Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 311–316

PVT FROM THE BURNETT AND ISOCHORIC MEASUREMENTS
Nitrous oxide

G. Di Nicola[1], *G. Giuliani*[1], *F. Polonara*[1*] *and R. Stryjek*[2]

[1]Dipartimento di Energetica, Università Politecnica delle Marche, Via Brecce Bianche, 60100 Ancona, Italy
[2]Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland

In this work, the PVT properties have been object of study. In particular, the experimental work was performed both in the two-phase region and in the superheated vapor region phase by means of two different methods: the isochoric and the Burnett methods.

The isochoric measurements were carried out at temperatures from 219 to 354 K and at pressures from 550 up to 5400 kPa. A total of 95 points, both in the two phases and in the superheated vapor region were obtained.

For the Burnett measurements, in total, 14 runs along 7 isotherms in a pressure range from 170 to 5200 kPa were performed. The second and third virial coefficients were derived and a good consistency was found after comparison with other literature sources in the reduced temperature range of interest ($0.9<T_r<1.2$).

Keywords: *nitrous oxide, PVT, superheated vapor, thermophysical properties, vapor pressure*

Introduction

Nitrous oxide (N_2O) is an inexpensive and widely available gas. Even if it is considered as contributing to the greenhouse effect, this is due to its expendable uses. As natural refrigerant [1], its GWP=310 for 100 years period can be considered low if compared with HFCs. However, the main part of experimental data on its thermophysical properties available in the literature is rather aged, except recent data on PVT obtained from ultrasound measurements.

In this work, a careful revision of the literature sources was carried out and, finally, the present vapor pressure and PVT measurements were compared with existing measurements.

Experimental

Reagents

N_2O was supplied by Sol SpA (www.sol.it), and its purity was checked by gas chromatographic analysis, using a thermal conductivity detector. It was found to be 99.99% on an area-response basis.

Experimental devices

In this paper, the adopted devices (reported in Figs 1 and 2) are the same described elsewhere [2, 3] with no modifications. Here, only a brief description is reported.

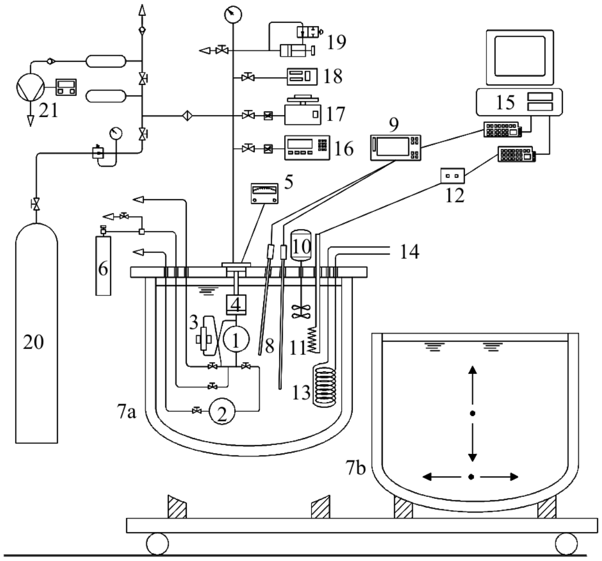

Fig. 1 Schematic view of the isochoric experimental apparatus; 1 – constant volume spherical cell, 2 – auxiliary cell, 3 – magnetic pump, 4 – differential pressure transducer, 5 – electronic null indicator, 6 – charging system, 7 – thermostatic baths, 8 – platinum thermo-resistances, 9 – thermometric bridge, 10 – stirrer, 11 – heater, 12 – power system, 13 – cooling coil, 14 – connections to auxiliary thermostatic bath, 15 – acquisition system, 16 – Bourdon gage, 17 – dead mass gage, 18 – vibrating cylinder pressure gage, 19 – precision pressure controller, 20 – nitrogen reservoir, 21 – vacuum pump system

