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Calculations of the Thermodynamic Properties of Nitrogen at High Pressures

By

J.L. Wilson and J.D. Regan

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Calculations of the Thermodynamic Properties of Nitrogen at High Pressures

- By -

J. L. Wilson and J. D. Regan

January, 1964

SUMMARY

The thermodynamic properties of nitrogen have been calculated in the range of temperatures from 600°K to 2 000°K and at pressures of up to 1 000 atmospheres. The virial coefficients used are those of Amdur and Mason, and the low pressure internal energy is taken from Hilsenrath et al.

Introduction

Both the N.P.L. hotshot hypersonic wind tunnel and the N.P.L. 2 in. shock tunnel[1] operate at pressures above 100 atmospheres and temperatures above 600°K where the effects of bulk compressibility of nitrogen cannot be ignored but where no tables including real-gas effects are available.

Hilsenrath et al[2] have published tables for nitrogen for pressures up to 100 atmospheres within the range of temperatures of present interest, and Little and Neel[3] give tables for pressures up to 1 000 atmospheres but only extending up to 600°K.

To cover the high temperature range at pressures up to 1 000 atmospheres, calculations of entropy, enthalpy, bulk compressibility and density are presented here as a function of pressure and temperature.

Thermodynamic Equations

The equation of state of a gas can be written in the form

$$PV = ZRT$$

where the bulk compressibility Z is given by:

$$Z = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \dots$$

For/

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For a diatomic molecule the assumption is made that the vibrational energy levels of the molecule are independent of Z, and that the virial coefficients are independent of the vibrational energy of the molecule. This assumption holds over the range of validity of the virial expansion.

The entropy and enthalpy of an undissociated gas[4] are then given by:

$$S = S' + \int_{T'}^{T} \frac{Cp_L}{T}\, dT - R\, \ell n \frac{T}{T'} + \left[\frac{\partial}{\partial T} \int \frac{RZT}{V}\, dV \right]_{V',T'}^{V,\,T}$$

$$H = E' + RT' + \int_{T'}^{T} Cp_L\, dT + R(Z-1) + \left[RT^2 \int \frac{\partial Z}{\partial T} \cdot \frac{dV}{V} \right]_{V',T'}^{V,\,T}$$

where the primes refer to a reference state of the gas, and Cp_L is the specific heat of the gas at low pressures.

Using the virial expansion for Z and neglecting terms higher than the fourth coefficient, we have:

$$\frac{S}{R} = \frac{S'}{R} + \int_{T'}^{T} \frac{Cp_L}{RT}\, dT - \ell n \frac{P}{P'} + \ell n\, Z - \left\{ \frac{B}{V} + \frac{C}{2V^2} + \frac{D}{3V^3} \right\}$$

$$- T \left\{ \frac{1}{V} \frac{dB}{dT} + \frac{1}{2V^2} \frac{dC}{dT} + \frac{1}{3V^3} \frac{dD}{dT} \right\}$$

$$\frac{H}{RT_o} = \frac{E'}{RT_o} + \frac{T'}{T_o} + \frac{1}{T_o} \int_{T'}^{T} \frac{Cp_L}{R}\, dT + (Z-1) \frac{T}{T_o}$$

$$- \frac{T^2}{T_o} \left\{ \frac{1}{V} \frac{dB}{dT} + \frac{1}{2V^2} \frac{dC}{dT} + \frac{1}{3V^3} \frac{dD}{dT} \right\}$$

where it is now assumed that the primed reference state is at a low pressure so that in this state $Z = 1$ and dZ/dT can be neglected. $T_o = 273{\cdot}16°K$.

We may put $$\frac{S_L}{R} = \frac{S'}{R} + \int_{T'}^{T} \frac{Cp_L}{RT}\, dT$$

and $$\frac{H_L}{RT_o} = \frac{E'}{RT_o} + \frac{T'}{T_o} + \frac{1}{T_o} \int_{T'}^{T} \frac{Cp_L}{R}\, dT$$

where/

where now S_L/R and H_L/RT_o are the values of entropy and enthalpy at low pressures and in these calculations have been taken from Hilsenrath et al.

