Nitrous oxide: Saturation properties and the phase diagram

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A B S T R A C T

The experimental values of the coordinates of the triple point and of the critical point of nitrous oxide registered in the literature were assessed and those judged as most reliable have been selected. Empirical equations have been found for the vapour pressure, sublimation and fusion curves. The virial coefficients and saturation properties as functions of temperature along the equilibrium curves are described by reduced equations. They were used in arriving at the molar enthalpies at the triple point and the normal boiling temperature. Equations for the sublimation and fusion curves resulting from the exactly integrated Clapeyron equation compare favourably with the results from the empirical treatment and the experimental data.

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1. Introduction

Nitrous oxide (or dinitrogen monoxide) is an important substance for its applications in medicine (as anaesthetic), in refrigeration, and in combustion reaction (as propellant). In environmental issues, its presence is not negligible due to the contribution of N_2O to the greenhouse effect. It also has played a relevant role in theoretical studies, namely in (vapour + liquid) equilibrium, because of the high quadrupole moment ($Q = -12.2 \cdot 10^{-40} \, C \cdot m^2$) and almost no dipole moment ($\mu = 0.55 \cdot 10^{-30} \, C \cdot m$) of its small-sized, relatively rigid molecule. In spite of all this, the thermodynamic properties of nitrous oxide have not been the object of recent systematic experimental investigations, with the possible exception of the research work due to Imhels and Gmelling [1] dedicated to volumetric measurements on the fluid under pressure, and those on the velocity of sound of the pressurized substance carried out by Hurly [2,3]. These studies do not explicitly include measurements on the saturation properties of the substance. However, there are dispersed experimental investigations taken over the years on the phase diagram of nitrous oxide and on its saturation properties. The main object of the present study is to analyse the published data, and to try and propose sufficiently accurate descriptions of the saturation properties of nitrous oxide.

2. Experimental data: the invariant points

2.1. Triple point

From a large number of measurements carried out in several reference laboratories from 1935 onwards, Staveley *et al.*, in a review article published in 1981[4], selected as the coordinates of the triple point of N_2O the values of T_t = 182.33 K (in the IPTS-68), and p_t = (659.04 ± 0.09) Torr = (87.865 ± 0.012) kPa. No figure was indicated there for the molar volume. Here we reassess those values in the light of the measurements published up to now, summarized in table 1. For the molar volume of the liquid at the triple point, there is only one direct measurement made at the Oxford laboratory, in which the sample was kept in a glass pycnometer surrounded by the same nitrous oxide substance melting slowly at its own triple point. We have adopted that value of $V_{m,t}^{\ell}$ = (35.847 ± 0.002) cm$^3 \cdot$ mol^{-1}, which is the average of six independent measurements taken over several years [10,11]. As far as the triple point temperature is concerned, there are three direct measurements, using different temperature scales. We favour the value of T_t = 182.26 K determined by Blue and Giauque [5] on a T scale where the melting point of water was taken as T_{ice} = 273.10 K. The conversion into ITS-90 gives T_t = 182.293 K, in our assessment. This is lower than the values determined by Hoge [7] and by Atake and Chihara [9], and also lower than that selected in reference [4]. While the measurements made by the Japanese research workers appear to be high, and probably uncertain as assessed by their corresponding values of the triple point pressure during melting, the triple point temperature found by Hoge has

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not been taken by himself in deriving his vapour pressure equation, and the vapour pressure seems not to have been measured at the triple point in that study. On the other hand, the vapour pressure of nitrous oxide has been extensively and rigorously measured at the triple point. The values reported oscillate around those firstly determined in the laboratories of Giauque [5] and of Clusius [6]. We have taken as most reliable the measurements made in Oxford [10,11]. In summary, the coordinates of the triple point of N_2O, used in the present work, have been taken as: $V_{m,t}^\ell = (35.847 \pm 0.002)$ cm$^3 \cdot$ mol^{-1}[10,11], $T_t = 182.293$ K [5], and $p_t = (87.866 \pm 0.001)$ kPa [10,11].