---

[*] Author for correspondence: f.polonara@univpm.it

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

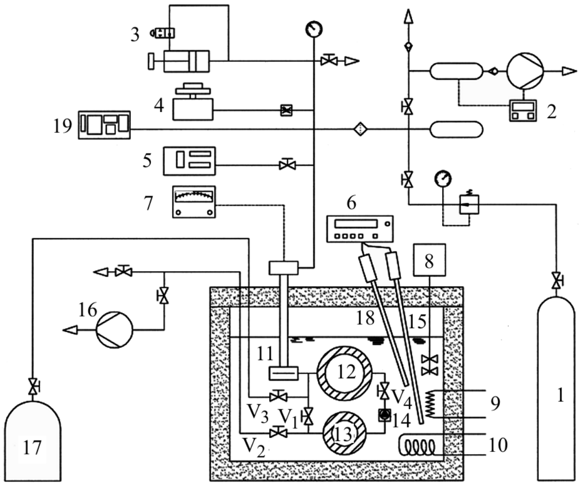

Fig. 2 Schematic view of the Burnett experimental apparatus; 1 – nitrogen reservoir, 2 – vacuum pump (Vacuubrand, mod. RZ2), 3 – precision pressure controller (Ruska, mod. 3981), 4 – gas lubricated dead mass gage (Ruska, mod. 2465), 5 – vibr. cylinder pressure gage (Ruska, mod. 6220), 6 – digital temperature indicator (Corradi, RP 7000), 7 – electronic null indicator (Ruska, mod. 2416), 8 – stirrer, 9 – heater, 10 – cooling coil connected with 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

The constant-volume apparatus with a volume of 273.5 mL was used for the two-phase measurements. A 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 two thermostatic baths containing different silicon oils and alternatively used for measurements at different temperature ranges. Both baths are controlled by a proportional integrative derivative (PID) device. An auxiliary bath, also controlled by a PID device, helps the system to keep the temperature constant. A platinum resistance thermometer is immersed near the cell and is connected to a digital indicator.

The Burnett apparatus used for the vapor phase measurements consists of two pressure vessels, the measurement chamber, and the expansion chamber, both spherical in shape, with a volume of approximately 70 and 35 mL, respectively. Some auxiliary systems for filling and mixing the compounds in the Burnett vessels, and for controlling and measuring the pressure and temperature complete the set-up. Also for the Burnett apparatus, the measurement vessel is connected to a diaphragm-type differential pressure transducer, coupled to an electronic null indicator. The pressure on either side of the diaphragm is balanced with nitrogen by means of a precision pressure controller, and the pressure is read by a digital pressure gauge. The vessels with the magnetic pump and the pressure transducer are immersed in a thermostatic bath filled with about 45 L of silicon oil. Again, the temperature of the bath is kept constant by means of a PID device. The temperature control and acquisition system relies on two platinum resistance thermometers. 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 using gaseous helium measurements. After taking measurements at several isotherms, the constant was found to be N=1.4969±0.0001 for all series excluding the last two series that were performed with N=1.4961±0.0001, after small modifications on valve volumes.

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 less than ±0.015 K and the uncertainty of the thermometer was found to be less than ±0.010 K in our temperature range. The total uncertainty in the temperature measurements was thus less than ±0.03 K for both apparatus. Any uncertainty in the pressure measurements is due to the transducer and null indicator system, and to the pressure gauge. The digital pressure indicator (Ruska, mod. 7000) has an uncertainty of ±0.003% of the full scale. The total uncertainty in the pressure measurement, also influenced by temperature fluctuations due to bath instability, was found to be less than ±1 kPa for both devices.

For the isochoric method, the uncertainty in the measurement of the mass inside the cell was estimated to amount to ±10 mg. The volume of the cell, piping and pressure transducer cavity is measured with an uncertainty of ±0.3 mL. From the uncertainties in the mass and volume measurements, the uncertainty in calculated molar volume was estimated to be always less than $\pm 0.08\ \mathrm{dm}^3\ \mathrm{mol}^{-1}$. The overall experimental uncertainty in terms of pressure, calculated using the laws of error propagation was estimated to be lower than ±0.8 kPa for measurements along the saturation line.

