Vanadium Nitride (VN$_{0.465}$)   **CRYSTAL** M_r = 57.4546 $N_{0.465}V_1$(cr)

$S°(298.15 \text{ K}) = 26.712 \pm 0.042 \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = -130.187 \pm 6.3 \text{ kJ·mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = -132.214 \pm 6.3 \text{ kJ·mol}^{-1}$

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹·mol⁻¹			kJ·mol⁻¹		
0	0.	0.	INFINITE	-4.623	-130.187	-130.187	INFINITE
100	10.647	4.977	47.673	-4.270	-130.995	-127.066	66.373
200	22.457	16.425	29.173	-2.550	-131.786	-122.808	32.074
298.15	28.877	26.712	26.712	0.	-132.214	-118.297	20.725
300	28.971	26.891	26.712	0.054	-132.219	-118.211	20.582
400	32.677	35.771	27.898	3.149	-132.365	-113.513	14.823
500	35.016	43.324	30.247	6.538	-132.318	-108.802	11.367
600	36.815	49.871	32.984	10.132	-132.138	-104.114	9.064
700	38.359	55.664	35.818	13.892	-131.860	-99.454	7.422
800	39.765	60.878	38.630	17.799	-131.508	-94.860	6.194
900	41.095	65.639	41.370	21.842	-131.104	-90.303	5.241
1000	42.376	70.036	44.020	26.016	-130.653	-85.793	4.481
1100	43.627	74.133	45.573	30.316	-130.165	-81.330	3.862
1200	44.852	77.982	49.032	34.740	-129.652	-76.913	3.348
1300	46.066	81.620	51.400	39.286	-129.119	-72.540	2.915
1400	47.262	85.078	53.683	43.953	-128.577	-68.208	2.545
1500	48.455	88.379	55.887	48.739	-128.026	-63.915	2.226
1600	49.643	91.544	58.017	53.644	-127.465	-59.659	1.948
1700	50.823	94.589	60.080	58.667	-126.904	-55.438	1.703
1800	51.999	97.529	62.079	63.810	-126.344	-51.251	1.487
1900	52.928	100.365	64.020	69.055	-125.814	-47.093	1.295
2000	53.974	103.106	65.906	74.401	-125.332	-42.963	1.122
2100	54.936	105.763	67.741	79.846	-124.880	-38.856	0.966
2200	55.940	108.342	69.528	85.390	-147.378	-34.665	0.823
2300	56.902	110.850	71.270	91.032	-147.199	-29.545	0.671
2400	57.907	113.293	72.971	96.774	-146.923	-24.435	0.532
2500	58.743	115.674	74.631	102.606	-146.560	-19.339	0.404
2600	59.622	117.995	76.255	108.524	-146.113	-14.258	0.286
2700	60.584	120.263	77.843	114.534	-145.576	-9.197	0.178
2800	61.505	122.483	79.398	120.639	-144.947	-4.157	0.078
2900	62.425	124.657	80.921	126.836	-144.227	0.859	-0.015
3000	63.304	126.789	82.414	133.123	-143.419	5.848	-0.102
3100	64.141	128.878	83.880	139.494	-142.527	10.809	-0.182
3200	65.019	130.928	85.318	145.952	-141.551	15.740	-0.257
3300	65.898	132.942	86.731	152.498	-140.488	20.639	-0.327
3400	66.777	134.923	88.119	159.132	-139.339	25.505	-0.392
3500	67.655	136.871	89.484	165.854	-138.103	30.336	-0.453

Vanadium Nitride (VN$_{0.465}$) $N_{0.465}V_1$(cr)