2.2. Critical point

The critical properties of nitrous oxide have been measured over the years (see table 2), but not all the experiments deserve the same confidence. The critical temperature is, certainly, the property which has been the most reliably measured. The direct method has been used by not many investigators. Among them, the research work developed by Levelt Sengers et al. [32] is to be preferred, in our view, by reason of the method used. They arrived at $t_c = 36.417$ °C, on the IPTS-48, which is $T_c = 309.548$ K after conversion into the ITS-90. This value was obtained by directly measuring the temperature at which the refractive index of the phases at equilibrium shows complete agreement with each other. This figure is not significantly different from the $T_c = 309.56$ K (on the IPTS-68) measured by Ohgaki et al. [34], also by direct observa-

tion. The measurements made by the latter investigators extend to the determination of the critical pressure and (indirectly) to that of the critical molar volume. The value of $p_c = 7.238$ MPa obtained by the direct method [34] is to be preferred to those published in previous studies [29–31,33]. The same happens with the critical molar density $\rho_{m,c} = 10.3$ kmol $\cdot$ m^{-3}, despite molar densities (and volumes) registered with more significant figures having been published. In view of the uncertainties attached to other techniques (viz. rectilinear diameters, extrapolation of vapour pressure equations, and similar ones), we selected as most reliable values of the critical properties of nitrous oxide: $T_c = 309.548$ K [32], $p_c = 7238$ kPa [34], and $V_{m,c} = 1/\rho_{m,c} = 97.087$ cm$^3 \cdot$ mol^{-1} [34].

3. Calculations and results

3.1. Vapourization

The vapour pressure of nitrous oxide has been rigorously measured since the first International Temperature Scale was established in 1927. Table 3 summarizes the results found in the literature. With the 296 experimental points resulting from tables 1 and 3 the parameters a_i in the Wagner vapour pressure equation

$$p = p_c \cdot \exp\{(a_1\tau + a_2\tau^{1.5} + a_3\tau^{2.5} + a_4\tau^5)/(T/T_c)\}, \quad (1)$$

where $\tau = (1 - T/T_c)$, were found to be $a_1 = -6.8657$, $a_2 = 1.9373$, $a_3 = -2.6440$, and $a_4 = 0.0387$. All the temperatures were previously converted into the ITS-90. In this fitting, the critical pressure p_c has

TABLE 1
Summary of the measurements on the triple point of nitrous oxide.

Year	Temperature[a]/K	T scale[b]	Pressure[c]/kPa	Molar volume/(cm$^3 \cdot$ mol^{-1})	Reference
1935	182.26	$T^{A,d}$	87.853		[5]
1941			87.882		[6]
1945	182.351	ITS-27			[7]
1960	(182.26)	$T^{A,d}$	87.851		[8]
1974	182.407	IPTS-68	87.91 to 87.99		[9]
1980;1983			87.866 ± 0.001[e,f]	35.487 ± 0.002[e,f]	[10,11]
1984;1986			87.912 ± 0.006[f]		[12,13]
1989			87.895 ± 0.007[f]		[14]
1994;1995			87.875 ± 0.012[f]		[15,16]
1996;1998;2000			87.815[f]		[17–20]
2000;2001;2002			87.869 ± 0.008[f]		[21–23]
2003;2005;2006			87.951 ± 0.015[f]		[24–27]

[a] Temperatures are as given in the original papers.
[b] T^A indicates a temperature scale used by a particular author.
[c] Pressures were converted into SI units.
[d] Giauque used $T_{ice} = 273.10$ K. Clusius et al. [8] used the same T scale.
[e] Average of six independent measurements made at different times with different samples.
[f] Measurements taken with the sample surrounded by purified N_2O melting at its own triple point.

TABLE 2
Summary of the measured coordinates of the critical point of nitrous oxide.

