International Journal of Thermophysics, Vol. 7, No. 3, 1986

A Thermodynamic Property Formulation for Nitrogen from the Freezing Line to 2000 K at Pressures to 1000 MPa[1]

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A new fundamental equation explicit in Helmholtz energy for thermodynamic properties of nitrogen from the freezing line to 2000 K at pressures to 1000 MPa is presented. A new vapor pressure equation and equations for the saturated liquid and vapor densities as functions of temperature are also included. The techniques used for development of the fundamental equation are those reported in a companion paper for ethylene. The fundamental equation and the derivative functions for calculating internal energy, enthalpy, entropy, isochoric heat capacity (C_v), isobaric heat capacity (C_p), and velocity of sound are also included in that paper. The property formulation using the fundamental equation reported here may generally be used to calculate pressures and densities with an uncertainty of $\pm 0.1\%$, heat capacities within $\pm 2\%$, and velocity of sound values within $\pm 2\%$. The fundamental equation is not intended for use near the critical point.

KEY WORDS: equation of state; nitrogen; saturation properties; thermodynamic properties.

1. INTRODUCTION

Commercial nitrogen is widely used in industry and in scientific and engineering laboratories throughout the world. A large base of experimental measurements and new correlation techniques have assisted the development of an accurate wide-range thermodynamic property for-

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[1] Paper presented at the Ninth Symposium on Thermophysical Properties, June 24–27, 1985, Boulder, Colorado, U.S.A.

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mulation for nitrogen at the Center for Applied Thermodynamic Studies at the University of Idaho in Moscow. The results of a recent study of thermodynamic properties of nitrogen are reported in Ref. 1. A companion formulation for the thermodynamic properties of nitrogen in the critical region is reported in Ref. 2. Conventions and notation used in this paper are those given in the preceding paper on ethylene [3].

Discussions of prior correlations of properties of nitrogen, experimental data sources, techniques of data analysis and correlation, and exhaustive comparisons to experimental data are given in Ref. 1. The fixed points for nitrogen used in this work are given in Table I. The sources and details of selection of these values are given in Ref. 1.

2. THE FUNDAMENTAL EQUATION

The fundamental equation used in this work is similar to that for ethylene described in Ref. 3, although the indices and coefficients are different. The procedures described in Ref. 3 for least-squares fitting taken from Ref. 4 were utilized in the determination of the coefficients of the fundamental equation. The fundamental equation and property calculation procedures are described in Ref. 3. The range of validity of the fundamental equation for nitrogen is from the freezing line to 2000 K at pressures to 1000 MPa. With a few exceptions, the equation presented here represents the selected experimental data to within the estimated accuracies of these data.

Table I. Fixed Points for Nitrogen

Symbol	Quantity	Value
T_c	Critical temperature	126.193 ± 0.003 K
P_c	Critical pressure	3.3978 ± 0.001 MPa
ρ_c	Critical density	11.177 ± 0.01 $\text{mol} \cdot \text{dm}^{-3}$
T_{tp}	Triple-point temperature	63.148 ± 0.002 K
P_{tp}	Triple-point pressure	0.01253 ± 0.00001 MPa
ρ_{tpv}	Triple-point density (vapor)	0.02410 $\text{mol} \cdot \text{dm}^{-3}$
T_{nbp}	Normal boiling-point temperature	77.348 K
ρ_{nbpv}	Normal boiling-point density (vapor)	0.1650 $\text{mol} \cdot \text{dm}^{-3}$
ρ_{nbpl}	Normal boiling density (liquid)	28.794 $\text{mol} \cdot \text{dm}^{-3}$
T_0	Reference temperature	298.15 K
P_0	Reference pressure	0.101325 MPa
H_0^0	Reference enthalpy at T_0	8669 $\text{J} \cdot \text{mol}^{-1}$
S_0^0	Reference entropy at T_0 and P_0	191.502 $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

