THEORETICAL STUDY OF THE THERMODYNAMIC PROPERTIES OF NITROGEN AT HIGH TEMPERATURES AND PRESSURES

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A theoretical analytical equation of state is derived and used to compute new thermodynamic data for nitrogen at high tempratures and pressures.

Reliable thermodynamic data of technologically important materials at high temperatures and pressures are necessary in many fields of science and technology. For example, the design and use of high-pressure hypersonic gasdynamical devices requires thermodynamic data for nitrogen at pressures up to 2000 MPa and at temperatues up to 2500°K. However for several reasons experimental P-v-T data on nitrogen for $T > 300°K$ and $P > 100$ MPa are very scarce, and experimental data on other thermodynamic properties are practically nonexistent in this temperature and pressure region.

Table 1 lists the relevant experimental papers, the intervals of the thermodynamic parameters, the method used, and the author's estimate of error in the data reported.

Figure 1 shows the deviation $\delta\rho$* between the experimental values of the density obtained in [1, 3, 6, 7] and the values given in [4]. The deviations are given in the temperature interval 373.15 to 673.15°K for the pressures 200, 400, 600, 800, and 1000 MPa. It is evident from Fig. 1 that the disagreement significantly exceeds the authors' estimates of error and reaches 1.6%. Comparison of the data of [6] and [7] at temperatures from 673.15 to 1273.15°K shows that the disagreement tends to increase with increasing temperature and reaches 3.5% for $T = 1273.15°K$. The disagreement is mainly due to the extreme difficulty of carrying out experiments at high temperatures and pressures. Above $T = 1800°K$ and $P = 550$ MPa experimental data does not exist.

The situation has stimulated the development of computational and theoretical methods of determining the thermodynamic properties of nitrogen in the dense fluid region. Among the papers in this field are the works of Jacobsen and Stewart [8], Zykov and Sevast'yanov [9], Kuznetsov [10], and Younglove [11].

Jacobsen and Stewart obtained an equation of state for nitrogen in the Strowbridge form with 32 empirical constants, which were found by a least squares fit to a large quantity of experimental data, including the data of [1, 4]. The resulting equation of state was then used to compute tables of the thermodynamic properties of nitrogen from the triple point up to $T = 2000°K$ for $P \leq$ MPa, and up to $T = 1200°K$ for $P \leq 1000$ MPa. The equation of state given in [8] closely approximate the experimental data used in the fit, however its extrapolation to higher densities is dubious, since it is purely empirical.

Zykov and Sevast'yanov considered a semiempirical equation of state of nitrogen for $T = 300$ to 1300°K and $P = 100$-1200 MPa. It contains theoretically motivated terms involving the constants ε and σ for a Lennard-Jones (12-7) potential, along with an empirical correction based on an analysis of the data of [3, 4, 6]. The resulting equation of state [9] leads to a satisfactory description of the P–v–T data for $T > 300°K$, but its extrapolation into the dense fluid region is unlikely to be satisfactory, in our opinion, since the use of a two-parameter Lennard-Jones potential at high temperatues and pressures and the use of the second virial coefficient to account for attractive forces is not completely justified.

The thermodynamic properties of nitrogen in the region $300 \leq T \leq 2500°K$ and $0 < \rho < 300$ kg/m^3 were calculated in [10]; this corresponds to a maximum pressure of $P \cong 300$ MPa at $T =$ 300 MPa at $T = 2500°K$. The equation of state was a virial expansion limited to the first

*$\delta\rho = [(\rho^{[\ ]} - \rho^{[4]}) / \rho^{[4]}] \cdot 100$, %.