Year	T_c [a]	T scale [b]	p_c[c]/kPa	$V_{m,c}$ or $\rho_{m,c}$ or ρ_c	Notes	Reference
1929				$\rho_c = 0.459$ g $\cdot$ cm^{-3}		[28]
1933	309.5 K	ITS-27	7265.0			[29]
1953	36.39 °C	IPTS-48	7234.6			[30]
1961	36.434 °C	T^A	7254.46	$\rho_c = 0.4525$ g $\cdot$ cm^{-3}	T_c by visual observation; p_c by equation; ρ_c by rectilinear diameter	[31]
1971	36.417 °C	IPTS-48			T_c by refraction index	[32]
1988	36.5 °C	IPTS-68	7270	$V_{m,c} = 95.5$ cm$^3 \cdot$ mol^{-1}	$V_{m,c}$ by visual observation	[33]
1990	309.56 K	IPTS-68	7238	$\rho_{m,c} = 0.0103$ mol $\cdot$ cm^{-3}	T_c, p_c, and $\rho_{m,c}$ by direct method	[34]
2006	309.57 K	ITS-90	7245			[35]
2006	309.52 K	ITS-90	7245	$\rho_{m,c} = 0.01027$ mol $\cdot$ cm^{-3}	Calculated	[36]

[a] Temperatures are as given in the original papers.
[b] T^A indicates a temperature scale used by a particular author.
[c] Pressures were converted into SI units.

TABLE 3
Summary of experimental data on the vapour pressure of nitrous oxide.

Year	No. of points	Range (T and p)[a]	T scale[b]	Reference
1935	5	$T = (182.26$ to $185.848)$ K; $p = (87.853$ to $109.180)$ kPa	T^A	[5]
1945	31	$T = (183.313$ to $236.860)$ K; $p = (93.219$ to $1069.891)$ kPa	ITS-27	[6]
1953	17	$t = (12.91$ to $36.39)$ °C; $p = (4265.783$ to $7234.605)$ kPa	IPTS-48	[30]
1961	19	$t = (30$ to $36.434)$ °C; $p = (1321.683$ to $7233.186)$ kPa	T^A	[31]
1974	26	$T = (182.405$ to $184.917)$ K; $p = (87.909$ to $102.419)$ kPa	IPTS-68	[9]
1975	163	$T = (182.26$ to $219.34)$ K; $p = (87.830$ to $558.363)$ kPa	T^A	[37]
1990	8	$T = (308.270$ to $309.365)$ K; $p = (4691$ to $7210)$ kPa	IPTS-68	[34]
2004	18	$T = (219.24$ to $273.08)$ K; $p = (554.7$ to $3119.9)$ kPa	ITS-90	[38]
2007	1	$T = 283.18$ K; $p = 4041.3$ kPa	ITS-90	[39]

[a] Temperatures are as given in the original papers; pressures were converted into SI units.
[b] T^A indicates a temperature scale used by a particular author.

been treated as the fifth adjustable parameter yielding $p_c = 7243$ kPa, not much different from the directly measured value selected in this study. The relative average absolute deviation (AAD) is 0.16%, and figure 1 shows a deviation plot for this fitting. The measurements of Atake and Chihara [9] are $(0.7$ to $0.8)$% too low, lying outside the limits in this figure. The sole point due to Wagner *et al.* [39] seems to be high by more than 0.9%.

The molar enthalpy of vapourization $\Delta_\ell^g H_m$ is readily calculated from equation (1) and the Clapeyron equation

$$dp/dT = \Delta_\ell^g H_m / (T \cdot \Delta_\ell^g V_m), \qquad (2)$$

once the molar volumes of the gaseous and liquid phases at equilibrium V_m^g and V_m^ℓ, respectively, or the difference between them $\Delta_\ell^g V_m = V_m^g - V_m^\ell$, are known. A summary of the experimentally determined molar volumes of the liquid and gas along the satura-

tion line found in the literature is compiled in table 4. Excluding the old measurements for the liquid density ρ^ℓ by Quinn and Vernimont [28] the 51 experimental points (tables 1 and 4) were fitted through the equation

