EQUATION OF STATE FOR LIQUID NITROGEN

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An equation of state has been found for nitrogen that satisfies the p, v, T data in the temperature interval 63.15–140° K at reduced densities ω = 1.8–3 (and pressures up to 700 bar).

Existing tables of the thermodynamic properties of nitrogen, even the most recent [1–3], do not contain sufficiently complete information about the properties of the liquid phase, although this information is valuable in a number of branches of technology. The available equations of state of nitrogen [2, 4–7], valid over a broad region of temperatures and pressures, and the equations of state of liquid nitrogen [8, 9] do not describe with experimental accuracy the p, v, T data for the liquid, including the saturation and solidification curves. This has made necessary the construction of an equation of state suitable for calculating the thermal and caloric properties of liquid nitrogen.

The equation of state was constructed on the basis of reference p, v, T data obtained as a result of the analysis and correlation of experimental data on the density of liquid nitrogen [4, 8, 10, 11]. The data were correlated with respect to isotherms and isobars, since the isobars of the liquid in ρ, T coordinates have a small curvature over a broad interval of variation of the parameters (except for the near-critical region).

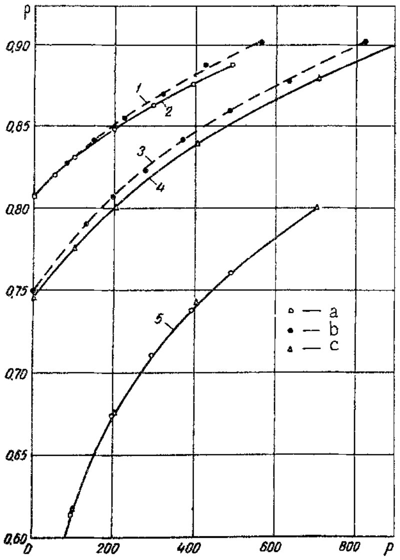

Fig. 1. Isotherms of liquid nitrogen from the experimental data of different authors: a) Golubev and Dobrovol'skii [11], b) Van Itterbeek and Verbeke [10], and c) Benedict [4]; 1) for 77.31° K; 2) 77.35; 3) 90.26; 4) 90.15; 5) 123.15; ρ in kg/dm^3; p in bar.

The most detailed experimental data on the density of liquid nitrogen are those obtained by Golubev and Dobrovol'skii [11] for the pressure interval 49.4–485 atm and the temperature interval −195.8° to −140° C.

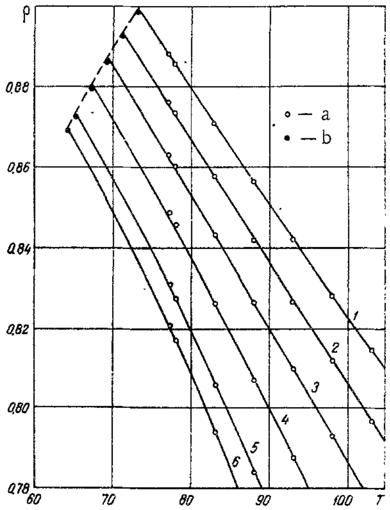

Fig. 2. Isobars of liquid nitrogen close to solidification curve: a) data of Golubev and Dobrovol'skii [11], b) Grilly and Mills [14]; 1) for 491.4 bar 2) 393.1; 3) 295.3; 4) 197.2; 5) 99.1; 6) 50.1; ρ in kg/dm^3; T in ° K.

The previously published data of Benedict [4] for the −150° C and −183° C isotherms, embracing the pressure range 700–1250 atm, agree with the values given in [11] correct to 0.1–0.2%. The experimental results of Van Itterbeek and Verbeke in the temperature interval 65.85–90.60° K at pressures up to 150 kgf/cm^2 [8] and on the 77.31° K and 90.26° K isotherms up to 574 kgf/cm^2 and 842 kgf/cm^2 [10] are for the most part too high (up to 0.7–1.3% at high pressures, Fig. 1). In [11] the hydrostatic weighing method was employed, and in [8, 10] the less reliable method of determining the dependence of the derivatives $(\partial\rho/\partial p)_T$ on pressure and then calculating the density by integration. Therefore the results of Golubev and Dobrovol'skii [11] and Benedict [4] were taken as standards for most isotherms. In the temperature interval 125°–135° K to obtain a smooth correlation with the data on gaseous nitrogen [3] the isobars were drawn between the points of [3, 11], fitted to within 0.1–0.2%. Correlation with the saturation and solidification curves had an important influence on the choice of reference data below 85° K. In this connection it is desirable to examine our data briefly for the above-mentioned curves.

