System

Series 1		Series 2		Series 3		Series 4	
$T = 303.25$ K		$T = 303.25$ K		$T = 303.25$ K		$T = 303.25$ K	
$x_1 = 0.3152$		$x_1 = 0.4308$		$x_1 = 0.5419$		$x_1 = 0.6613$	
P (kPa)	z	P (kPa)	z	P (kPa)	z	P (kPa)	z
3012.1	0.7838	3489.6	0.7542	3408.6	0.7716	2933.8	0.8174
2185.1	0.8507	2565.1	0.8294	2486.5	0.8421	2099.0	0.8749
1541.6	0.8979	1825.8	0.8832	1760.9	0.8922	1467.5	0.9152
1068.3	0.9309	1272.3	0.9208	1222.8	0.9269	1010.4	0.9427
731.3	0.9534	874.1	0.9464	838.3	0.9507	688.8	0.9615
496.7	0.9688	595.0	0.9638	569.8	0.9668	466.4	0.9740
335.5	0.9789	402.6	0.9756	385.1	0.9775	314.4	0.9824
225.8	0.9858	271.2	0.9832	259.3	0.9847	211.4	0.9879
151.7	0.9906	182.2	0.9882	174.2	0.9896	141.8	0.9915
Series 5		Series 6		Series 7		Series 8	
$T = 303.25$ K		$T = 303.25$ K		$T = 323.44$ K		$T = 323.43$ K	
$x_1 = 0.7758$		$x_1 = 0.2248$		$x_1 = 0.3580$		$x_1 = 0.5105$	
P (kPa)	z	P (kPa)	z	P (kPa)	z	P (kPa)	z
3965.1	0.7449	3303.6	0.8119	3557.0	0.8069	3632.8	0.8131
2929.0	0.8233	2366.6	0.8701	2553.4	0.8666	2601.4	0.8711
2090.5	0.8791	1657.1	0.9115	1790.3	0.9091	1820.9	0.9123
1459.1	0.9180	1142.3	0.9400	1235.2	0.9384	1255.0	0.9406
1003.6	0.9446	779.4	0.9596	843.2	0.9583	856.1	0.9600
683.7	0.9628	528.1	0.9726	571.6	0.9720	579.9	0.9729
462.7	0.9749	356.1	0.9814	385.6	0.9809	391.0	0.9814
311.9	0.9830	239.5	0.9872	259.3	0.9869	262.8	0.9870
209.6	0.9883	160.7	0.9910	174.0	0.9909	176.4	0.9908

The PVT measurements obtained by experiment were used to derive the second, B, and third, C, virial coefficients of the truncated virial equation:

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

The procedure used for the pure compounds was also applied to find the virial coefficients for the mixtures.

Each run was treated separately in the regression and $(\mathrm{d}P)^2$ was used as an objective function, applying the Burnett constant obtained by means of the calibration with helium. The pressure distortion of the Burnett cells was taken into account, as explained elsewhere [3].

Table I. *Continued*

Series 9		Series 10		Series 11		Series 12	
$T = 323.44\,\mathrm{K}$		$T = 323.44\,\mathrm{K}$		$T = 343.95\,\mathrm{K}$		$T = 343.95\,\mathrm{K}$	
$x_1 = 0.6428$		$x_1 = 0.7792$		$x_1 = 0.2403$		$x_1 = 0.4174$	
P (kPa)	z	P (kPa)	z	P (kPa)	z	P (kPa)	z
3379.9	0.8354	3585.4	0.8302	4242.9	0.8135	4359.1	0.8205
2399.2	0.8872	2551.0	0.8837	3030.8	0.8708	3105.8	0.8761
1669.1	0.9234	1777.2	0.9210	2117.9	0.9119	2166.3	0.9157
1145.9	0.9485	1221.0	0.9467	1457.5	0.9405	1488.7	0.9431
779.5	0.9653	831.2	0.9642	992.7	0.9599	1013.0	0.9617
527.1	0.9764	562.3	0.9759	671.3	0.9728	684.7	0.9741
354.9	0.9837	378.9	0.9837	451.8	0.9812	460.6	0.9821
238.4	0.9886	254.5	0.9888	303.2	0.9866	308.9	0.9871
159.9	0.9917	170.7	0.9920	202.9	0.9897	206.8	0.9901
				135.6	0.9910	138.2	0.9917
				90.5	0.9910	92.3	0.9925