Virial Coefficients

The virial coefficients chosen are those of Amdur and Mason[5]. These are calculated from an intermolecular potential function[6] found by Mason and Rice[7] from a fit to experimental data.

This potential function is basically an exponential-six function which at large radii is fitted to the crystal lattice spacing, PVT data and transport properties, all at low and moderate temperatures, and at small radii is fitted to molecular scattering experiments.

For a monatomic gas it is found that a spherically symmetric potential function in this form is an extremely good fit to the experimental data. Nitrogen, a diatomic gas, is not spherically symmetric and this exhibits itself by requiring two potential functions to fit the experimental data: one for the transport properties, and one for the crystalline and PVT data[7].

In addition, the virial coefficients derived from this potential function by Amdur and Mason are calculated for a spherically symmetric molecule. The lack of spherical symmetry has little effect on the second virial coefficient B, but has an increasing effect on higher coefficients, since the angle of scattering of multiple collisions depends on the shape of the molecule[8].

Hence the higher virial coefficients which are used here, although fitting the available PVT data, are not necessarily correct at high temperatures, but since Z approaches unity in this region it is presumed that this will not introduce appreciable errors.

Below 1 000°K the second virial coefficient is tabulated by Mason and Rice[7], while the third and fourth were found by extrapolation of the data of Amdur and Mason[5].

Calculations

The calculations were carried out using V as independent parameter rather than P, in which the results are presented, since the convergence of the virial expansion in V is much better. $Z = 1 \cdot 5$ was selected as the limit to which calculations should proceed since at greater values of Z the term containing D, which for reasons given in the previous section may be inaccurate, becomes appreciable. Also the higher terms in the virial expansion may not necessarily be neglected.

The values of S_L/R and H_L/RT_o were taken from Hilsenrath et al[2].

The calculated values are presented in Table 1 non-dimensionalised with respect to STP conditions and the appropriate constants to convert them to dimensional form are in Table 2.

Appended/

Appended to this report is a Mollier diagram drawn from this data, the data of Hilsenrath at pressures below 100 atmospheres, and Little and Neel below 600°K. This chart shows the agreement of the three tables and is useful for approximate flow calculations.

Accuracy

No attempt has been made to search for experimental information which might be available in the 600°K to 2 000°K range and which would be relevant to these calculations.

However, the recent work of Saurel[9] shows excellent agreement with Hilsenrath et al in the range of temperatures up to 1 000°K and confirms the values of the virial coefficients chosen.

The agreement with Hilsenrath et al at 100 atmospheres is necessarily good since their data was used in the calculations. The fit to Little and Neel at high pressures is close.

Since these calculations were commenced a report by C. E. Smith[10] has been received, which calculates the properties of nitrogen from 1 000°K upwards in the range of pressures considered here. He takes the internal energy to be that of a set of harmonic oscillators and his agreement with Hilsenrath et al is to within 1% at low pressures. These calculations also agree with those presented here to within about 1%.

The range of temperatures and pressures considered here are well outside those at which dissociation occurs.

At values of Z greater than 1·3, the percentage accuracy of Table 1 is in doubt because of the truncation of the virial expansion at the fourth term, due to a lack of theoretical and experimental values of higher coefficients. As a rough estimate, from an examination of the terms in the virial expansion, an accuracy of 5% is claimed where $Z = 1{\cdot}5$, reducing to 1% where $Z = 1{\cdot}3$.

For Z less than 1·3, an accuracy of better than 1% is not claimed because of the uncertainty in the value of even the second and third coefficients.