As reference data for the saturation curve of nitrogen we took mainly the data of [12], which generalize a large amount of accumulated experimental material.

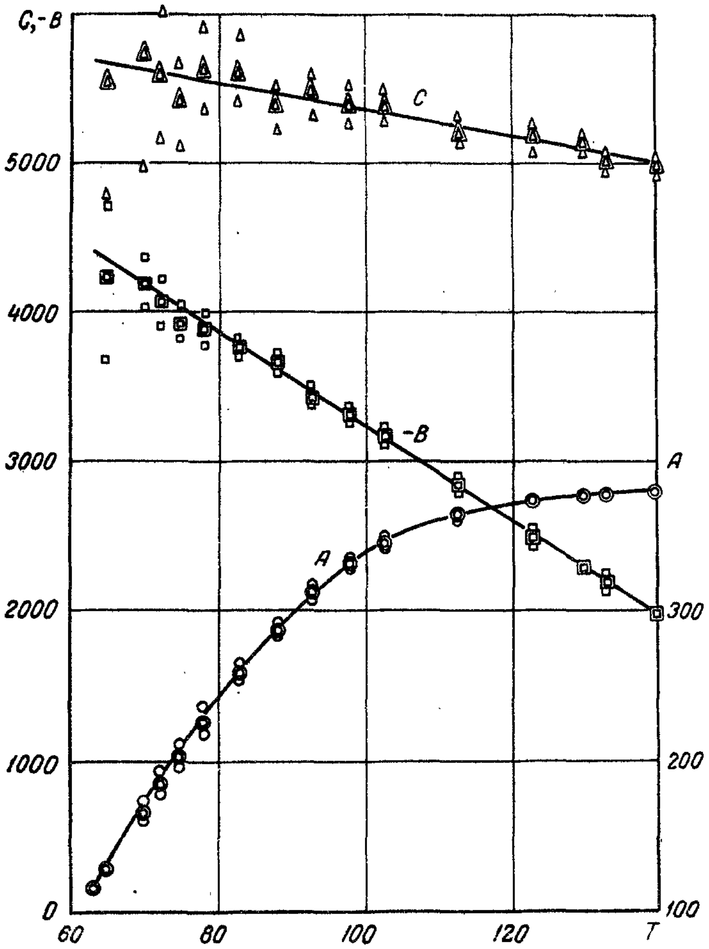

Fig. 3. Temperature functions A(T), B(T) and C(T) of the equation of state for liquid nitrogen.

In the interval 63.15°–74° K the densities of the boiling liquid were corrected slightly to fit the value at the triple point determined from the results of [14]. For the solidification curve we used the reliable data obtained by Mills and Grilly [13, 14]. In [13] these authors investigated the dependence of solidification pressure on temperature in the interval 3.5–3600 kgf/cm^2, and in [14] determined the specific volumes on the solidification curve at pressures of 79–3556 kgf/cm^2; in both studies the experimental data were described analytically with experimental accuracy.

Upon extrapolating the isobars constructed on the basis of the data of [11] to solidification temperatures we obtain values of the density exceeding the values of [14] by 0.2–0.6%. In order to fit the solidification curve, at temperatures below 85° K the isobars were drawn between the points of [11] and [14], so that the deviations did not exceed 0.1–0.3% (Fig. 2). As a result we obtained a reference network of isotherms and isobars embracing the temperature interval 63.15°–140° K at pressures up to 700 bar.

In order to describe the thermodynamic properties of liquid nitrogen we used an equation of state in the form

$$p = A(T)\rho^{n} + B(T)\rho^{n+2} + C(T)\rho^{n+4}. \tag{1}$$

A check showed that for this limited number of terms the experimental data on most of the isotherms are well satisfied when n is taken equal to unity.