Series 13		Series 14		Series 15	
$T = 343.95\,\mathrm{K}$		$T = 343.95\,\mathrm{K}$		$T = 343.87\,\mathrm{K}$	
$x_1 = 0.5360$		$x_1 = 0.6698$		$x_1 = 0.7837$	
P (kPa)	z	P (kPa)	z	P (kPa)	z
4125.5	0.8374	3898.2	0.8519	4273.0	0.8401
2920.0	0.8882	2743.8	0.8986	3026.4	0.8901
2027.4	0.9241	1897.6	0.9313	2103.1	0.9254
1389.0	0.9489	1296.6	0.9537	1442.6	0.9497
943.2	0.9656	879.0	0.9688	980.8	0.9660
636.6	0.9767	592.7	0.9789	663.0	0.9769
428.0	0.9839	398.2	0.9857	446.5	0.9842
287.0	0.9886	266.9	0.9901	299.8	0.9888
192.0	0.9915	178.9	0.9945	201.0	0.9917
128.4	0.9933	119.5	0.9953		
		79.8	0.9965		

In the present work, the second and third virial coefficients obtained for the pure compounds [1, 2], summarized in Table III, were used because the same samples were also used for the mixture measurements.

For nitrous oxide, the second and third virial coefficients are reported elsewhere [1], together with the coefficients published in the literature [5–10]. For the case of the second virial coefficients, comparisons at the same reduced temperatures showed a good degree of consistency with the other sources of data (taking the mutual uncertainties into account). Only one data source was available for the third virial coefficients [7], which again proved consistent with our data. The same good level of agreement with

Table II. Experimental and Calculated Second and Third Virial Coefficients for the N_2O (1) + R23 (2) System

T (K)	x_1	B_m exp (cm^3·mol^{-1})	B_m calc (cm^3·mol^{-1})	dB_m (cm^3·mol^{-1})	C_m exp (cm^6·mol^{-2})	C_m calc (cm^6·mol^{-2})	dC_m (cm^6·mol^{-2})
303.25	0.3152	−156.2	−154.9	−1.3	9440	9380	60
303.25	0.4308	−149.3	−148.8	−0.5	8380	8450	−70
303.25	0.5419	−143.8	−143.6	−0.1	7660	7590	60
303.25	0.6613	−137.7	−138.8	1.1	6620	6780	−170
303.25	0.7758	−134.2	−134.8	0.7	6320	6180	140
323.44	0.2248	−136.5	−136.0	−0.5	8030	8190	−170
323.44	0.3580	−129.5	−129.1	−0.4	7180	7160	20
323.43	0.5105	−123.1	−122.5	−0.5	6370	6150	220
323.44	0.6428	−117.6	−118.0	0.4	5470	5480	−10
323.44	0.7792	−113.6	−114.4	0.9	4860	5020	−160
343.95	0.2403	−113.7	−114.3	0.6	6250	6360	−100
343.95	0.4134	−106.4	−106.6	0.3	5250	5230	20
343.95	0.5360	−102.7	−102.4	−0.3	4840	4740	100
343.95	0.6698	−99.7	−99.0	−0.7	4490	4420	70
343.87	0.7837	−97.2	−97.2	0.0	4110	4270	−160

Table III. Averaged Second and Third Virial Coefficients for the N_2O (1) + R23 (2) System

T (K)	B_{11} (cm^3·mol^{-1})	B_{12} (cm^3·mol^{-1})	B_{22} (cm^3·mol^{-1})	C_{111} (cm^6·mol^{-2})	C_{112} (cm^6·mol^{-2})	C_{122} (cm^6·mol^{-2})	C_{222} (cm^6·mol^{-2})
303.25	−129.0	−139.0	−175.0	5780	5400	9940	11480
323.44	−111.1	−115.3	−150.1	4950	4360	7190	10120
343.95	−95.7	−95.1	−128.3	4120	4350	4230	9040

other literature results was also obtained for R23, as reported elsewhere [2, 11–14].

The values of the second and third virial coefficients (Table II) were used in combination with the virial coefficients for the pure compounds (smoothed as a function of reduced temperature) to derive the cross virial coefficients shown in Table III.