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TABLE 1. List of Experimental Papers on Nitrogen at High Temperatures and Pressures

Author(s) and publ. year	Parameters studied	Range		Method used	Author's estimate of error, %	Lit. source
		ΔT, K	ΔP, MPa			
Michels, Wouters, and De Boer (1936)	P, v, T	273—423	20—304	PV	0,02	[1]
Tsiklis (1951)	P, v, T	323—423	658—1013	D	0,3	[2]
Tsiklis and Polyakov	P, v, T	295—673	152—1013	D	0,3	[3]
Robertson, Babb (1969)	$P, v. T$	308—673	150—1000	PV—PC	0,3	[4]
Voronov, Pitaevskaya, and Bilevich (1969)	Speed sound	298—448	20—405	Pulse	0,3	[5]
Malbrunot, Vodar (1973)	P, v, T	473—1273	76—494	PC	0,3	[6]
Antanovich, Plotnikov (1977)	P, v, T	400—1800	100—800	D	1,2	[7]

Note: PV) variable volume piezometer; PC) constant volume piezometer; D) displacement.

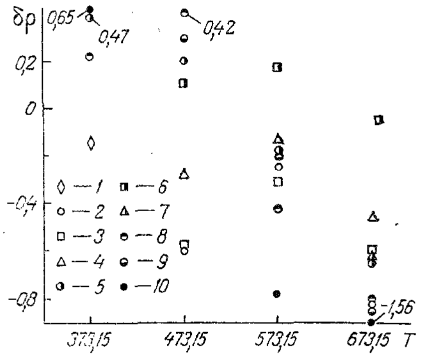

Fig. 1

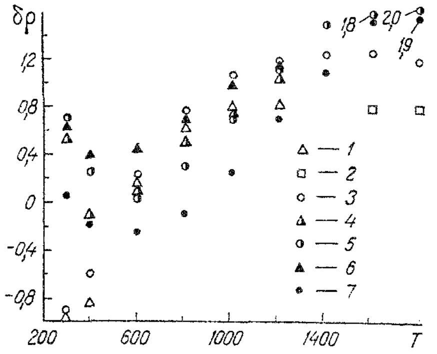

Fig. 2

Fig. 1. Deviations between the experimental values of the density of nitrogen, obtained by different authors, and the data of [4] for the following pressures: 1) 200 MPa [1]; 2) 200 [3]; 3) 200 [6]; 4) 200 [7]; 5) 400 [3]; 6) 400 [6]; 7) 400 [7]; 8) 600 [3]; 9) 800 [3]; 10) 1000 MPa [3]. δρ, %; T, K.

Fig. 2. Deviations between the values of the density of nitrogen calculated from equation (2) and the data of other authors for the following pressures: 1) 200 MPa [9]; 2) 200 [10]; 3) 200 [11]; 4) 600 [9]; 5) 600 [11]; 6) 1000 [9]; 7) 1000 MPa [11].

five coefficients, which were calculated theoretically using a Lennard-Jones (12-6) potential. This equation of state becomes incorrect for densities exceeding the critical density of $\rho_c = 313.1$ kg/m^3.

The tables of thermodynamic properties of nitrogen calculated by Younglove [11] were based on the equation of state obtained in [8]. The region of temperature and pressure in these tables was expanded up to 1800°K and 1000 MPa. Therefore these tables involve a larger extrapolation of the empirical equation of state then in the tables of [8].

Comparison of the densities calculated using the equations of state of [9-11] in the temperature interval T = 300-1200°K and pressure interval P = 100-1000 MPa shows that they are consistent with one another to within an error of 0.8% or less (see Fig. 2). This is not surprising, since the use of the same experimental data often leads to good agreement of the thermal parameters. Above 800°K the consistency between the calculated values [9-11] of the caloric properties is also quite acceptable. However, at lower temperatures and higher densities there is serious disagreements between them (see Figs. 3 and 4). For example, at T = 300°K the disagreement between the calculated values of the heat capacity at constant pressure in [9] and [11] is about 36%, and for the speed of sound it is about 9%. We note that this situation is typical for other materials in the dense fluid state as well, although most of them have been studied to a lesser degree than nitrogen. Hence further study is needed in the direction of reliable, theoretically based methods of