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Table 1/

Table 1

Properties of Nitrogen

$\frac{P}{P_o}$	$\frac{\rho}{\rho_o}$	Z	$\frac{H}{RT_o}$	$\frac{S}{R}$
T = 600°K				
100	43·505	1·046	7·737	20·851
200	82·930	1·098	7·764	20·119
300	118·44	1·153	7·810	19·682
400	150·43	1·211	7·871	19·368
500	179·31	1·270	7·943	19·122
600	205·51	1·329	8·024	18·921
700	229·49	1·389	8·111	18·751
800	251·58	1·448	8·203	18·604
900	271·89	1·507	8·299	18·473
1000	290·92	1·565	8·395	18·356
T = 700°K				
100	37·365	1·044	9·111	21·430
200	71·529	1·091	9·164	20·713
300	102·61	1·141	9·232	20·289
400	131·27	1·189	9·305	19·984
500	157·47	1·239	9·388	19·748
600	181·53	1·290	9·478	19·552
700	203·63	1·341	9·575	19·383
800	224·40	1·391	9·672	19·242
900	243·60	1·442	9·773	19·114
1000	261·47	1·492	9·877	19·000
T = 800°K				
100	32·782	1·042	10·502	21·939
200	62·973	1·084	10·573	21·228
300	90·795	1·128	10·652	20·808
400	116·49	1·172	10·740	20·508
500	140·24	1·217	10·833	20·272
600	162·31	1·262	10·931	20·080
700	182·95	1·306	11·032	19·918
800	202·14	1·351	11·137	19·776
900	220·16	1·396	11·244	19·650
1000	237·07	1·440	11·353	19·537
T = 900°K				
100	29·218	1·039	11·917	22·394
200	56·299	1·078	12·001	21·688
300	81·436	1·118	12·092	21·271
400	104·83	1·158	12·187	20·973
500	126·64	1·198	12·288	20·741
600	147·04	1·238	12·392	20·521
700	166·19	1·278	12·499	20·390
800	184·12	1·319	12·609	20·248
900	201·09	1·358	12·720	20·124
1000	217·15	1·398	12·832	20·014

T = 1000°K/

Table 1 contd.

$\frac{P}{P_o}$	$\frac{\rho}{\rho_o}$	Z	$\frac{H}{RT_o}$	$\frac{S}{R}$
T = 1000°K				
100	26·363	1·036	13·357	22·809
200	50·935	1·073	13·451	22·106
300	73·887	1·109	13·551	21·691
400	95·369	1·146	13·654	21·395
500	115·52	1·182	13·761	21·165
600	134·47	1·219	13·871	20·976
700	152·37	1·255	13·982	20·817
800	169·24	1·291	14·088	20·675
900	185·24	1·327	14·211	20·554
1000	200·44	1·363	14·327	20·444
T = 1100°K				
100	24·012	1·034	14·820	23·190
200	46·517	1·068	14·924	22·489
300	67·633	1·102	15·032	22·076
400	87·499	1·135	15·142	21·782
500	106·23	1·169	15·255	21·553
600	123·93	1·202	15·370	21·365
700	140·70	1·235	15·486	21·207
800	156·61	1·269	15·604	21·069
900	171·72	1·302	15·724	20·946
1000	186·14	1·334	15·843	20·837
T = 1200°K				
100	22·066	1·032	16·304	23·542
200	42·822	1·063	16·416	22·843
300	62·394	1·095	16·530	22·432
400	80·887	1·126	16·646	22·140
500	98·390	1·157	16·765	21·912
600	114·99	1·188	16·884	21·725
700	130·81	1·218	17·004	21·568
800	145·86	1·249	17·125	21·431
900	160·21	1·279	17·240	21·308
1000	173·93	1·309	17·371	21·201
T = 1300°K				
100	20·408	1·030	17·806	23·871
200	39·681	1·059	17·924	23·173
300	57·922	1·088	18·044	22·763
400	75·223	1·117	18·165	22·472
500	91·662	1·146	18·287	22·245
600	107·32	1·175	18·411	22·059
700	122·24	1·203	18·535	21·902
800	136·50	1·231	18·660	21·765
900	150·16	1·259	18·785	21·645
1000	163·25	1·287	18·910	21·538

T = 1400°K/

Table 1 contd.