The cross second virial coefficients were calculated from the formula,

$$B_m = \sum_{i=1}^{2} \sum_{j=1}^{2} B_{i,j} x_i x_j \qquad (2)$$

for each experimental point. Then, the B_{12} values obtained for each temperature were averaged (Table III) and used to calculate the deviations of B_m from the experimental values in Table II. The cross third virial coefficients were calculated from the defining equation,

$$C_m = \sum_{i=1}^{2}\sum_{j=1}^{2}\sum_{k=1}^{2} C_{i,j,k} x_i x_j x_k \tag{3}$$

The averaged values of the third cross virial coefficients (Table III) were used to recalculate the third virial coefficients for the mixtures at each point. Table II shows the results, together with the deviations. The overall *AAD* for B_m was $1.4\,\text{cm}^3\cdot\text{mol}^{-1}$, while the *AAD* for C_m was $123\,\text{cm}^6\cdot\text{mol}^{-2}$.

The second and third virial coefficients for the system plotted against the mole fraction in Figs. 2 and 3 show minimal positive and negative deviations, respectively, from the ideal, which is defined here as

$$B_{12} = (B_{11} + B_{22})/2 \tag{4}$$

$$C_{112} = (2C_{111} + C_{222})/3 \tag{5}$$

$$C_{122} = (C_{111} + 2C_{222})/3 \tag{6}$$

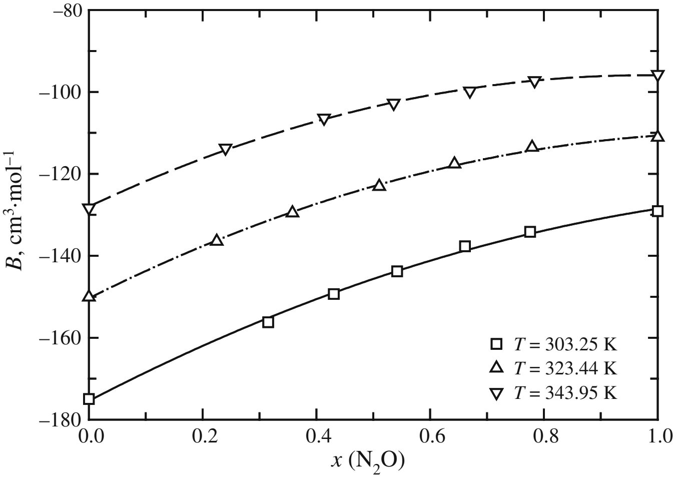

Fig. 2. Second virial coefficients for the N$_2$O (1) + R23 (2) system versus mole fraction at temperatures, (□) = 303.25 K; (△) = 323.44 K; (▽) = 343.95 K, including the values smoothed in relation to temperatures for the pure compounds. Lines represent the trend of the values.

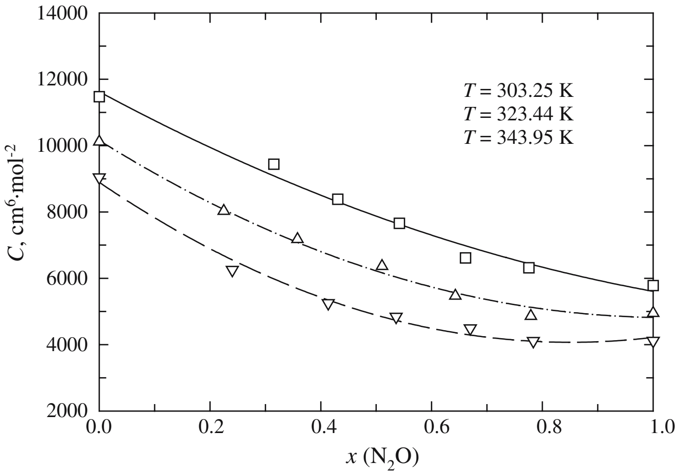

Fig. 3. Third virial coefficients for the N_2O (1) + R23 (2) system versus mole fraction at temperatures, (□) = 303.25 K; (△) = 323.44 K; (▽) = 343.95 K, including the values smoothed in relation to temperatures for the pure compounds. Lines represent the trend of the values.

4. CONCLUSIONS

Our experimental results obtained with the Burnett method for the R23 + N_2O system are reported here. Measurements for the two pure fluids, N_2O and R23, used to check the performance of the apparatus, revealed good consistency between the virial coefficients we obtained and those published elsewhere. The R23 + N_2O system was studied for three isotherms to derive second and third cross virial coefficients. The former revealed positive deviations from the ideal over the entire temperature range, while the latter revealed negative deviations. No other *PVTx* data are available in the literature for this specific binary system.

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