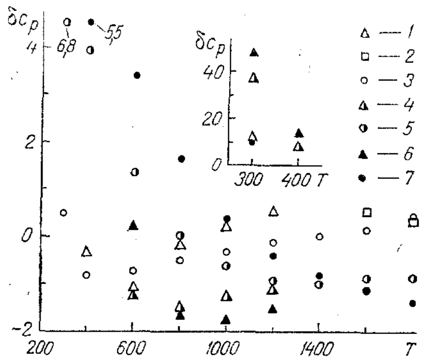

Fig. 3

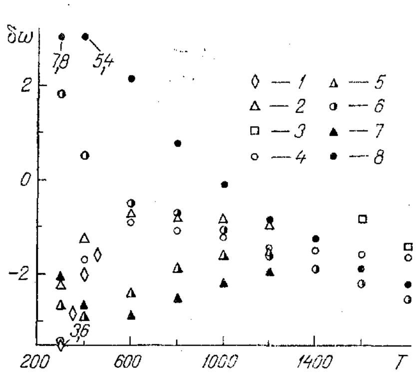

Fig. 4

Fig. 3. Deviation between the calculated heat capacity at constant pressure for nitrogen and the data of other authors for the pressures given in Fig. 2.

Fig. 4. Deviation between the calculated values of the speed of sound and the data of other authors for the following pressures: 1) 202.65 MPa [5]; 2) 200 [9]; 3) 200 [10]; 4) 200 [11]; 5) 600 [9]; 6) 600 [11]; 7) 1000 [9]; 8) 1000 MPa [11] δw, %.

calculating the thermodynamic parameters of materials in the region of the state variables where experiments are either difficult or impossible to perform with current methods.

As a model of a nonpolar, pure material in the dense fluid state, we consider a system of N spherically symmetric particles inside a volume V. The total pair interaction potential U(r) can be written in the form:

$$U(r) = \varphi_{RS}(r) + \Phi(r), \tag{1}$$

where $\varphi_{RS}(r)$ is the arbitrary interaction potential of a reference system (RS) and corresponds to the repulsive part of the total pair potential; $\Phi(r)$ is a perturbing attractive potential, chosen in the form of a square well.

Thermodynamic perturbation theory was used by the present authors [12] to obtain a general analytical equation of state for a system of this kind, including terms to second order in $1/kT$. The equation of state (in terms of the compressibility factor $z = P/(\rho kT)$) can be written in the form

$$z = z_{RS}(x) + (\varepsilon/kT)\, z_1(\lambda,\ x) + (\varepsilon/kT)^2 z_2(\lambda,\ x). \tag{2}$$

In this equation $x = (\pi/6)\rho\sigma^3$, $\lambda = R/\sigma$, where $\rho = N/V$ is the number density of particles in the system; σ is the range of the potential $\varphi_{RS}(r)$. The functions $z_1(\lambda,\ x)$ and $z_2(\lambda,\ x)$ have the following forms:

$$\begin{gathered}
z_1 = 0{,}5x\,(D_2 - 8\lambda^3) + \Delta z_1,\\
z_2^{MC} = 2x\,[\lambda^3(xD_2 - D_1) + 0{,}25D_2(D_1 - 0{,}5)] + \Delta z_2^{MC},\\
z_2^{LC} = 2x\,[\lambda^3(xD_2 - D_1) - 0{,}125\,(xD_2^2 - D_1D_2 - xD_1D_2')] + \Delta z_2^{LC},\\
\Delta z_1 = 12x\,(G_1 + xG_1'),\\
\Delta z_2^{MC} = 6x\,[(D_1 - xD_2)\,G_1 + xD_1G_1'],\\
\Delta z_2^{LC} = 6x\,[(D_1 - xD_2)\,G_1 + (3xD_1 - x^2D_2)\,G_1' + x^2D_1G_1''];
\end{gathered} \tag{3}$$

here

$$D_1 = [\partial(z_{RS}x)/\partial x]_T^{-1};\ D_2 = -\partial D_1/\partial x;\ D_2' = \partial D_2/\partial x;\ G_1^{(n)} = \partial^n G_1/\partial x^n;$$

G_1 depends on the radial distribution function $g_{RS}(L,\ x)$ for the reference system:

$$G_1(\lambda,\ x) = \int_{\lambda}^{\infty} L^2\,[g_{RS}(L,\ x) - 1]\,dL, \tag{4}$$

where $L = r/\sigma$. The superscripts MC and LC in the expressions for $z_2(\lambda, x)$ refer to the approximations of macroscopic and local compressibilities in the thermodynamic perturbation theory [12].