$$\rho^\ell / (g \cdot cm^{-3}) = \rho_c / (g \cdot cm^{-3}) \cdot \exp(c_1 \tau^{1/3} + c_2 \tau^{2/3} + c_3 \tau^{7/3} + c_4 \tau^4), \qquad (3)$$

with the parameters $c_1 = 1.6779$, $c_2 = -0.5810$, $c_3 = 1.3148$, and $c_4 = -2.9806$. The AAD is 0.27%, and the standard deviation is $\sigma(\rho^\ell) = \pm 0.003$ g $\cdot$ cm^{-3}.

For the molar volumes V_m^g of the saturated gaseous phase along the temperature interval from T_t to T_c the calculations are more involved. Discarding the much scattered (and out of the trend) series of values in reference [28], the measurements on the saturated gas only extend from about $T = 240$ K upwards to the critical point.
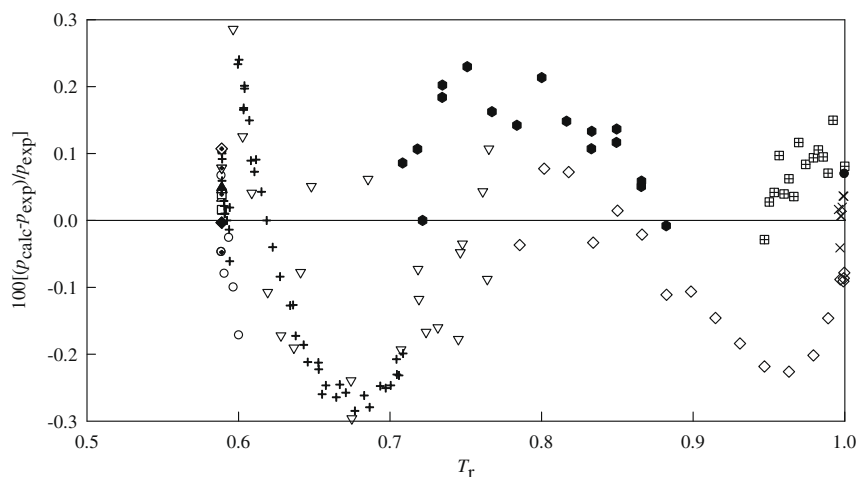
FIGURE 1. Vapour pressure deviation plot of N$_2$O. The p_{calc} represents the values calculated from equation (1), with the parameters given in the text. Legend: the symbols are: ○, reference [5]; △, reference [6]; ▽, reference [7]; ⊞, reference [30]; ▼, reference [8]; ◇, reference [31]; +, reference [37]; ▲, reference [10,11]; ♦, reference [12,13]; □, reference [14]; ×, reference [34]; ⊡, reference [15,16]; ◈, reference [17–20]; ▲, reference [21–23]; ⊙, reference [24–27]; ●, reference [38]; ▼, triple point, this work; ●, critical point, this work.

TABLE 4
Summary of the experimental data on the density of the saturated fluid phases of nitrous oxide.

Year	No. of points	T scale[a]	(T and ρ^ℓ or ρ_m^ℓ)[b]	(T and ρ^g or ρ_m^g)[b]	Reference
1929	18	T^A	$t = (-50$ to $38.8)$ °C; $\rho^\ell = (1.079$ to $0.451)$ g $\cdot$ cm^{-3}	$t = (-50$ to $38.8)$ °C; $\rho^g = (0.032$ to $0.459)$ g $\cdot$ cm^{-3}	[28]
1953	14	IPTS-48	$t = (-20.00$ to $34.02)$ °C; $\rho^\ell = (0.789$ to $0.617)$ g $\cdot$ cm^{-3}	$t = (-20.00$ to $34.02)$ °C; $\rho^g = (1.159$ to $0.295)$ g $\cdot$ cm^{-3}	[30]
1961	13	T^A	$t = (-30.0$ to $36.4)$ °C; $\rho^\ell = (1.0341$ to $0.4854)$ g $\cdot$ cm^{-3}	$t = (-30.0$ to $36.4)$ °C; $\rho^g = (0.0343$ to $0.4188)$ g $\cdot$ cm^{-3}	[31]
1964	17	T^A	$T = (182.4$ to $184.5)$ K; $\rho^\ell = (1.241$ to $1.235)$ g $\cdot$ cm^{-3}		[40]
1990	7(3)	IPTS-68	$T = (308.270$ to $309.365)$ K; $\rho_m^\ell = (13.28$ to $12.02)$ kmol $\cdot$ m^{-3}	$T = (308.575; 308.739; 309.226)$ K; $\rho_m^g = (7.68; 7.87; 8.29)$ kmol $\cdot$ m^{-3}	[34]