Enthalpy of Formation

Pankratz et al.[1] measured the enthalpy of combustion of vanadium subnitride at 303.15 K. The composition of their sample was VN$_{0.465}$ which corresponds to the nitrogen rich boundary of the subnitride phase (see Phase Data section). Chemical analysis also showed that the sample contained 0.74 weight percent VO and trace amounts of CaO and Mo as impurities. The composition of the combustion products fell between V$_2$O$_4$ and V$_2$O$_5$. JANAF data[2] for these two oxides are used to correct their combustion values to correspond to the formation of the pentoxide as the final state. Our values for this correction are roughly 3 cal·K⁻¹·mol⁻¹ subnitride greater than those used by Pankratz et al.[1] Impurity corrections for VO and Mo are also based on JANAF[2] data and amount to 9.03 and 0.37 cal g⁻¹ subnitride, respectively. For the process VN$_{0.465}$(cr) + 1.25 O$_2$(g) = 0.5 V$_2$O$_5$(cr) + 0.2325 N$_2$(g), we obtain $\Delta_f H° = 153.69 \pm 0.75$ kcal·mol⁻¹ at unit fugacities of oxygen and nitrogen. When this value is combined with $\Delta_f H°$(V$_2$O$_5$, cr, 298.15 K)[2], that for vanadium subnitride is $\Delta_f H°$(VN$_{0.465}$, cr, 298.15 K) = -31.6 ± 1.5 kcal·mol⁻¹. We adopt this value and include in the overall uncertainty (±1.5 kcal·mol⁻¹) the error associated with correcting the combustion values to correspond to the pentoxide as the final state. The only other value for $\Delta_f H°$ is derived from dissociation pressure data for VN$_{0.43}$ which were reported by Brauer and Schnell[3] for the temperature range 1655–1879 K (corrected to IPTS 68) JANAF functions for VN$_{0.465}$ are used to analyze these pressures by the 3rd law method. These calculations lead to $\Delta_f H°$ for the subnitride phase of -25.2 ± 1.7 kcal·mol⁻¹. The 2nd law value is $\Delta_f H°$(298.15 K) = -10.7 kcal·mol⁻¹; the 3rd law drift is 8.3 ± 1.1 cal·K⁻¹·mol⁻¹. These results show considerable scatter and are believed to be less reliable than those obtained by combustion calorimetry.

Heat Capacity and Entropy

Pankratz et al.[1] have measured low temperature heat capacities (9 to 307 K) for VN$_{0.465}$ in an adiabatic calorimeter. The composition of the subnitride sample was similar to that employed in their combustion work. Their $C_p°$ data are adopted and used to obtain a value (6.384 cal·K⁻¹·mol⁻¹) for S°(298.15 K). This latter value is based on S°(9 K) = 0.004 cal·K⁻¹·mol⁻¹.

In the same paper, Pankratz et al.[1] reported measurements of the high temperature enthalpies (401–1794 K) for VN$_{0.465}$ which were obtained in a copper-block drop calorimeter. The subnitride sample was the same as that used in their combustion work and was contained in Pt-Rh alloy capsules during the "drop" experiments. Temperature enthalpy measurements were based on the IPTS–68 scale. A technique employing orthogonal polynomials is used to fit their experimental enthalpies by computer. The curve is constrained to join smoothly with the low temperature $C_p°$ data near 298.15 K. The average deviation of the smoothed enthalpies from the experimental values is +0.46%; the maximum deviation is +0.73% at 702 K. $C_p°$ data above 1800 K are obtained by graphical extrapolation. No anomalies are observed in either the low temperature $C_p°$ data or the high temperature enthalpies.