For the Burnett method, the uncertainty of the mixture's composition was found to be constantly lower than 0.5% in mole fraction. The experimental uncertainty in second and third virial coefficients is estimated to be within $\pm 1.5\ \mathrm{mL\ mol}^{-1}$ and $\pm 500\ \mathrm{mL}^2\ \mathrm{mol}^{-2}$, respectively.

Results

In total, 221 experimental points for nitrous oxide were obtained. By the isochoric method, 18 data points were collected in the two-phase region and reported elsewhere [4], while 77 data were collected along 5 isochores in the superheated vapor region. The vapor phase data are reported in Table 1. By the Burnett method, 126 experimental points along 7 isotherms were collected and reported elsewhere [4]. A summary of the experimental survey is showed in Fig. 3.

Vapor pressure data

The 18 vapor pressure points were obtained at temperatures from (219 to 273) K and for pressures from (550 to 3100) kPa. The analysis of the literature showed that a total of 11 data sources are available [5–15]. Taking into account only data following a common trend (considering also the 18 data points obtained by us), a total of 119 points were regressed as a combined set with the Wagner equation in the following form:

$$\ln\frac{P}{P_c}=\frac{T_c}{T}[A_1\tau+A_2\tau^{1.5}+A_3\tau^{2.5}] \qquad (1)$$

Table 1 Experimental PVT data for N_2O

T_{90}/K	P/kPa	V/mL mol^{-1}	T_{90}/K	P/kPa	V/dm^3 mol^{-1}
227.36	685.9	2470.447			
232.43	707.0	2470.998			
237.50	726.5	2471.549			
242.57	745.6	2472.100			
252.71	783.3	2473.204	313.74	3538.5	590.786
262.86	820.5	2474.308	319.05	3628.4	590.923
273.02	857.3	2475.413	323.97	3710.4	591.051
283.36	895.1	2476.538	328.99	3793.7	591.181
293.55	931.5	2477.645	334.09	3878.1	591.313
303.74	968.2	2478.754	339.14	3961.0	591.444
308.83	985.8	2479.307	344.20	4043.9	591.575
313.91	1003.6	2479.859	349.30	4126.9	591.707
319.01	1021.4	2480.415	354.34	4208.8	591.838
324.10	1039.2	2480.968			
329.20	1057.0	2481.523			
339.38	1092.4	2482.631			
344.48	1110.0	2483.185			
			278.08	3263.4	505.851
247.56	1329.0	1303.792	283.00	3373.7	505.960
252.61	1368.1	1304.081	288.38	3491.7	506.080
257.71	1407.1	1304.374	293.46	3602.2	506.193
267.82	1481.0	1304.953	298.60	3711.5	506.307
272.71	1517.3	1305.234	303.68	3818.6	506.420
282.62	1588.3	1305.803	308.77	3924.9	506.533
293.55	1666.0	1306.429	313.85	4030.2	506.646
303.73	1737.1	1307.013	318.95	4134.8	506.759
313.91	1807.7	1307.596	324.04	4238.5	506.872
324.09	1877.9	1308.180	329.13	4341.9	506.985
334.16	1946.3	1308.758	334.23	4444.5	507.099
344.37	2015.9	1309.344	339.33	4546.7	507.212
354.52	2084.8	1309.926	344.43	4648.2	507.325
			354.61	4849.5	507.551
			283.31	3696.8	438.916
			288.40	3831.1	439.014
			293.51	3964.4	439.112
267.92	2707.7	589.598	298.60	4093.6	439.210
272.98	2822.6	589.730	303.69	4221.5	439.308
277.86	2912.4	589.856	308.78	4348.1	439.407
283.26	3010.1	589.996	313.86	4473.4	439.505
288.31	3100.0	590.127	318.95	4597.8	439.603
293.34	3189.0	590.257	324.04	4721.1	439.701
298.50	3278.6	590.391	329.16	4844.2	439.799
303.58	3365.9	590.522	334.23	4965.2	439.897
308.65	3452.3	590.654	339.34	5086.3	439.996
			344.44	5206.7	440.094
			354.63	5445.1	440.290