[a] T^A indicates a temperature scale used by a particular author.
[b] Temperatures are as given in the original papers; $\rho_m = 1/V_m = \rho/M$, where $M = 44.0128$ g $\cdot$ mol^{-1}.

These results are of little use in extrapolating to the far temperature region in which we are interested for the present calculations, *viz.* the short temperature range from T_t to that of the normal boiling temperature T_b. In view of this, for the molar volume of the gaseous phase V_m^g in this region the Leiden form of the virial equation of state truncated after the third term

$$pV_m/(RT) = 1 + B/V_m + C/V_m^2, \tag{4}$$

where B and C are the second and third virial coefficients, respectively, has been judged to be adequate. The reduced second virial coefficients were expressed by fitting polynomials of the form

$$B/\{V_{m,c}/(\text{cm}^3 \cdot \text{mol}^{-1})\} = \sum_{i=0}^{2} b_i/(T/T_c)^i, \tag{5}$$

where $V_{m,c}$ is the critical molar volume and the b_i are numeric adjustable parameters to the 77 experimental values summarized in table 5. The early results obtained by Johnston and Weimar [41], which along the years have been shown to be not of the best quality, were discarded in this fitting. The following values have been obtained for the parameters in equation (5): $b_0 = 0.2957$, $b_1 = -0.1801$ and $b_2 = -1.3754$, with $\sigma(B) = \pm 4 \text{ cm}^3 \cdot \text{mol}^{-1}$. The third virial coefficients C were calculated through the empirical equation due to Chueh and Prausnitz [51]:

$$C/\{V_{m,c}/(\text{cm}^3 \cdot \text{mol}^{-1})\}^2 = (0.232T_r^{-0.25} + 0.468T_r^{-5}) \cdot \{1 - \exp(1 - 1.89T_r^2)\} + d \cdot \exp(-2.49 + 2.30T_r - 2.70T_r^2), \tag{6}$$

where $T_r = T/T_c$ and d is an empirical parameter specific to each particular substance. In this study, the parameter d has been adjusted in order to obtain from equation (6) the best fit to the experimental values of C in table 5. In spite of the scatter of the data points, this gives $d = (2.83 \pm 0.18)$. With these values of B and C, and equations (1) to (6) the molar enthalpy of vapourization is easily calculated.

The normal boiling temperature of nitrous oxide as assessed from the Wagner equation (1) is $T_b = 184.646$ K, which is to be compared with 184.59 K given in reference [5], and 184.695 K [7], 184.81 K [9], 184.67 K [35], and 184.68 [36]. At this temperature the molar enthalpy of vapourization as calculated from equations (1) to (4) is $\Delta_\ell^g H_m(T_b) = 16384 \text{ J} \cdot \text{mol}^{-1}$, significantly lower than the experimentally determined $\Delta_\ell^g H_m(T_b) = 16564 \text{ J} \cdot \text{mol}^{-1}$ [5] and $\Delta_\ell^g H_m(T_b) = 16544 \text{ J} \cdot \text{mol}^{-1}$ [9].