The reference system is shown to be a system of soft spheres with an exponential repulsive potential; the so-called Born–Maier potential:

$$\varphi_{\mathrm{RS}}(r) = \gamma \exp(-r/\delta), \tag{5}$$

where γ and δ are positive constant with the dimensions of energy and length, respectively. This potential is a good model for materials consisting of spherically symmetric or nearly spherically symmetric molecules in the dense fluid state [13, 14].

It was shown in [15] that the equation of state of a system with the interaction potential (5) can be replaced with the equation of state for hard spheres with a temperature-dependent diameter σ:

$$\sigma(T) = \delta \ln(\alpha\gamma/kT), \tag{6}$$

where $\ln \alpha$ is Euler's constant.

Choosing the Percus–Yevick approximation for hard spheres as the simplest and the most valid theoretically, a simple analytical approximation for $G_1(\lambda, x)$ was obtained in [12], which can be used to present the equation of state (2) with the functions z_1 and z_2 given by (3) in a form convenient for the calculation of any of the thermodynamic properties of dense fluids. The example of nitrogen was used to illustrate the application of the resulting equation of state to the calculation of thermodynamic properties of real, pure materials at high temperatures and pressures [12, 16].

However it is known that the Percus–Yevick approximation for hard spheres is not sufficiently accurate. It was shown in [17] that this approximation inadequately describes the properties of hard sphere at high densities. For example, at $x \cong 0.5$ the error reaches $\delta z \cong 6\%$ in comparison with the molecular-dynamics calculations for a system of hard spheres. These calculations also show [18] that there are significant deficiencies in the radial distribution function $g(L, x)$ in the Percus–Yevich approximation. For these reasons we attempt to obtain an equation of state in the form (2) using the Carnahan–Starling approximation [17] for a system of hard spheres:

$$z_{\mathrm{RS}}(x) = (1+x+x^2-x^3)/(1-x)^3. \tag{7}$$

Equation (7) lacks the deficiencies of the Percus–Yevick approximation mentioned above, is quite simple, and accurately describes the results of the molecular-dynamics calculations for a system of hard spheres.

The radial distribution function $g_{\mathrm{RS}}(L, x)$ corresponding to the approximation (7) was calculated using the method suggested in [18]:

$$g_{\mathrm{RS}}(L, x) = g_{\mathrm{PY}}(L_w, x_w) + g_1(L, x_w), \tag{8}$$

where $g_{\mathrm{PY}}(L_w, x_w)$ is the Percus–Yevick radial distribution function, calculated in the usual way [19]:

$$x_w = x(1-0{,}0625x), \quad L_w = L/(1-0{,}0625x)^{1/3},$$

$$g_1(L, x_w) = [f(x_w)/L] \exp\{-24f(x_w)(L-1)/[x_w\varphi(x_w)]\} \cos\{24f(x_w)(L-1)/[x_w\varphi(x_w)]\}, \tag{9}$$

where

$$f(x_w) = 0{,}75x_w^2(1-0{,}7117x_w-0{,}114x_w^2)/(1-x_w)^4,$$

$$\varphi(x_w) = (1+0{,}5x_w)/(1-x_w)^2.$$

The integral $G_1(\lambda, x)$ for the Carnahan–Starling approximation was evaluated numerically using the method described in [12] in the interval of reduced densities $0.025 \le \rho\sigma^3 \le 1.100$ with the granularity $\Delta(\rho\sigma^3) = 0.025$ and for $\lambda = 2.0$.