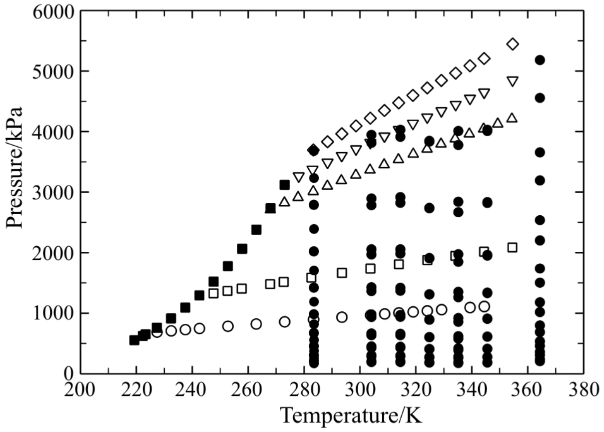

Fig. 3 Summary of the experimental PVT data; ■ – isochoric vapor pressure data, ● – Burnett PVT data, ○ – isochoric PVT data, m=4.86 g, □ – isochoric PVT data, m=9.21 g, △ – isochoric PVT data, m=20.40 g, ▽ – isochoric PVT data, m=23.79 g and ◇ – isochoric PVT data, m=27.42 g

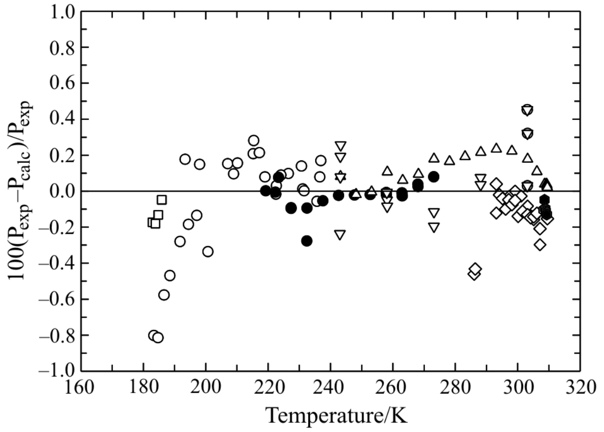

Fig. 4 Scatter diagram of the relative saturated pressure deviations (in percent) from the fit with the Wagner equation, Eq. (1); ○ – Hoge, △ – Couch *et al.*, ⬢ – Ohgaki *et al.*, □ – Blue et Giaque, ▽ – Hirth, ◇ – Cook and ● – present work

where $\tau=(T_c-T)/T_c$; the critical temperature T_c=309.54 K and the critical pressure P_c=7249.27 kPa were taken as fixed values. The critical values were estimated averaging the values reported in reliable literature sources, as reported elsewhere [4]. The following values were found for the parameters: A_1=–6.88269266, A_2=1.94458967, A_3=–2.58663757, with deviations bias(dP/P) and absolute (dP/P) equal to –0.03 and 0.14%. Scatter diagrams of the relative deviations in pressure are reported in Fig. 4.

PVT data from Burnett apparatus

The 126 experimental points along 7 isotherms were obtained in the temperature range from (283 to 364) K and in the pressure range from (170 to 5200) kPa. The experimental PVT measurements were used to derive the second virial coefficient, B, and the third virial coefficient, C, as described elsewhere [3, 16, 17].

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 taken into account, as explained elsewhere [16, 17].