Table II. Parameters Considered in the Determination of the Equation of State for Nitrogen[a]

k	i	j	l	k	i	j	l
1	1	0.25	0	51	2	2.00	2
2	1	0.50	0	52	2	3.00	2
3	1	0.75	0	53	2	4.00	2
4	1	1.00	0	54	2	5.00	2
5	1	1.25	0	55	2	7.00	2
6	1	1.50	0	56	2	8.00	2
7	1	1.75	0	57	2	8.00	4
8	1	2.00	0	58	2	10.00	4
9	1	2.50	0	59	2	12.00	4
10	1	3.00	0	60	2	14.00	4
11	1	4.00	0	61	2	16.00	4
12	1	5.00	0	62	2	18.00	4
13	1	6.00	0	63	2	20.00	4
14	1	7.00	0	64	2	22.00	4
15	2	0.25	0	65	2	8.00	6
16	2	0.50	0	66	2	12.00	6
17	2	0.75	0	67	2	16.00	6
18	2	1.00	0	68	2	20.00	6
19	2	1.50	0	69	2	24.00	6
20	2	2.00	0	70	2	28.00	6
21	2	2.50	0	71	2	32.00	6
22	2	3.00	0	72	3	8.00	3
23	2	3.50	0	73	3	10.00	3
24	3	0.25	0	74	3	12.00	3
25	3	0.50	0	75	3	14.00	3
26	3	0.75	0	76	3	16.00	3
27	3	1.00	0	77	3	18.00	3
28	3	1.50	0	78	3	20.00	3
29	3	2.00	0	79	3	22.00	3
30	3	2.50	0	80	4	4.00	2
31	4	1.00	0	81	4	5.00	2
32	4	2.00	0	82	4	6.00	2
33	4	3.00	0	83	4	7.00	2
34	4	4.00	0	84	4	8.00	2
35	4	5.00	0	85	4	9.00	2
36	6	1.00	0	86	4	10.00	2
37	6	2.00	0	87	4	10.00	4
38	6	3.00	0	88	4	12.00	4
39	6	4.00	0	89	4	14.00	4
40	6	5.00	0	90	4	16.00	4
41	6	6.00	0	91	4	18.00	4
42	1	3.00	3	92	4	20.00	4
43	1	4.00	3	93	4	22.00	4
44	1	5.00	3	94	4	24.00	4
45	1	6.00	3	95	8	4.00	2
46	1	7.00	3	96	8	5.00	2
47	1	8.00	3	97	8	6.00	2
48	1	9.00	3	98	8	7.00	2
49	1	10.00	3	99	8	8.00	2
50	2	1.00	2	100	8	9.00	2

[a] $\gamma = 0$ for terms with $l = 0$; $\gamma = 1$ for terms with l greater than 0.

The real-fluid contribution to dimensionless Helmholtz energy [Eq. (6) from Ref. 3] is given by

$$\bar{\alpha}(\delta, \tau) = \sum_{k=1}^{100} N_k\, \delta^i \tau^j \exp(-\gamma\, \delta^l), \tag{1}$$

where the N_k are the coefficients of the fundamental equation, and γ is a parameter which has a value of 0 or 1. The terms in Eq. (1) are similar to those used by Schmidt and Wagner for oxygen [5].

The bank of terms used for nitrogen is given in Table II. The coefficients of Eq. (1) given in Table III were determined by a least-squares fit

Table III. Coefficients for the Fundamental Equation [Eq. (1)] for Nitrogen[a] (Coefficients Not Listed are Zero)

	i	j	l
$N_1 = 0.9499541827$	1	0.25	0
$N_4 = -2.049741504$	1	1.00	0
$N_6 = 0.2650110798$	1	1.50	0
$N_{10} = -0.3785445194$	1	3.00	0
$N_{15} = 0.2481718513$	2	0.25	0
$N_{16} = -0.1748429008$	2	0.50	0
$N_{20} = 0.07311459372$	2	2.00	0
$N_{22} = 0.1895290433$	2	3.00	0
$N_{24} = -0.2046287122$	3	0.25	0
$N_{25} = 0.6387017148$	3	0.50	0
$N_{26} = -0.5272986168$	3	0.75	0
$N_{31} = 0.05551383553$	4	1.00	0
$N_{32} = -0.0281308071$	4	2.00	0
$N_{33} = 0.007001895093$	4	3.00	0
$N_{36} = -0.0008191106396$	6	1.00	0
$N_{37} = 0.001659823569$	6	2.00	0
$N_{42} = -0.04927710927$	1	3.00	3
$N_{43} = 0.1138121942$	1	4.00	3
$N_{50} = 0.05032519699$	2	1.00	2
$N_{51} = 0.06012817812$	2	2.00	2
$N_{54} = -0.09551409802$	2	5.00	2
$N_{57} = -0.01100721771$	2	8.00	4
$N_{63} = -0.0001484600538$	2	20.00	4
$N_{79} = -0.005806483467$	3	22.00	3
$N_{80} = 0.06512013679$	4	4.00	2
$N_{82} = 0.02118354140$	4	6.00	2
$N_{89} = 0.01284432210$	4	14.00	4
$N_{91} = -0.01054474910$	4	18.00	4

[a] $\gamma = 0$ for terms 1 through 37 and $\gamma = 1$ for terms 42 through 91.

to 2112 selected data points including P–ρ–T data, velocity of sound data, second virial coefficients, and calculated smoothed values from the revised and extended scaling equation of Ref. 2 and from ancillary equations for the phase equilibrium properties. Details of the data selection are given in Ref. 1.