$\frac{P}{P_o}$	$\frac{\rho}{\rho_o}$	Z	$\frac{H}{RT_o}$	$\frac{S}{R}$
T = 1400°K				
100	18·986	1·028	19·323	24·178
200	36·976	1·055	19·447	23·482
300	54·058	1·083	19·571	23·072
400	70·319	1·110	19·697	22·782
500	85·815	1·137	19·823	22·556
600	100·61	1·164	19·950	22·371
700	114·77	1·190	20·077	22·214
800	128·34	1·216	20·204	22·078
900	141·36	1·242	20·332	21·959
1000	153·86	1·268	20·459	21·851
T = 1500°K				
100	17·746	1·026	20·856	24·467
200	34·616	1·052	20·984	23·771
300	50·689	1·078	21·112	23·363
400	66·023	1·103	21·243	23·073
500	80·685	1·129	21·370	22·847
600	94·720	1·154	21·500	22·663
700	108·18	1·178	21·630	22·507
800	121·11	1·203	21·759	22·371
900	133·55	1·227	21·889	22·252
1000	145·52	1·251	22·019	22·145
T = 1600°K				
100	16·661	1·025	22·401	24·739
200	32·545	1·049	22·532	24·044
300	47·715	1·073	22·664	23·636
400	62·230	1·097	22·796	23·347
500	76·144	1·121	22·928	23·122
600	89·495	1·145	23·060	22·938
700	102·32	1·168	23·192	22·782
800	114·68	1·191	23·324	22·647
900	126·58	1·214	23·455	22·528
1000	138·06	1·237	23·587	22·421
T = 1700°K				
100	15·701	1·023	23·957	24·997
200	30·708	1·047	24·091	24·302
300	45·076	1·069	24·226	23·895
400	58·858	1·092	24·360	23·606
500	72·090	1·114	24·495	23·381
600	84·820	1·137	24·629	23·197
700	97·072	1·159	24·764	23·041
800	108·90	1·180	24·897	22·907
900	120·31	1·202	25·031	22·788
1000	131·35	1·223	25·162	22·682

T = 1800°K/

Table 1 contd.

$\frac{P}{P_o}$	$\frac{\rho}{\rho_o}$	Z	$\frac{H}{RT_o}$	$\frac{S}{R}$
		T = 1800°K		
100	14·846	1·022	25·523	25·241
200	29·070	1·044	25·660	24·547
300	42·720	1·066	25·797	24·140
400	55·836	1·087	25·933	23·851
500	68·456	1·108	26·070	23·627
600	80·621	1·129	26·206	23·444
700	92·293	1·151	26·347	23·283
800	103·69	1·171	26·477	23·154
900	114·66	1·191	26·612	23·036
1000	125·26	1·212	26·747	22·930
		T = 1900°K		
100	14·080	1·021	27·097	25·474
200	27·598	1·042	27·237	24·780
300	40·597	1·062	27·376	24·373
400	53·113	1·083	27·514	24·085
500	65·177	1·103	27·652	23·861
600	76·824	1·123	27·790	23·678
700	88·079	1·143	27·927	23·523
800	98·971	1·162	28·064	23·389
900	109·52	1·181	28·200	23·270
1000	119·74	1·201	28·336	23·164
		T = 2000°K		
100	13·390	1·020	28·679	25·696
200	26·269	1·040	28·821	25·002
300	38·647	1·060	28·968	24·595
400	50·641	1·079	29·103	24·307
500	62·201	1·098	29·242	24·084
600	73·374	1·117	29·381	23·901
700	84·192	1·136	29·519	23·746
800	94·666	1·154	29·657	23·612
900	104·83	1·173	29·794	23·494
1000	114·70	1·191	29·931	23·388

Table 2/

Table 2

Values of the Dimensional Constants

P_o = $1{\cdot}01371 \times 10^5$ Newt.m^{-2} (= 1 atmosphere)

ρ_o = $1{\cdot}25046$ Kg.m^{-3} (= 1 amagat)