Defining the average absolute deviation in pressure as:

$$AAD=\sum_{i=1}^{n} abs(\mathrm{d}P)\,/\,n \qquad (2)$$

where the AAD=0.190 kPa for N_2O was found to be within the estimated experimental uncertainty. The derived second and third virial coefficients for N_2O are given in Table 2, together with the pressure deviations from the fit, that always proved to be less than 0.1%. In Figs 5 and 6, the second and the third virial coefficients for N_2O are plotted and compared with values in [18–22] and with the calculated recommended equation [23].

A good agreement of the present and the most of the literature data measured in the reduced temperature range of interest ($0.9<T_r<1.2$) are evident both for the second and the third virial coefficients.

PVT data from isochoric apparatus

The 77 experimental points along 5 isochores were obtained in the temperature range from (227 to 354) K and for pressures from (700 to 5400) kPa.

The experimental findings were compared with the PVT results obtained by the Burnett method. First, a polynomial temperature dependence for the experi-

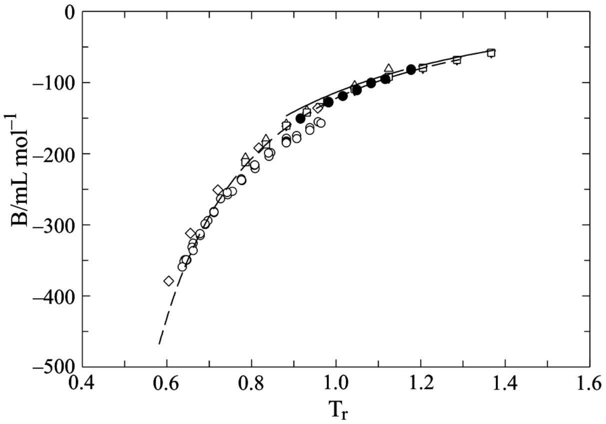

Fig. 5 Experimental second virial coefficients for N_2O *vs.* reduced temperature, T/T_c, where T_c=309.54 K is the critical temperature; ○ – Johnston and Weimer, ▽ – Schamp *et al.*, ● – present work, —– Ihmels and Gmehling, △ – Turlington and McKetta, □ – Couch *et al.*, ◇ – Elias *et al.*, — — – Dymond *et al.*

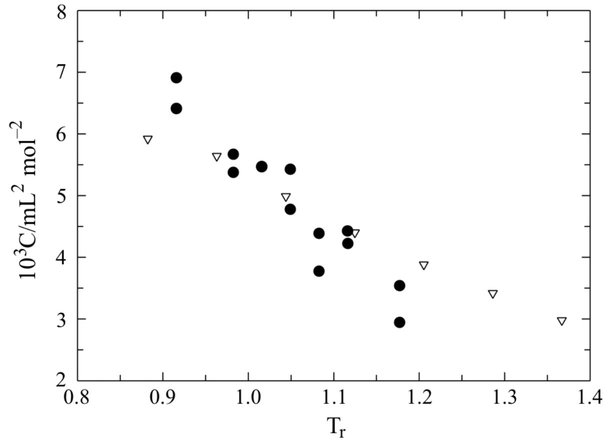

Fig. 6 Experimental third virial coefficients for N_2O *vs*. reduced temperature; ▽ – Schamp *et al*. and ● – present work

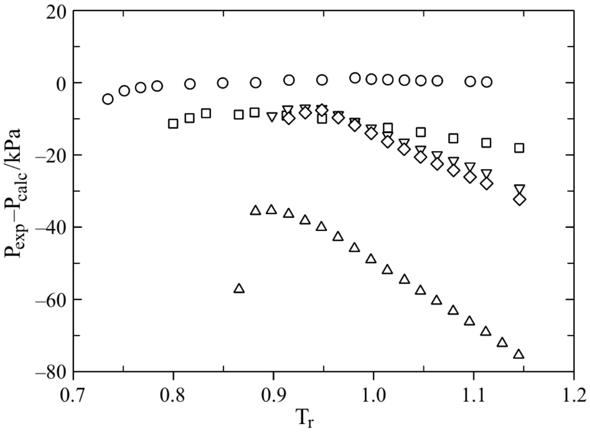

Fig. 7 Absolute pressure deviations between the isochoric and the Burnett experimental PVT data