3. ANCILLARY EQUATIONS

A new vapor pressure equation and equations for the density of the saturated liquid and the saturated vapor as functions of temperature have been developed to include the critical region. New equations for coexistence properties consistent with the revised and extended scaling formulation of Jahangiri and Jacobsen [2] in the critical region are given in this section. Coefficients for these equations are given in Table IV.

3.1. The Vapor Pressure Equation

The vapor pressure equation is

$$\frac{P}{P_c}=\frac{T}{T_c}\left[1+N_1\tau+N_2\tau^{1.9}+N_3\tau^2+N_4\tau^{2.4}+N_5\tau^3+\sum_{i=6}^{17}N_i\tau^{(i+1)/2}\right] \quad (2)$$

where $\tau=(T_c/T)-1$, and P_c and T_c are the critical pressure and critical temperature, respectively. The values of P_c and T_c for nitrogen listed in Table I are taken from Zozulya and Blagoi [6].

3.2. The Equation for the Saturated Vapor Density

The equation for the saturated vapor density of nitrogen is

$$\ln\frac{\rho_{sv}}{\rho_c}=\sum_{i=1}^{23}N_i\tau^{(i+1)/3}+N_{24}\ln\theta+N_{25}\tau^{0.325} \quad (3)$$

where $\tau=[1-(T/T_c)]$, $\theta=T_c/T$, and ρ_{sv} is the density of the saturated vapor.

3.3. The Equation for the Saturated Liquid Density

The equation for the saturated liquid density of nitrogen is

$$\frac{\rho_{sl}}{\rho_c}-1=\sum_{i=1}^{23}N_i\tau^{(i+1)/3}+N_{24}\tau^{0.325}+N_{25}\ln\theta \quad (4)$$

where $\tau=[1-(T/T_c)]$, $\theta=T_c/T$, and ρ_{sl} is the density of the saturated liquid.

Table IV. Coefficients for Liquid–Vapor Coexistence Property Equations for Nitrogen[a]

Vapor pressure equation [Eq. (2)]

$N_1 = -5.072183802$
$N_2 = 13.67990776$
$N_4 = -11.94002133$
$N_6 = 2.641788411$
$N_{10} = -0.3781265428$
$N_{13} = 0.07593697713$

Saturated vapor density equation [Eq. (3)]

$N_1 = 1.345167397$
$N_2 = 27.21335451$
$N_3 = 118.9562787$
$N_4 = -268.1972897$
$N_5 = 329.2110413$
$N_6 = -138.1052419$
$N_{10} = 34.47426258$
$N_{24} = -57.24027229$
$N_{25} = -1.592975033$

Saturated liquid density equation [Eq. (4)]

$N_1 = 17.80437699$
$N_3 = 1202.958313$
$N_4 = -4601.087081$
$N_5 = 10512.65347$
$N_6 = -11885.82325$
$N_8 = 17409.12806$
$N_9 = -19342.02934$
$N_{10} = 7191.464655$
$N_{24} = 0.8015275102$
$N_{25} = -189.5717510$

[a] Coefficients not listed are zero.

3.4. The Melting Pressure Equation

Pressures on the melting curve are given by the equation determined by Watson [7].

$$\ln\left(\frac{P}{P_\mathrm{t}}\right) = \sum_{i=1}^{5} N_i \left(\frac{T}{T_\mathrm{t}} - 1\right)^{i/10} \tag{5}$$

The coefficients, N_i, are listed in Table V. T_t and P_t are the triple-point

Table V. Coefficients of the Melting Curve Equation for Nitrogen

$N_1 = -22.207134$
$N_2 = 114.63633$
$N_3 = -155.53829$
$N_4 = 95.230366$
$N_5 = -21.764068$

temperature and pressure given by Watson [7] as 63.148 K and 0.01253 MPa, respectively.