T_o = $273{\cdot}16$ °K

R = $296{\cdot}774$ joules Kg^{-1} $°K^{-1}$

RT_o = $81{\cdot}0669 \times 10^3$ joules Kg^{-1}

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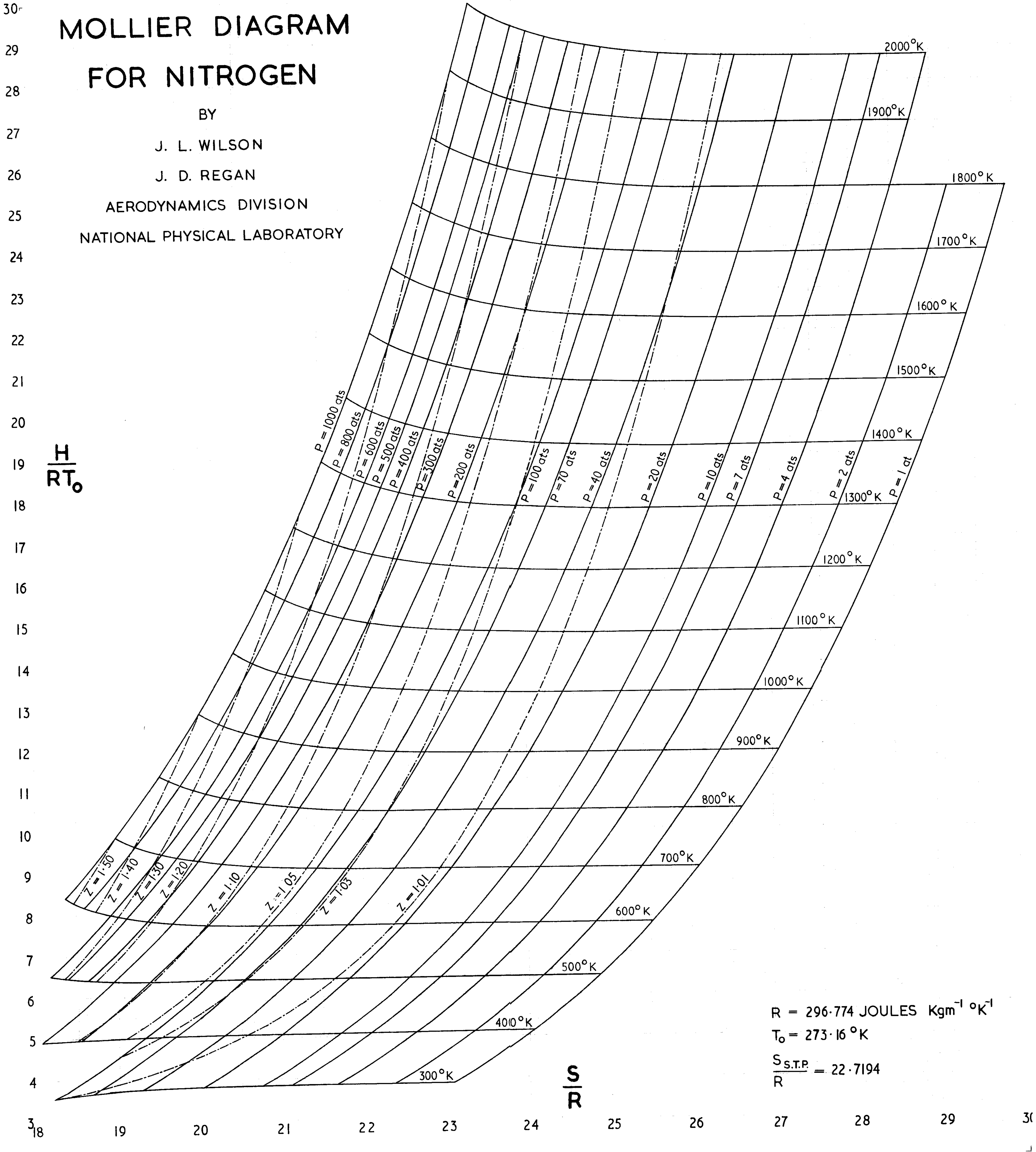
MOLLIER DIAGRAM
FOR NITROGEN

BY

J. L. WILSON
J. D. REGAN
AERODYNAMICS DIVISION
NATIONAL PHYSICAL LABORATORY



$R = 296{\cdot}774$ JOULES $Kgm^{-1}\ {}^{\circ}K^{-1}$

$T_o = 273{\cdot}16\ {}^{\circ}K$

$\frac{S_{S.T.P.}}{R} = 22{\cdot}7194$

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