mental second and third virial coefficients obtained by the Burnett method was found. Then, the values of the second and third virial coefficients were calculated at the isochoric experimental temperatures. Finally, the pressure values were calculated according to the virial equation of state in the Leiden form, expressed in terms of inverse molar volume, and truncated after the third term as follows:

$$P=\frac{RT}{V}\left(1+\frac{B}{V}+\frac{C}{V^2}\right) \qquad (3)$$

where R=8.31451 J mol^{-1} K^{-1} is the universal gas constant, V is the isochoric experimental molar volume. Absolute and relative deviations between the experimental and calculated pressures are reported in Figs 7 and 8. Here, it is worth to point out that the two differ-

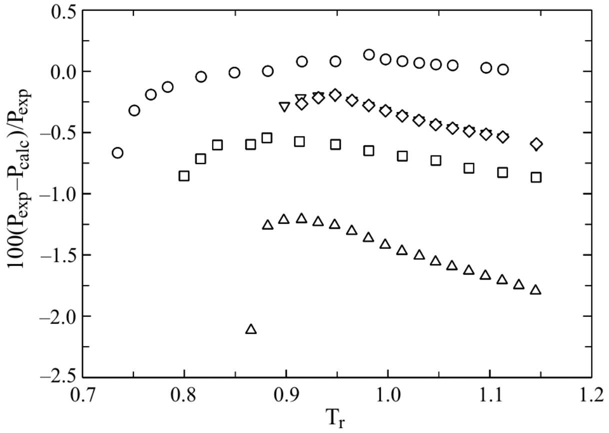

Fig. 8 Relative pressure deviations between the isochoric and the Burnett experimental PVT data

Table 2 Second and third virial coefficients for N_2O; ρ(1) denotes regressed initial density

Series	Temperature/K	B/mL mol^{-1}	10^3C/mL^2 mol^{-2}	$10^3\rho(1)$/mol mL^{-1}	$100(P-P_{calc})P^{-1}$	abs$\{100(P-P_{calc})P^{-1}\}$
1	283.51	–150.3	6.41	1.84017	0.04	0.05
2	283.50	–151.1	6.91	2.24384	0.03	0.04
3	304.09	–127.3	5.38	1.95324	0.02	0.03
4	304.10	–128.4	5.67	2.05230	0.03	0.04
5	314.42	–119.1	5.47	1.95477	0.03	0.03
6	314.41	–119.2	5.47	1.88231	0.03	0.04
7	324.78	–109.9	4.78	1.72071	0.01	0.01
8	324.79	–111.2	5.43	1.72815	0.02	0.02
9	335.18	–101.5	4.39	1.71467	0.02	0.02
10	335.16	–100.1	3.77	1.59518	0.03	0.03
11	345.58	–95.0	4.22	1.62894	0.01	0.01
12	345.52	–95.5	4.43	1.63968	0.01	0.01
13	364.36	–82.7	3.54	2.01752	–0.03	0.03
14	364.36	–81.3	2.94	1.73236	–0.04	0.04

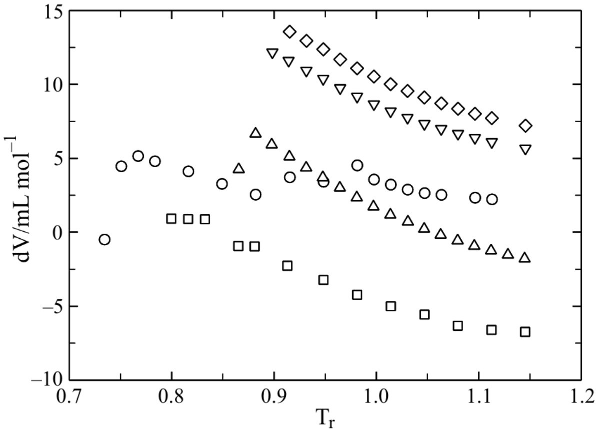

Fig. 9 Molar volume deviations between the isochoric experimental data and data calculated by the recommended equation [23]

ent experimental devices produced mutually consistent results, being deviations between 0 and –2%.