The temperature functions of the equation of state (1) were determined by linearization of the isotherms. From the reference data on the isotherms we calculated the complexes*

$$Y_1 = \left(\frac{p}{\rho} - \frac{p_s}{\rho_s}\right)\frac{1}{\rho^2 - \rho_s^2} = B + C(\rho^2 + \rho_s^2), \tag{2}$$

the construction of which as a function of $\rho^2 + \rho_s^2$ made it possible to determine the values of C. After smoothing and analytical representation of the function C(T) the new complexes

$$Y_2 = \frac{p - C\rho^5}{\rho} = A + B\rho^2 \tag{3}$$

were formed. By constructing Y_2 as a function of ρ^2 on the isotherms we found values of the function B(T), which was also smoothed and described analytically. Then from all the reference data we determined the function A(T).

In Fig. 3 the single symbols relate to the limiting, and the double symbols to the optimal values of the functions giving best satisfaction of the reference data. In order to obtain good correlation between the theoretical values of the thermodynamic properties of the liquid and the data for the gas at high densities the temperature functions were determined up to 140° K. Within the assumed limits the functions C(T) and B(T) are linear and are described by the expressions

$$C(T) = 6237.03 - 8.826T, \tag{4}$$

$$B(T) = -6405.70 + 31.675T. \tag{5}$$

The function A(T) has a more complicated configuration and is approximated by the polynomial

$$A(T) = 377.556 - 1.22038\theta^2 - 0.098336\theta^4 + 0.0007383\theta^6, \tag{6}$$

where $\theta = 0.1(T - 140)$.

Substitution of expressions (4)–(6) in Eq. (1) with n = 1 leads to an equation of state for liquid nitrogen in which the pressure is measured in bar, density in kg/dm^3, and temperature in ° K.

Equation of state (1) closely describes the thermal properties of nitrogen in the temperature interval 63.15°–140° K and the reduced density interval $\omega = 1.8$–3.1 (up to 700 bar). A comparison of the calculated density values and the reference values, including data on the supercritical isotherms at high densities, showed that for 192 points out of 235 the deviations do not exceed 0.1% and only at two points reach 0.22 and 0.33%; the mean square deviation is 0.08%.

The overwhelming majority of the experimental data of Golubev and Dobrovol'skii [11] in the temperature interval 88.15–133.15° K are satisfied by the equation of state within the limits of experimental error ±0.1% (Table 1). In the interval 77.35–83.15° K the calculated density values are lower than the experimental values of [11] by 0.1–0.3%, which is a consequence of the choice of reference data (Fig. 2).

The density values calculated from the equation of state on the isotherms 90.15° K and 123.15° K at pressures up to 700 bar are in agreement with the experimental data of Benedict [4] correct to ±0.1%. There are deviations from the data of Van Itterbeek and Verbeke that have the same magnitude and sign as the deviations of the data of [8, 10] from the reliable results of [4, 11].

It is of interest to compare the experimental density values on the saturation and solidification curves with the calculated values obtained using the equation of state and also the equations of the vapor pressure [12] and fusion [13] curves.

It is clear from Table 2 that the equation of state describes with high accuracy the saturation curve at temperatures up to 103.15° K, and only at higher temperatures does the discrepancy exceed the error of the reference data [12]. On the solidification curve the calculated values are somewhat higher than the experimental data of [14] (Table 3), but the deviations lie within the limits of experimental error (0.2%). We note that in constructing the network of reference data we admitted a systematic deviation from the points of [14], since satisfying them more closely would have led to a greater deviation from the data of [11] at low temperatures.

In order to check the possibility of using the proposed equations of state for determining the caloric properties, on the basis of the thermodynamic relations we obtained expressions for calculating the entropy and enthalpy of liquid nitrogen:

$$s = s' - 0.1 \times \left[A' \ln\frac{\rho}{\rho_s} + \frac{B'}{2}(\rho^2 - \rho_s^2) + \frac{C'}{4}(\rho^4 - \rho_s^4)\right], \tag{7}$$

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*Here and in what follows the subscript s denotes the density and pressure in the saturation state.