3.2. Sublimation

Perhaps due to the relatively high value of the triple point pressure of nitrous oxide the sublimation pressure of this substance has been measured a number of times in several laboratories, as summarized in table 6. After the temperatures were converted into the ITS-90, the 160 experimental points in tables 1 and 6 have been used in fitting the empirical equation

$$\ln p = \ln p_t + (e_1\theta + e_2\theta^f)/(T/T_t), \tag{7}$$

to the data. In this equation p is the sublimation pressure, $\theta = (1 - T/T_t)$, and e_1, e_2, and f are numerical adjustable parameters. These are: $e_1 = -6.6551$, $e_2 = -9.8076$, and $f = 1.0364$. The relative average absolute deviation for this fitting is AAD = 4% (in the pressure). Considering the scatter affecting the lower values of the sublimation pressure which are of the order of 10^{-5} Pa at temperatures of about 75 K, this AAD is not too high. In spite of this, we decided to try and use the exact integrated form of the Clapeyron equation for the sublimation equilibrium as reported in reference [55], since the values of the ancillary data needed for the calculations are available in the literature. For these calculations, the molar volumes of the gas are obtained from equation (4) and those of the solid phase V_m^c can be calculated by fitting a second degree polynomial in the temperature to the data in reference [56]. The molar heat capacity of the saturated gaseous phase $C_{p,m}^g$ can be calculated from the normal modes of vibration of N_2O [57], and that of the solid $C_{p,m}^c$ is obtained from fitting a polynomial form of the second degree in the temperature to the experimental results in references [5,9]. For the enthal-

TABLE 5
Summary of the data on the virial coefficients of nitrous oxide.

| Year	No. of points	Temperature range	Virial coefficients	Reference
1934	46	$T = (196.87 \text{ to } 298.51) \text{ K}$	$-B = (359.4 \text{ to } -155.3) \text{ cm}^3 \cdot \text{mol}^{-1}$	[41]
1961	10	$t = (-30 \text{ to } 150) \,^\circ\text{C}$	$-B = (212.0 \text{ to } 58.2) \text{ cm}^3 \cdot \text{mol}^{-1}$	[31]
1961	7	$t = (-30.0 \text{ to } 75.0) \,^\circ\text{C}$	$-B' = -B/RT = (10.32 \text{ to } 2.83) \text{ atm}^{-1}$	[42]
1962	7	$t = (0 \text{ to } 150) \,^\circ\text{C}$	$-B = (160.92 \text{ to } 58.3) \text{ cm}^3 \cdot \text{mol}^{-1}$ $C \cdot 10^{-3} = (5.92 \text{ to } 2.98) \text{ cm}^6 \cdot \text{mol}^{-2}$	[43]
1973	3	$t = (6.5; 30.1; 75.1) \,^\circ\text{C}$	$-B = (146.4; 119.7; 101.2) \text{ cm}^3 \cdot \text{mol}^{-1}$	[44]
1986	5	$T = (187.0 \text{ to } 296.2) \text{ K}$	$-B = (379 \text{ to } 136) \text{ cm}^3 \cdot \text{mol}^{-1}$	[45]
1987	24	$t = (0 \text{ to } 3000) \,^\circ\text{C}$	$-B = (153.69 \text{ to } -31.24) \text{ cm}^3 \cdot \text{mol}^{-1a}$	[46]
2004	4	$T = (283.5 \text{ to } 345.6) \text{ K}$	$C \cdot 10^{-3} = (6.64 \text{ to } 4.16) \text{ cm}^6 \cdot \text{mol}^{-2}$	[47]
2004; 2005; 2006	14(+4)	$T = (283.51 \text{ to } 364.36) \text{ K}$	$-B = (150.3 \text{ to } 81.3) \text{ cm}^3 \cdot \text{mol}^{-1}$ $C = (6410.51 \text{ to } 2943.91) \text{ cm}^6 \cdot \text{mol}^{-2}$	[47,38,48,49]
2006	3	$T = (303.25; 323.44; 343.95) \text{ K}$	$-B = (129.0; 111.1; 95.7) \text{ cm}^3 \cdot \text{mol}^{-1}$ $C = (5780; 4950; 4120) \text{ cm}^6 \cdot \text{mol}^{-2}$	[50]

[a] Calculated.

