THE EQUATION OF STATE AND THERMODYNAMIC PROPERTIES OF MOLECULAR NITROGEN

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An equation of state has been obtained for nitrogen in the pressure range (1-1,000) · 10^5 n/m^2 for temperatures up to 1,000°K. This equation shows good agreement with the experimental data. A detailed table of thermodynamic properties of nitrogen, based on the new equation, is presented.

Nitrogen is now being used more and more in the power, refrigeration, and chemical industries as a heat-transfer agent or working fluid, both in the pure state and as a component of gas mixtures.

There is accordingly an urgent need for data on the thermodynamic properties of nitrogen over a wide range of temperatures and pressures. This paper presents an equation of state for molecular nitrogen, based on experimental data on compressibility, and gives detailed tables of thermodynamic properties for pressures in the range (1-1,000) · 10^5 newton/m^2 and temperatures up to 1,000°K.

These tables are of practical interest, since the existing tables of [13], although covering a temperature range to 3,000°K, are limited in respect of pressure to 100 · 10^5 newton/m^2, while those of [1] for pressures exceeding 1,000 · · 10^5 newton/m^2 are limited in respect of temperature to 600°K.

The thermal data on gaseous nitrogen in [2-9] cover a range of temperatures t = −150−800°C at pressures up to 3,000 · 10^5 newton/m^2.

Analysis of the data cited indicates that, for the most part, they are in mutual agreement correct to 0.3%, except for the data of [3] which diverge from the data of the other authors by 0.5% on the average. The data on the compressibility of nitrogen [4] at the isochores (Amagat units) d_A = 80, d_A = 200, d_A = 280, d_A = 319.86 show poor agreement with [8] (discrepancy of the order of 1%). Therefore the data of [3] and [4] cannot be considered reliable. The foregoing analysis and the measure of agreement between the data allow a choice of the most reliable data to be made and a table of reference points to be constructed on which an equation of state for nitrogen can be based.

A method of formulating an equation of state in terms of elementary functions has been developed in detail in [10]. The form of the equation of state used in the present paper is that obtained theoretically in [11], namely:

$$\frac{pv}{RT_k} = \alpha_0 + \alpha_1\tau + \beta\psi + \gamma\psi^2 + \delta\psi^3 + \ldots \quad (1)$$

The temperature function ψ was obtained from data on the second virial coefficient, determined by experiments on the compressibility of nitrogen, and takes the form:

$$\psi = \tau^{-0.515} \quad (2)$$

An analysis carried out by the authors has shown that to achieve a reliable description of the thermal properties of nitrogen in the range of parameters under examination it is sufficient to limit the expansion on the right hand side of (1) to five terms, and to represent the elementary volume functions α_0, α_1, β, λ and δ by polynomials of the seventh degree in the reduced density ω.

Following the general method, polynomials were constructed for the five base isotherms (t = −146.96°C; −100; 0; 150; 400) necessary for an analytic representation of the elementary volume functions. The final equation of state has the form:

$$\frac{pv}{RT_k} = \alpha_0 + \alpha_1\tau + \beta\psi + \gamma\psi^2 + \delta\psi^3.$$

$$\alpha_0 = -10{,}292060\omega + 36{,}803085\omega^2 - 35{,}210254\omega^3 - 0{,}908527\omega^4 + 13{,}371784\omega^5 - 1{,}892588\omega^6 - 1{,}0195504\omega^7,$$

$$\alpha_1 = 1 + 0{,}778225\omega - 1{,}113880\omega^2 + 1{,}083803\omega^3 + 0{,}194683\omega^4 - 0{,}386645\omega^5 + 0{,}113358\omega^6 + 0{,}094367\omega^7,$$

$$\beta = 31{,}028822\omega - 121{,}229141\omega^2 + 120{,}595000\omega^3 - 1{,}350716\omega^4 - 45{,}741585\omega^5 + 11{,}075360\omega^6 + 1{,}710686\omega^7,$$

Table 1. Specific Volume of Molecular Nitrogen (cm^3/g)