Table 1

Comparison of Calculated Values of the Density of Nitrogen ρ (kg/dm^3) and the Experimental Data of [11]

p, bar	78.15° K		83.15° K		88.15° K	
	ρ_{exp}	ρ	ρ_{exp}	ρ	ρ_{exp}	ρ
50.05	0.8168	0.8144	0.7935	0.7928	0.7700	0.7700
99.10	0.8272	0.8245	0.8052	0.8044	0.7837	0.7833
197.2	0.8456	0.8426	0.8262	0.8244	0.8066	0.8061
295.3	0.8602	0.8584	0.8432	0.8418	0.8262	0.8251
393.1	0.8738	0.8725	0.8578	0.8570	0.8418	0.8416
491.4	0.8858	0.8850	0.8710	0.8706	0.8565	0.8562
$\delta\rho_{av}$, %	0.25		0.13		0.06	
$\delta\rho_{max}$, %	0.34		0.22		0.13	

p, bar	93.15° K		98.15° K		103.15° K	
	ρ_{exp}	ρ	ρ_{exp}	ρ	ρ_{exp}	ρ
50.05	0.7460	0.7464	0.7215	0.7215	0.6955	0.6952
99.10	0.7613	0.7617	0.7392	0.7393	0.7163	0.7163
197.2	0.7872	0.7875	0.7680	0.7684	0.7488	0.7495
295.3	0.8094	0.8084	0.7925	0.7915	0.7758	0.7749
393.1	0.8265	0.8263	0.8116	0.8111	0.7964	0.7957
491.4	0.8420	0.8420	0.8281	0.8279	0.8143	0.8140
$\delta\rho_{av}$, %	0.06		0.06		0.08	
$\delta\rho_{max}$, %	0.12		0.13		0.12	

p, bar	113.15° K		123.15° K		133.15° K	
	ρ_{exp}	ρ	ρ_{exp}	ρ	ρ_{exp}	ρ
50.05	0.6352	0.6350	0.5552	0.5546		
99.10	0.6683	0.6683	0.6139	0.6140	0.5528	0.5514
197.2	0.7107	0.7109	0.6728	0.6724	0.6322	0.6325
295.3	0.7422	0.7419	0.7092	0.7092	0.6757	0.6765
393.1	0.7670	0.7663	0.7370	0.7373	0.7086	0.7087
491.4	0.7868	0.7868	0.7600	0.7603	0.7338	0.7338
$\delta\rho_{av}$, %	0.04		0.06		0.12	
$\delta\rho_{max}$, %	0.09		0.11		0.25	

Table 2

Comparison of Calculated Values of the Density of Liquid Nitrogen on the Saturation Curve and Reference Values

T, °K	p, bar	ρ_{exp}, kg/dm^3	ρ, kg/dm^3	$\delta\rho$, %	T, °K	p, bar	ρ_{exp}, kg/dm^3	ρ, kg/dm^3	$\delta\rho$, %
63.15	0.1253	0.8653	0.8653	0	93.15	4.672	0.7294	0.7297	—0.04
70	0.3859	0.8390	0.8384	0.07	98.15	6.823	0.7016	0.7020	—0.06
78.15	1.113	0.8038	0.8031	0.09	100	7.775	0.6906	0.6913	—0.10
80	1.369	0.7959	0.7947	0.15	103.15	9.616	0.6707	0.6721	—0.21
83.15	1.907	0.7806	0.7799	0.09	110	14.67	0.6227	0.6263	—0.58
88.15	3.064	0.7557	0.7555	0.03	113.15	17.54	0.5966	0.6018	—0.87
90	3.600	0.7463	0.7461	0.03	120	25.15	0.5242	0.5285	—0.82