TABLE 6
Summary of the experimental data on the sublimation pressure of nitrous oxide.

Year	No. of points	(T and p)[a]	T scale[b]	Reference
1930	7	$t = (-170.0 \text{ to } -150.0) \,^\circ\text{C}; p = (0.17 \text{ to } 40.8) \text{ Pa}$	ITS-27	[52]
1935	9	$T = (148.476 \text{ to } 182.258) \text{ K}; p = (2429 \text{ to } 87853) \text{ Pa}$	T^A	[5]
1974	38	$T = (68.1 \text{ to } 80.2) \text{ K}; p = (1.14 \cdot 10^{-7} \text{ to } 1.21 \cdot 10^{-4}) \text{ Pa}$		[53]
1974	26	$T = (146.071 \text{ to } 182.210) \text{ K}; p = (1765 \text{ to } 82243) \text{ Pa}$	IPTS-68	[9]
1975	56	$T = (143.88 \text{ to } 182.25) \text{ K}; p = (1309 \text{ to } 87739) \text{ Pa}$	T^A	[37]
1983	12	$T = (125.10 \text{ to } 147.54) \text{ K}; p = (60.86 \text{ to } 2119.8) \text{ Pa}$	IPTS-68	[54]

[a] Temperatures are as given in the original papers; pressures were converted into SI units.
[b] T^A indicates a temperature scale used by a particular author.
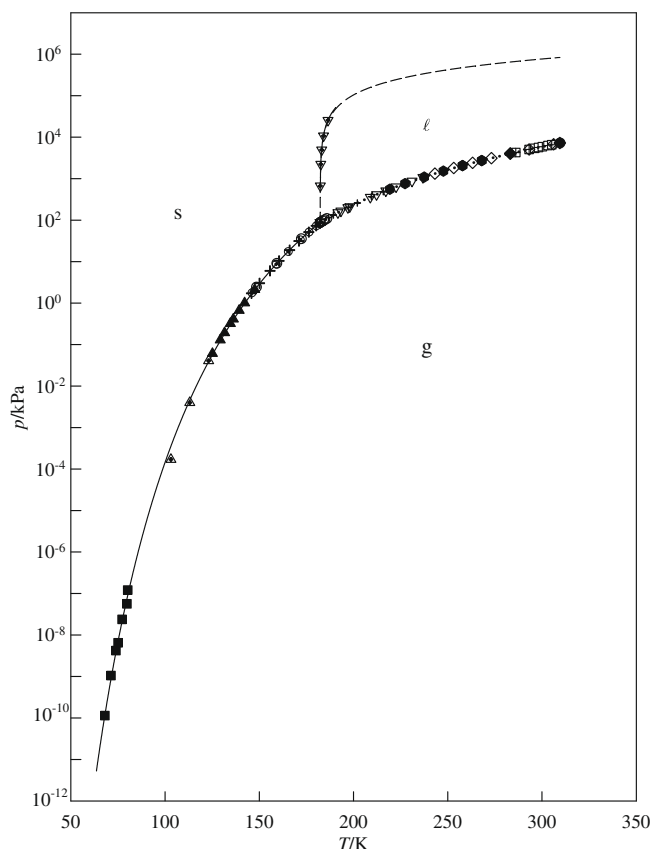
FIGURE 2. Phase diagram of N_2O. Legend: the symbols are: ○, reference [5]; △, reference [6]; ▽, reference [7]; ▼, reference [8]; ⊙, reference [9]; ⊞, reference [30]; ◇, reference [31]; ×, reference [34]; +, reference [37]; ♦, reference [39]; ●, reference [47,38,48,49]; ▲, reference [52]; ■, reference [53]; ▲, reference [54]; ▼, triple point, this work; ●, critical point, this work. The solid, liquid and gaseous phases are represented by s, ℓ, g, respectively. The curves are: sublimation, solid line from equation (7); vapourization, dotted line from equation (1); fusion, dashed line from equation (9).