Phase Data

In a review of vanadium binary systems, Rostoker and Yamamoto[4] have questioned the existence of a subnitride phase, since Muthmann et al.[5] were unable to recognize its presence. However, several recent investigations[3,6] have reported the preparation of the subnitride at temperatures in excess of 1300 K. Using x-ray techniques, Brauer and Schnell[3] and Hahn[6] found that the phase had an extensive homogeneity range which extends from about VN$_{0.37}$ to VN$_{0.49}$ (27 to 33 atomic percent nitrogen). Pankratz et al.[1] reported the composition of the nitrogen rich phase boundary as VN$_{0.465}$. These results are in agreement with the earlier x-ray work.[3,6] The structure of vanadium subnitride has been determined to be hexagonal.[6,7] Further information on the vanadium vanadium nitride system has been reviewed by Storms.[9]

Decomposition Data

No information is available on the melting behavior of VN$_{0.465}$ at elevated temperatures. Mass spectrometric evidence[10] has been presented which indicates that vanadium mononitride decomposes to its elements rather than melting. By analogy with VN, we assume the process VN$_{0.465}$(cr) – V(l) + 0.2325 N$_2$(g) to be the mode of decomposition upon heating the solid. T_{dcm} ~ 2875 K is the temperature at which the VN$_{0.465}$(cr) – V(l) + 0.2325 N$_2$(g) to be the mode of decomposition upon heating the solid. T_{dcm} ~ 2875 K is the temperature at which the fugacity for the above process approaches 1 atm. $\Delta_{dcm} H° = 34.3$ kcal·mol⁻¹ is the negative of the enthalpy of formation of VN$_{0.465}$ at T_{dcm}.

References

[1] L. B. Pankratz, J. M. Stuve, H. O. Poppleton, L. L. Oden, and A. D. Mah, U. S. Bur. Mines RI 7585, (1971).
[2] JANAF Thermochemical Tables: V$_2$O$_4$(cr) and VO(cr), 12-31-73; V$_2$O$_5$(cr), 6-30-73; MoO$_3$(cr), 6-30-67.
[3] G. Brauer and W. D Schnell, J. Less Common Metals 6, 326 (1964).
[4] W. Rostoker and A. Yamamoto, Trans. ASM 46, 1136 (1954).
[5] W. Muthmann, L. Weiss, and R. Riedelbauch, Liebigs Ann. Chem. 355, 58 (1907).
[6] H. Hahn, Z. Anorg. Chem. 58, 258 (1949).
[7] D. Potter and R. Geils, Sci. Met. 6, 395 (1972).
[8] E. T. Turkdogan and E. M. Fenn, J. Iron Steel Inst. 181, 343 (1955).
[9] E. K. Storms, Los Alamos Scientific Laboratory, LA 2942, (August, 1964).
[10] M. Farber and R. D. Srivastava, J. Chem. Soc. Faraday Trans. 1, 69, 390 (1973).

Nitrogen (N) $N_1(g)$

Nitrogen (N)   IDEAL GAS $A_r = 14.0067$

$\Delta_f H^\circ(0 \text{ K}) = 470.82 \pm 0.10 \text{ kJ·mol}^{-1}$
$\Delta_f H^\circ(298.15 \text{ K}) = 472.68 \pm 0.10 \text{ kJ·mol}^{-1}$
$S^\circ(298.15 \text{ K}) = 153.300 \pm 0.02 \text{ J·K}^{-1}\text{·mol}^{-1}$

Electronic Levels and Quantum Weights

State	ϵ, cm^{-1}	g_i
$^4S_{3/2}$	0.000	4
$^2D^\circ_{5/2}$	19224.464	6
$^2D^\circ_{3/2}$	19233.177	4
$^2P^\circ_{1/2}$	28838.920	2
$^2P^\circ_{3/2}$	28839.306	4

Enthalpy of Formation

$\Delta_f H^\circ$ is based on the D°_0 value for $N_2(g)$ adopted by the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions.[1] The adopted value for $\Delta_f H^\circ$(N, 298.15, 0 K) is derived using $D^\circ_0(N_2, g) = 78715 \pm 50$ cm^{-1} (225.057 ± 0.143 kcal·mol^{-1}) from Buttenbender and Herzberg,[2] Tanaka, Ogawa, and Jursa,[3] and Telford, Vanderslice, and Wilkinson.[4] This is discussed further by Gaydon[5] and Lofthus and Krupenie.[6]