Table 3

Comparison of Calculated Values of the Density of Nitrogen on the Solidification Curve and the Experimental Data of [14]

p, bar	T, °K	ρ_{exp}, kg/dm^3	ρ, kg/dm^3	$\delta\rho$, %	p, bar	T, °K	ρ_{exp}, kg/dm^3	ρ, kg/dm^3	$\delta\rho$, %
19.61	63.57	0.8668*	0.8669	—0.01	294.2	69.38	0.8864	0.8868	—0.05
58.84	64.43	0.8698*	0.8699	—0.01	343.2	70.38	0.8897	0.8900	—0.03
98.07	65.28	0.8715	0.8730	—0.17	392.3	71.35	0.8930	0.8931	—0.01
137.3	66.12	0.8746	0.8759	—0.15	441.3	72.32	0.8960	0.8962	—0.02
166.7	66.74	0.8769	0.8781	—0.14	490.3	73.29	0.8990	0.8991	—0.01
196.1	67.36	0.8792	0.8801	—0.10	588.4	75.18	0.9046	0.9051	—0.06
245.2	68.37	0.8828	0.8837	—0.10	686.5	77.04	0.9099	0.9107	—0.09

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*Value calculated from the equation given in [14].

Table 4

Comparison of Enthalpy and Entropy Differences Calculated from the Data of Stobridge [2], Din [1], and Equation of State (1)

T, °K	$\Delta i_{206.8}$, kJ/kg		δ, kJ/kg	$\Delta i_{202.6}$, kJ/kg		δ, kJ/kg
	[2]	(1)		[1]	(1)	
70	16.6	16.8	—0.2			
80	15.1	15.1	0			
90	13.1	13.0	0.1	11.2	12.7	—1.5
100	9.8	9.9	—0.1	8.6	9.6	—1.0
110	4.2	4.8	—0.6	1.9	4.6	—2.7
120	—7.1	—6.9	—0.2	—13.5	—7.1	—6.4

T, °K	$\Delta s_{206.8}$, kJ/kg·deg		δ, kJ/kg·deg	$\Delta s_{202.6}$, kJ/kg·deg		δ, kJ/kg·deg
	[2]	(1)		[1]	(1)	
70	—0.107	—0.105	—0.002			
80	—0.125	—0.124	—0.001			
90	—0.146	—0.147	0.001	—0.144	—0.144	0
100	—0.174	—0.173	—0.001	—0.166	—0.171	0.005
110	—0.217	—0.212	—0.005	—0.222	—0.209	—0.013
120	—0.299	—0.296	—0.003	—0.348	—0.293	—0.055

$$i = i' + 0.1\left[(A - TA')\ln\frac{\rho}{\rho_s} + \frac{1}{2}(3B - TB')\times\right.$$
$$\left.\times(\rho^2 - \rho_s^2) + \frac{1}{4}(5C - TC')(\rho^4 - \rho_s^4)\right]. \qquad (8)$$

Calculations based on Eqs. (7) and (8) do not present difficulties, since the values of s' and i' were previously determined in [3].

The calculated values of the caloric properties of liquid nitrogen have been compared with literature data; in view of the differences in reference points we compared the quantities $\Delta i = i - i'$ and $\Delta s = s - s'$ on the isotherms. The broadest range of pressures is covered by Din's tables [1], which contain only five liquid isotherms. On the 90° K, 100° K, and 110° K isotherms at a pressure of 700 atm the discrepancies with respect to Δi do not exceed 3 kJ/kg, and the discrepancies with respect to Δs, 0.02 kJ/kg · deg. At temperatures of 120 and 125° K, close to the critical temperature, the deviations roughly double. More detailed than the tables given in [1] are those of Stobridge [2] which cover the temperature interval 63.3°–300° K, but in this case the maximum pressure is only 3000 psia (206.8 bar). For this pressure the values of Δi and Δs according to the data of [2] and Eq. (1) are in good agreement (Table 4). The same table gives the results of a comparison with the data of [1] at 202.6 bar. The agreement with the latter is not so good, which is evidently attributable to shortcomings of the method used to compile the tables in [1].

Mage and coworkers [15] have also published a table of the enthalpy of nitrogen in the temperature range 77.37°–283.15° K at pressures from 1.013 to 206.8 bar obtained on the basis of experimental data on the specific heat c_p [15] and the adiabatic throttle effect [16]. The values of Δi for liquid nitrogen at 206.8 bar obtained from equation of state (1) and the data of [15] coincide to within 1–3 kJ/kg, the greatest deviations being observed on the near-critical isotherms.

The results presented in Tables 1–4 indicate the reliability of the equation of state obtained, which can be recommended for calculating detailed tables of the thermodynamic properties of liquid nitrogen.

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16 August 1966

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