3.5. The Ideal-Gas Heat Capacity Equation

The ideal-gas heat capacity for nitrogen is given by

$$C_p^0/R = N_1/T^3 + N_2/T^2 + N_3/T + N_4 + N_5 T + N_6^2 + N_7 T^3 + N_8 u^2 e^u/(e^u - 1)^2 \tag{6}$$

where C_p^0/R is the reduced ideal-gas heat capacity, T is the temperature in Kelvins, and $u = N_9/T$. This equation is taken from Ref. 8. The coefficients for Eq. (6) are given in Table VI.

4. COMPARISONS OF CALCULATED PROPERTIES TO EXPERIMENTAL DATA

Detailed comparisons of calculated properties to experimental data are given in Ref. 1. Space limitations do not permit the inclusion of graphical comparisons in this paper. Table VII is an abbreviated table of ther-

Table VI. Coefficients for the Ideal-Gas Heat Capacity Equation for Nitrogen from Ref. 7

$N_1 = -0.837079888737309 \times 10^3$
$N_2 = 0.379147114487423 \times 10^2$
$N_3 = -0.6017378442\ 75135$
$N_4 = 3.50418363823414$
$N_5 = -0.874955653028497 \times 10^{-5}$
$N_6 = 0.148968607238516 \times 10^{-7}$
$N_7 = -0.256370354277089 \times 10^{-11}$
$N_8 = 1.00773735767351$
$N_9 = 0.33534061 \times 10^4$

Table VII. Thermodynamic Properties of Nitrogen

Temperature (K)	Density $(\mathrm{mol \cdot dm^{-3}})$	Internal energy $(\mathrm{J \cdot mol^{-1}})$	Enthalpy $(\mathrm{J \cdot mol^{-1}})$	Entropy $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	C_v $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	C_p $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	Velocity of sound $(\mathrm{m \cdot s^{-1}})$
			0.101325-MPa isobar				
64	30.920	−4180.7	−4177.4	68.63	31.22	56.48	1010
70	29.984	−3842.4	−3839.0	73.68	30.64	56.45	934
80	0.15850	1602.6	2241.8	152.55	23.32	33.51	177
100	0.12432	2040.0	2855.0	159.41	20.96	29.89	202
150	0.08173	3093.4	4333.2	171.40	20.84	29.37	249
200	0.06107	4138.5	5797.7	179.83	20.82	29.23	288
300	0.04063	6222.7	8716.6	191.66	20.82	29.17	353
600	0.02030	12572.	17563.	212.07	21.80	30.12	496
1200	0.01015	26800.	36780.	234.12	25.41	33.73	688
			3.5-MPa isobar				
64	31.128	−4214.5	−4102.1	68.09	31.49	56.10	1035
70	30.231	−3882.4	−3766.6	73.11	30.87	55.84	961
80	28.680	−3327.6	−3205.5	80.60	29.79	56.56	853
100	25.148	−2174.0	−2034.8	93.64	27.74	61.53	650
150	3.6176	2441.6	3409.1	137.51	23.15	46.65	229
200	2.2658	3776.5	5321.3	148.59	21.55	34.17	286
300	1.4083	6028.3	8513.6	161.58	21.05	30.71	360
600	0.69115	12499.	17563.	182.50	21.86	30.42	505
1200	0.34714	26780.	36862.	204.65	25.44	33.78	695

Thermodynamic properties of nitrogen for the coexistence states

Temperature (K)	Pressure (MPa)	Density $(\mathrm{mol \cdot dm^{-3}})$	Enthalpy $(\mathrm{J \cdot mol^{-1}})$	Entropy $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	C_v $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	C_p $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	Velocity of sound $(\mathrm{m \cdot s^{-1}})$
64	0.01460	30.915	−4179.3	68.64	31.21	56.49	1010
		0.02776	1828.8	162.52	24.10	33.51	160
80	0.13699	28.351	−3268.9	81.28	29.63	57.65	821
		0.21801	2202.7	149.67	26.52	38.34	174
100	0.77881	24.584	−2050.5	94.58	27.84	65.09	601
		1.1436	2451.0	139.59	27.43	47.46	181
120	2.5125	18.643	−493.19	107.95	29.06	128.9	309
		4.4632	2082.1	129.41	31.78	131.2	171

modynamic properties of nitrogen which may be used to verify programming of the equations presented here for system analysis and other engineering applications.

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