$p \cdot 10^{-5}$, n/$м^2$	T, °K																	
	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	900	950	1000
1	442,2	592,1	741,3	890,2	1039	1187	1336	1484	1633	1781	1930	2078	2227	2375	2523	2671	2820	2969
10	41,53	57,96	73,61	88,91	104,0	119,0	134,0	149,0	163,9	178,8	193,7	208,6	223,5	238,3	253,2	268,1	283,0	297,9
20	19,29	28,33	36,54	44,41	52,11	59,72	67,27	74,79	82,35	89,78	97,26	104,7	112,2	119,6	127,1	134,6	142,0	149,5
30	11,86	18,48	24,20	29,59	34,81	39,94	45,02	50,07	55,07	60,11	65,12	70,11	75,1	80,09	85,08	90,06	95,04	100,0
40	8,124	13,58	18,05	22,19	26,17	30,06	33,90	37,71	41,48	45,28	49,04	52,81	56,56	60,31	64,06	67,84	71,54	75,29
50	5,865	10,66	14,37	17,75	20,99	24,14	27,23	30,36	33,35	36,38	39,40	42,42	45,43	48,44	51,45	54,45	57,45	60,45
60	4,383	8,733	11,93	14,81	17,54	20,19	22,79	25,36	27,89	30,45	32,98	35,50	38,02	40,53	43,04	45,55	48,05	50,56
70	3,443	7,372	10,19	12,71	15,08	17,37	19,62	21,84	24,03	26,22	28,39	30,56	32,72	34,88	37,04	39,19	41,34	43,49
80	2,898	6,368	8,898	11,14	13,24	15,27	17,24	19,19	21,12	23,04	24,95	26,85	28,75	30,64	32,53	34,42	36,31	38,19
90	2,582	5,602	7,900	9,921	11,81	13,63	15,40	17,14	18,87	20,58	22,27	23,97	25,66	27,35	29,03	30,71	32,39	34,07
100	2,383	5,003	7,108	8,952	10,67	12,32	13,92	15,50	17,06	18,60	20,14	21,67	23,19	24,71	26,23	27,74	29,26	30,77
200	1,778	2,680	3,728	4,705	5,618	6,488	7,328	8,147	8,951	9,745	10,53	11,31	12,09	12,86	13,63	14,39	15,16	15,93
300	1,604	2,123	2,755	3,392	4,005	4,596	5,168	5,726	6,273	6,812	7,344	7,872	8,395	8,916	9,435	9,951	10,46	10,98
400	1,506	1,877	2,319	2,779	3,233	3,676	4,108	4,531	4,946	5,355	5,758	6,158	6,554	6,947	7,339	7,729	8,118	8,506
500	1,438	1,733	2,072	2,429	2,786	3,137	3,483	3,823	4,156	4,486	4,948	5,133	5,452	5,769	6,084	6,397	6,709	7,021
600	—	1,635	1,911	2,202	2,495	2,785	3,072	3,354	3,633	3,909	4,181	4,451	4,719	4,984	5,248	5,510	5,771	6,031
700	—	1,563	1,796	2,042	2,290	2,536	2,781	3,022	3,262	3,498	3,733	3,965	4,195	4,423	4,650	4,876	5,101	5,325
800	—	1,507	1,709	1,922	2,137	2,351	2,564	2,775	2,984	3,191	3,397	3,600	3,803	4,003	4,203	4,401	4,598	4,795
900	—	1,461	1,640	1,828	2,018	2,208	2,395	2,582	2,768	2,952	3,135	3,317	3,497	3,676	3,854	4,031	4,207	4,382
1000	—	1,422	1,584	1,752	1,823	2,092	2,261	2,428	2,595	2,761	2,926	3,089	3,252	3,414	3,575	3,735	3,893	4,053

Translator's note: commas represent decimal points

Table 2. Enthalpy of Molecular Nitrogen (kj/kg)