Finally, deviations in molar volumes between our experimental isochoric results and the second virial coefficients predicted by the based on literature survey recommended equation [23] were calculated, truncating Eq. (3) after the second term:

$$\mathrm{d}V = \left(\frac{PV}{RT} - 1\right)V - B \tag{4}$$

The analysis of results showed a good agreement between our data and the prediction equation, as witnessed by Fig. 9.

Conclusions

In this work, the PVT properties of nitrous oxide have been measured, both in the saturation region and in the superheated vapor region. The results in the two phase region were correlated, together with a selection of literature sources, with the Wagner equation. The Burnett PVT data were used to derive the second and the third virial coefficients, while the isochoric PVT data were compared with the Burnett and with the literature ones. A good agreement with the literature sources was found for all experimental data. Besides, the mutual consistency between the PVT data obtained by the two different methods was found.

Acknowledgements

This work was supported by MIUR, Ministry of Instruction, University and Research and by the government of Marche region.

References

1 ASHRAE Standard 34-2001. ‘Designation and Safety Classification of Refrigerant’. ASHRAE, Atlanta, GA 2001.
2 G. Di Nicola, G. Giuliani, F. Polonara and R. Stryjek, J. Chem. Eng. Data, in press.
3 G. Di Nicola, G. Giuliani, F. Polonara and R. Stryjek, Fluid Phase Equilib., 199 (2002) 161.
4 G. Di Nicola, G. Giuliani, R. Ricci and R. Stryjek, J. Chem. Eng. Data, in press.
5 R. W. Blue and W. F. Giaque, J. Am. Chem. Soc., 57 (1935) 991.
6 D. Cook, Proc. Roy. Soc. Lond., Ser. A, 219 (1953) 245.
7 D. Cook, Trans. Far. Soc., 49 (1953) 716.
8 E. J. Couch, K. A Kobe and L. J. Hirth, J. Chem. Eng. Data, 6 (1961) 229.
9 L. J. Hirth, Ph.D. Dissertation, Austin, University of Texas, USA 1958.
10 H. J. Hoge, J. Res. Natl. Bur. Stand., 34 (1945) 281.
11 K. Ohgaki, S. Umezono and T. Katayama, J. Supercrit. Fluids, 3 (1990) 78.
12 M. A. Hunter, J. Phys. Chem., 10 (1906) 330.
13 J. P. Kuenen, J. Philos. Mag., 40 (1895) 173.
14 W. P. Parrish and W. G. Steward, J. Chem. Eng. Data, 20 (1975) 412.
15 H. Zeininger, J. Chem. Ing. Tech., 44 (1972) 607.
16 S. Glowka, Pol. J. Chem., 64 (1990) 699.
17 S. Glowka, Fluid Phase Equilib., 78 (1992) 285.
18 B. L. Turlington and J. J. McKetta, AIChE J., 7 (1961) 336.
19 H. W. Jr. Schamp, E. A. Mason and K. Su, J. Phys. Fluids, 5 (1962) 769.
20 H. L. Johnston and H. R. Weimer, J. Am. Chem. Soc., 56 (1934) 625.
21 E. C. Ihmels and J. Gmehling, Int. J. Thermophys., 23 (2002) 709.
22 E. Elias, N. Hoang, J. Sommer and B. Schramm, Ber. Bunsenges Phys. Chem., 90 (1986) 342.
23 J. H. Dymond, K. N. Marsh, R. C. Wilhoit and K. C. Wong, The Virial Coefficients of Pure Gases and Mixtures, Springer-Verlag; Berlin 2002.