The resulting values $\{G_{1\lambda}(x)_i\}$ were approximated with the help of the program ORFU [20] which provides a statistically optimum choice of regression functions from a given set of functions. The result has the form

TABLE 2. Coefficients of (10) for $\lambda = 2.0$

i	n_i	a_i	i	n_i	a_i
1	1	$-4{,}297094 \cdot 10^{-4}$	8	8	$1{,}153326 \cdot 10^{4}$
2	2	$-2{,}162878 \cdot 10^{0}$	9	13	$-6{,}835093 \cdot 10^{4}$
3	3	$1{,}797249 \cdot 10^{1}$	10	16	$9{,}364344 \cdot 10^{5}$
4	4	$6{,}397568 \cdot 10^{1}$	11	18	$-6{,}060627 \cdot 10^{6}$
5	5	$-1{,}129693 \cdot 10^{3}$	12	19	$9{,}529928 \cdot 10^{6}$
6	6	$5{,}454744 \cdot 10^{3}$	13	20	$-4{,}457087 \cdot 10^{6}$
7	7	$-1{,}247009 \cdot 10^{4}$			

$$G_{1\lambda}(x) = \sum_{i=1}^{m} a_i x^{n_i}, \qquad (10)$$

where $n_i > 0$. The coefficients $\{a_i\}$ and $\{n_i\}$ are given in Table 2. The mean square error in the approximation was ≅0.032%. Substituting (7) for $z_{RS}(x)$ and (10) for G_1 into (3), and performing some simple reductions, we obtain an analytical equation of state in the form (2) for the reference system in the Carnahan–Starling approximation.

Explicit expressions for the quantities appearing in (3) are:

$$D_1 = (1-x)^4[(1+2x)^2 - 4x^3 + x^4],$$
$$D_2 = 4(1-x)^3(2+5x-x^2)/[(1+2x)^2 - 4x^3 + x^4]^2, \qquad (11)$$
$$D_2' = -4(1-x)^2\varphi_1(x)/[(1+2x)^2 - 4x^3 + x^4]^3,$$
$$\varphi_1(x) = 17 + 82x + 39x^2 - 80x^3 + 77x^4 - 30x^5 + 3x^6;$$
$$\Delta z_1 = 12xB_1, \quad \Delta z_2^{MC} = 6x(D_1B_1 - xD_2B_0);$$
$$\Delta z_2^{LC} = 6x(D_1B_2 - xD_2B_1), \qquad (12)$$

$$B_0 = \sum_{i=1}^{m} a_i x^{n_i}, \quad B_1 = \sum_{i=1}^{m} (n_i + 1) a_i x^{n_i}, \quad B_2 = \sum_{i=1}^{m} (n_i + 1)^2 a_i x^{n_i}.$$

Calculations show that the functions of (3) with the corrections (12) accurately (to within 0.1% in z_1 and 1% in z_2) reproduce the corresponding quantities obtained in thermodynamic perturbation theory (with the help of a numerical integration of the radial distribution function $g_{RS}(L, x)$) in the region of reduced densities $0 \leq \rho\sigma^3 \leq 1.0$. These results show that the analytical equation of state can be used up to densities close to the density of the liquid–solid phase transition, provided that $(\varepsilon/kT) \ll 1$.

The equation of state contains three potential parameters, two of which appear in expression (6) for $\sigma(T)$. For convenience in practical calculations we write (6) in the form

$$\sigma(T) = C - q \ln T, \qquad (13)$$

where $C = \delta \ln(\alpha\gamma/k)$, $q = \delta$. The third parameter is ε/k, the depth of the potential well. The parameters C, q, and ε/k must be determined from the experimental data for nitrogen. This was done using the P–v–T data of [1, 4] as the most reliable and self-consistent. A total of 204 points were chosen in the temperature and density intervals T = 298.15-673.15 °K and $\rho/\rho_c = 0.8\text{-}3.5$.

The equation of state (2) is obviously nonlinear in the parameters C and q and linear in ε/k. Therefore the program FUMILI [21] was used to determine these parameters. The program uses a nonlinear normal regression scheme to estimate the parameters. The results are: $C = 4.47 \pm 0.03$ Å, $q = 0.178 \pm 0.005$ Å/K, $\varepsilon/k = 49.4 \pm 0.4$ K. The errors of the parameters were determined for a significance level of 0.05.