$p \cdot 10^{-5}$, П/м²	T, °K																	
	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	900	950	1000
1	399,6	452,0	504,2	556,3	608,8	660,6	713,0	765,7	818,8	872,1	986,3	981,0	1036,2	1092,0	1148,5	1205,5	1263,1	1321,2
10	391,1	446,7	500,9	554,3	607,5	659,8	712,5	765,4	818,6	872,2	926,5	981,1	1036,4	1092,3	1148,7	1205,8	1263,5	1321,6
20	381,2	441,0	497,4	552,1	606,1	658,9	712,0	765,1	818,4	872,2	926,5	981,3	1036,6	1092,5	1149,1	1206,2	1263,9	1322,1
30	370,5	435,4	494,0	549,9	604,7	658,0	711,4	764,8	818,2	872,2	926,6	981,5	1036,9	1092,8	1149,4	1206,6	1264,3	1322,5
40	358,6	429,9	490,7	547,8	603,3	657,2	710,9	764,5	818,1	872,2	926,7	981,7	1037,2	1093,2	1149,8	1207,0	1264,8	1323,0
50	345,3	424,5	487,5	545,8	602,1	656,3	710,4	764,2	818,0	872,3	926,8	981,9	1037,4	1093,5	1150,2	1207,4	1265,2	1323,5
60	330,5	419,3	484,4	543,8	600,8	655,5	709,9	763,9	817,9	872,3	927,0	982,1	1037,7	1093,8	1150,6	1207,9	1265,7	1324,0
70	316,3	414,2	481,4	541,9	599,4	654,7	709,4	763,7	817,9	872,4	927,1	982,4	1038,0	1094,2	1151,0	1208,3	1266,2	1324,6
80	305,4	409,3	478,6	540,1	598,4	654,0	709,0	763,5	817,9	872,5	927,3	982,6	1038,4	1094,6	1151,4	1208,8	1266,7	1325,1
90	297,8	404,6	475,8	538,3	597,3	653,3	708,6	763,3	817,9	872,6	927,5	982,9	1038,7	1095,0	1151,8	1209,2	1267,2	1325,6
100	292,6	400,1	473,1	536,6	596,2	652,6	708,2	763,1	818,0	872,7	927,7	983,2	1039,0	1095,4	1152,3	1209,7	1267,7	1326,2
200	277,8	371,5	453,5	523,6	587,8	647,6	705,7	762,5	818,7	874,7	930,6	986,8	1043,3	1100,1	1157,4	1215,2	1273,5	1332,2
300	278,5	363,6	444,8	517,3	583,9	645,7	705,5	763,7	821,1	878,0	934,7	991,5	1048,5	1105,7	1163,4	1221,5	1280,0	1339,0
400	282,9	363,7	442,8	515,7	583,4	646,4	707,3	766,6	824,8	882,4	939,7	997,0	1054,5	1112,1	1170,1	1228,5	1287,2	1346,4
500	288,6	367,2	444,7	517,3	585,4	649,1	710,5	770,6	829,4	887,6	945,5	1003,2	1061,0	1119,0	1177,3	1235,9	1294,9	1354,2
600	—	372,5	448,7	521,0	589,3	653,3	715,3	775,6	834,9	893,5	951,8	1009,9	1068,1	1126,3	1184,9	1243,7	1302,9	1362,4
700	—	378,9	454,0	526,0	594,4	658,5	721,0	781,4	841,0	900,0	958,6	1017,0	1075,5	1134,0	1192,8	1251,8	1311,2	1370,8
800	—	385,9	460,3	532,0	600,3	664,6	727,1	787,9	847,7	906,9	965,8	1024,5	1083,2	1141,9	1200,9	1260,2	1319,7	1379,5
900	—	393,3	467,2	538,6	606,9	671,4	734,0	794,9	854,9	914,2	973,3	1032,1	1091,1	1150,0	1209,2	1268,6	1328,4	1388,3
1000	—	401,1	474,6	545,7	614,0	678,6	741,2	802,3	862,4	921,9	981,0	1040,1	1099,1	1158,3	1217,7	1277,3	1337,1	1397,2

Translator's note: commas represent decimal points

Table 3. Entropy of Molecular Nitrogen (kj/kg · degree)