py of sublimation at the triple point $\Delta_c^g H_m (T_t)$ which is also needed in the calculations, the experimental molar enthalpy of fusion $\Delta_c^\ell H_m(T_t) = 6529 \, J \cdot mol^{-1}$, which is the average of the two values reported in the literature [5,9], has been added to the molar enthalpy of vapourization measured by the same authors at the normal boiling point extrapolated to the triple point temperature. This extrapolation is small (just above 2 K) but not negligible. We arrived at a value of $\Delta_c^g H_m(T_t) = 23\,205 \, J \cdot mol^{-1}$. At zero Kelvin, the molar enthalpy of sublimation is $\Delta_c^g H_m \, (T = 0 \, K) = 24\,489 \, J \cdot mol^{-1}$, and the maximum value of $\Delta_c^g H_m = 25\,214 \, J \cdot mol^{-1}$ occurs at $T = 50 \, K$, the temperature at which $C_{p,m}^c = C_{p,m}^g$ as predicted in reference [55]. For the reference point in the calculation of the sublimation pressure, the coordinates of the triple point have been used. With these data, following the procedure developed in reference [55], we obtained the sublimation curve represented in figure 2. This curve is almost exactly the same as that calculated from equation (7).

3.3. Fusion

The existing experimental results for the fusion of nitrous oxide consist of the measurements carried out by Clusius *et al.* [8] from the triple point up to pressures just above 25 MPa. The data were correlated through the Simon equation

$$p = p_t + g\{(T/T_t)^h - 1\}, \tag{8}$$

where g/MPa = 330.4 and h = 3.27 are adjusted parameters. The molar enthalpy of fusion at the triple point derived from equation (8) is $\Delta_c^\ell H_m(T_t) = 6720 \, J \cdot mol^{-1}$ which is to be compared with the measured $\Delta_c^\ell H_m(T_t) = 6529 \, J \cdot mol^{-1}$ mentioned above.

One of the exact integrated forms of the Clapeyron equation was used to find and extend the fusion curve up to higher temperatures. The final form of the fusion curve equation [55] is

$$p = p_t + \{j_1 + j_2 T \ln T + j_3 T\}/\Delta_c^\ell V_m(T_t), \tag{9}$$

where the j_i are

$$j_1 = \Delta_c^\ell C_{p,m}(T_t) \cdot T_t - \Delta_c^\ell H_m(T_t),$$
$$j_2 = \Delta_c^\ell C_{p,m}(T_t), \tag{10}$$
$$j_3 = \Delta_c^\ell H_m(T_t)/T_t - \Delta_c^\ell C_{p,m}(T_t) - \Delta_c^\ell C_{p,m}(T_t) \ln T_t.$$

The calculations give j_1/(Pa · m³ · mol⁻¹) = –3326, j_2/(Pa · m³ · mol⁻¹ · K⁻¹) = 17.566, and j_3/(Pa · m³ · mol⁻¹ · K⁻¹) = –73.198. The fusion curve is shown in figure 2 along with the entire equilibrium phase diagram.

Recently, Iota *et al.* [58] have studied solid N_2O by X-ray at much higher pressures (from 5 GPa up to 40 GPa) and apparently found three more solid phases stable at those pressures. Their data are given only in graphical form with no numeric complementary information.

4. Conclusions

In conclusion, in this study we have selected experimentally measured coordinates of the triple point and the critical point of nitrous oxide. Also, empirical equations have been found for the vapourization, sublimation and fusion curves. The results of the exact integrated Clapeyron equation compare favourably with those from the aforementioned empirical equations. The molar enthalpies of vapourization at T_b, sublimation at T_t, and fusion at this same temperature have been derived. The molar enthalpy of sublimation at 0 K is also given. The phase diagram has been constructed.

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