With the help of well-known thermodynamic relations, the equation of state (2) was used to obtain analytical expressions (in the form of functions of T and ρ) for the following quantities: the enthalpy, entropy, heat capacities at constant volume and pressure, speed of sound, adiabatic Joule–Thomson coefficient, coefficient of volume expansion, thermal pressure coefficient, the adiabatic index, and the fugacity. In addition, analytical

TABLE 3. Deviations Between the Densities Calculated from the Equation of State (2) and the Experimental data of [1]

P, MPa	$\delta\rho$, %		
	T=323,15 K	T=373,15 K	T=423,15 K
50	+0,39	+0,92	+1,13
100	—1,17	—0,54	—0,04
150	—1,18	—0,78	—0,39
200	—0,86	—0,65	—0,37
250	—	—0,39	—0,21
300	—	—	+0,03

TABLE 4. Deviations Between the Densities Calculated from the Equation of State (2) and the Experimental Data of [4]

P, MPa	$\delta\rho$, %				
	T=308,15 K	T=373,15 K	T=473,15 K	T=573,15 K	T=673,15 K
150	—1,27	—	—	—	—
200	—0,89	—0,79	—0,54	—	—
250	—0,49	—0,55	—0,35	—0,17	—0,09
400	+0,35	+0,06	+0,02	0,00	+0,11
600	+0,66	+0,38	+0,19	+0,08	—0,02
800	+0,45	+0,30	+0,11	—0,03	—0,16
1000	+0,01	+0,00	—0,15	—0,22	—0,40

expressions were found for the derivatives of all of these functions with respect to the parameters C, q, and ε/k. These derivatives can be used, along with the covariance matrix, to calculate the errors in all of these quantities at any point on the thermodynamic surface. The expressions obtained in this way were used to calculate the thermodynamic properties of nitrogen and the corresponding errors on a computer. For input values of T and P, the value of ρ was calculated by solving (2) using Newton's method. The values of the ideal gas functions were calculated using the expressions of [22].

The thermodynamic properties of nitrogen were calculated in the temprature interval T = 300-2000°K and pressure interval P = 100-1200 MPa, and were computed with the data of other authors. Tables 3 and 4 present the deviations between the calculated values of the density ρ^c and the experimental values ρ^e [1, 4]:

$$\delta\rho = [(\rho^c - \rho^e)/\rho^e] \cdot 100, \ \%.$$

Comparing Tables 3 and 4 and Fig. 1, it is evident that δρ does not exceed the maximum of the deviations between the experimental data of different authors.

Figures 2 through 4 show the relative deviations between the values of certain thermodynamic quantities calculated using our equation of state (f^{es}) and the data of other authors (f):

$$\delta f = [(f^{es} - f)/f] \cdot 100, \ \%.$$

Values of δf are given in the temperature interval T = 300 to 1800°k for three pressures: P = 200, 600, and 1000 MPa.

We see from Fig. 2 that the deviations in the density between our values and the data of other authors (for the intervals of the parameters studied experimentally) are normally less than the total errors in the experimental data (see Fig. 1). The deviations between the calculated values of the heat capacity at constant pressure and the data of other authors (Fig. 3) normally do not exceed 5%, and this is consistent with the author's estimates of error in [11]. An exception is the data of [9] on the isotherms 300 and 400°K, which apparently are not very accurate. As seen from Fig. 4, the calculated values of the speed of sound are too low on average by 1.5% both in the experimental and calculated regions of the parameters. The cause of these systematic deviations is difficult to explain without additional experimental information.

Therefore the theoretical equation of state obtained here for the dense fluid state can be used not only to compute the thermodynamic functions of nitrogen and to determine confidence intervals for their errors, but can also be used to test the extrapolation possibilities of the empirical equations of state. Hence it would be of interest to extend this method of calculating thermodynamic properties to other pure materials with nearly spherically symmetric molecules in the temperature region from the Boyle temperature to the thermal dissociation temperature, and in the density interval from ρ_c to $4\text{-}5\rho_c$.

NOTATION

N, number of paticles in the system; V, volume; U(r), total pair interaction potential; $\varphi_{RS}(r)$, interaction potential for the reference system; $\Phi(r)$, perturbing potential; P, pressure; T, temperature; ρ, density; k, Boltzmann constant; z, compressibility factor; σ, effective hard sphere diameter; R width of the potential well; ε, depth of the potential well; g_{RS}, radial distribution function for the reference system; c_p, heat capacity at constant pressure; w, speed of sound.

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