$p \cdot 10^{-5}$, n/м²	T, °K																	
	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	900	950	1000
1	6,1245	6,4255	6,6585	6,8487	7,0093	7,1489	7,2720	7,3830	7,4844	7,5774	7,6640	7,7449	7,8211	7,8931	7,9617	8,0266	8,0890	8,1485
10	5,4023	5,7222	5,9644	6,1589	6,3218	6,4626	6,5866	6,6980	6,7997	6,8929	6,9797	7,0606	7,1369	7,2089	7,2777	7,3426	7,4051	7,4645
20	5,1501	5,4947	5,7469	5,9463	6,1116	6,2538	6,3785	6,4905	6,5927	5,6859	6,7727	6,8539	6,9303	7,0024	3,0712	7,1362	7,1987	7,2582
30	4,9782	5,3530	5,6152	5,8191	5,9868	6,1304	6,2559	6,3683	6,4705	6,5643	6,6514	6,7326	6,8091	6,8813	6,9501	7,0151	7,0775	7,1372
40	4,8339	5,2466	5,5186	5,7270	5,8970	6,0419	6,1682	6,2811	6,3836	6,4776	6,5650	6,6463	6,7228	6,7951	6,8640	6,9291	6,9917	7,0513
50	4,6988	5,1599	5,4415	5,6542	5,8265	5,9726	6,0997	6,2131	6,3161	6,4101	6,4977	6,5792	6,6558	6,7279	6,7969	6,8622	6,9248	6,9844
60	4,5665	5,0854	5,3768	5,5936	5,7681	5,9155	6,0433	6,1573	6,2603	6,3549	6,4425	6,5241	6,6008	6,6732	6,7421	6,8074	6,8701	6,9297
70	4,4462	5,0199	5,3208	5,5416	5,7182	5,8668	5,9952	6,1098	6,2133	6,3079	6,3957	6,4774	6,5542	6,6267	6,6958	6,7609	6,8237	6,8835
80	4,3523	4,9612	5,2713	5,4958	5,6744	5,8242	5,9537	6,0684	6,1723	6,2671	6,3551	6,4369	6,5138	6,5863	6,6555	6,7207	6,7835	6,8432
90	4,2837	4,9078	5,2267	5,4549	5,6355	5,7864	5,9164	6,0318	6,1361	6,2310	6,3191	6,4010	6,4781	6,5507	6,6199	6,6852	6,7479	6,8077
100	4,2322	4,8589	5,1862	5,4179	5,6003	5,7523	5,8831	5,9989	6,1035	6,1986	6,2869	6,3689	6,4460	6,5187	6,5876	6,6533	6,7161	6,7760
200	4,0007	4,5405	4,9077	5,1639	5,3604	5,5216	5,6582	5,7780	5,8854	5,9825	6,0723	6,1553	6,2333	6,3066	6,3763	6,4421	6,5052	6,5653
300	3,8938	4,3833	4,7462	5,0109	5,2151	5,3816	5,5223	5,6451	5,7546	5,8534	5,9444	6,0284	6,1070	6,1808	6,2510	6,3171	6,3805	6,4409
400	3,8195	4,2844	4,6378	4,9040	5,1114	5,2813	5,4244	5,5492	5,6604	5,7605	5,8524	5,9372	6,0165	6,0908	6,1614	6,2278	6,2912	6,3520
500	3,7598	4,2120	4,5577	4,8230	5,0318	5,2031	5,3480	5,4743	5,5867	5,6877	5,7805	5,8660	5,9457	6,0205	6,0915	6,1582	6,2221	6,2827
600	—	4,1545	4,4942	4,7583	4,9676	5,1398	5,2856	5,4129	5,5261	5,6279	5,7214	5,8074	5,8876	5,9628	6,0342	6,1010	6,1651	6,2259
700	—	4,1064	4,4416	4,7044	4,9137	5,0866	5,2331	5,3608	5,4748	5,5772	5,6711	5,7576	5,8382	5,9138	5,9853	6,0525	6,1168	6,1773
800	—	4,0649	4,3967	4,6583	4,8678	5,0409	5,1877	5,3160	5,4303	5,5331	5,6274	5,7143	5,7953	5,8711	5,9429	6,0103	6,0748	6,1360
900	—	4,0281	4,3574	4,6179	4,8275	5,0008	5,1480	5,2765	5,3910	5,4942	5,5888	5,6760	5,7573	5,8333	5,9053	5,9730	2,0376	6,0990
1000	—	3,9949	4,3225	4,5820	4,7916	4,9652	5,1125	5,2412	5,3560	5,4593	5,5542	5,6414	5,7231	5,7992	5,8716	5,9395	6,0043	6,0658

Translator's note: commas represent decimal points

$$\gamma = -37{,}597512\omega + 142{,}373383\omega^2 - 142{,}925291\omega^3 - 1{,}152781\omega^4 + 60{,}568071\omega^5 - 18{,}837233\omega^6 - 0{,}439433\omega^7,$$

$$\delta = 14{,}806714\omega - 55{,}587103\omega^2 + 54{,}373002\omega^3 + 6{,}041763\omega^4 - 29{,}859194\omega^5 + 10{,}490170\omega^6 - 0{,}440696\omega^7,$$

$$\psi = \tau^{-0.515}.$$

This equation describes the thermal data for nitrogen in the density range $\omega = 0-2.3$ at temperatures T = 126.2–1000°K.

On the basis of this equation, using known thermodynamic relations, the thermal quantities for nitrogen were calculated. Comparison of the calculated values of the specific heat c_p with the experimental data of [12] and with the data of [1] and [8] shows good agreement, except in the low-temperature region up to 300°K, when discrepancies relative to the data of [1] and [8] reach 10%. These discrepancies are attributable to the fact that in [1] and [8] a method of graphical differentiation was used that is known to be inaccurate in a region of inflections of the isobars.

A comparison with respect to compressibility and c_p gives reason to believe that the above equation of state may serve as a basis for calculating detailed tables of thermodynamic properties of nitrogen in the pressure interval $(1-1000) \cdot 10^5$ newton/m^2 for temperatures up to 1,000°K (Tables 1–3).

The equation was used to calculate density, enthalpy, entropy, specific heats c_p and c_v, coefficient of volume expansion, speed of sound, and adiabatic coefficient.

The following values of the critical parameters were used: $p_k = 33.94 \cdot 10^5$ newton/m^2; $T_k = 126.2$°K; $d_k = 0.311$ g/cm^3.

Values of the enthalpy and entropy in the ideal-gas state were obtained from [13], the zero reference readings being taken as: for enthalpy 244.93 kj/kg, for entropy 0 kj/kg•degree.

All the thermodynamic quantities were calculated on a high-speed electronic computer.

NOTATION

τ – reduced temperature ($\tau = T/T_k$); ω – reduced density ($\omega = d/d_k$); Ψ – monotonically decreasing function of duced temperature τ; α_0, α_1, β, γ, δ – elementary volume functions, polynomials in the reduced density ω.

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