Heat Capacity and Entropy

The electronic levels for N(g) are given in the compilation by Moore.[7] Our calculations indicate that, except for the five states lying below 29000 cm^{-1}, the inclusion of levels up to $n = 12$ has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the fifth excited state lies at 83284.070 cm^{-1} above the ground state. Since the inclusion of these upper levels has no effect on the thermodynamic function (to 6000 K) we list only the lowest lying states ($\epsilon_i < 29000$ cm^{-1}). The reported uncertainty in S°(298.15 K) is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures.[8]

References

[1]CSU–CODATA Task Group, J. Chem. Thermodynamics 4, 331 (1972).
[2]G. Buttenbender, and G. Herzberg, Ann. Phys. Leipzig [5] 21, 577 (1935).
[3]Y. Tanaka, M. Ogawa, and A. S Jursa, J. Chem. Phys. 40. 3690 (1964).
[4]S. G. Telford, J. T. Vanderslice, and P. G. Wilkinson, Astrophys. J. 142, 1203 91965).
[5]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", 3rd ed., Chapman and Hall Ltd., London, (1968).
[6]A. Lofthus and P. H. Krupenie, J. Phys. Chem. Ref. Data 6, 113 (1977).
[7]C E. Moore, NSRDS–NBS3, Section 5 (1975).
[8]J. R. Downey, AFOSR–TR 78–0960, (March 9, 1978).

Nitrogen (N) $N_1(g)$

T/K	C°_p	S°	$-(G^\circ-H^\circ(T_r))/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log K_f$
0	0.	0.	INFINITE	-6.197	470.820	470.820	INFINITE
100	20.786	130.593	171.780	-4.119	471.448	466.379	-243.611
200	20.786	145.001	155.201	-2.040	472.071	461.070	-120.419
250	20.786	149.639	153.642	-1.001	472.383	458.283	-95.753
298.15	20.786	153.300	153.300	0.	472.683	455.540	-79.809
300	20.786	153.429	153.300	0.038	472.694	455.434	-79.298
350	20.786	156.633	153.554	1.078	473.005	452.533	-67.537
400	20.786	159.408	154.116	2.117	473.314	449.587	-58.710
450	20.786	161.857	154.843	3.156	473.621	446.603	-51.840
500	20.786	164.047	155.655	4.196	473.923	443.584	-46.341
600	20.786	167.836	157.379	6.274	474.510	437.461	-38.084
700	20.786	171.041	159.108	8.353	475.067	431.242	-32.180
800	20.786	173.816	160.777	10.431	475.591	424.945	-27.746
900	20.786	176.264	162.364	12.510	476.081	418.584	-24.294
1000	20.786	178.454	163.866	14.589	476.540	412.171	-21.530
1100	20.786	180.436	165.284	16.667	476.970	405.713	-19.266
1200	20.786	182.244	166.623	18.746	477.374	399.217	-17.377
1300	20.786	183.908	167.889	20.824	477.756	392.688	-15.778
1400	20.786	185.448	169.089	22.903	478.118	386.131	-14.407
1500	20.786	186.882	170.228	24.982	478.462	379.548	-13.217
1600	20.786	188.224	171.311	27.060	478.791	372.943	-12.175
1700	20.786	189.484	172.344	29.139	479.107	366.318	-11.256
1800	20.787	190.672	173.329	31.218	479.411	359.674	-10.437
1900	20.790	191.796	174.272	33.296	479.705	353.014	-9.705
2000	20.790	192.863	175.175	35.375	479.990	346.339	-9.045
2100	20.793	193.877	176.042	37.454	480.266	339.650	-8.448
2200	20.797	194.844	176.874	39.534	480.536	332.947	-7.905
2300	20.804	195.769	177.676	41.614	480.799	326.233	-7.409
2400	20.813	196.655	178.448	43.695	481.057	319.507	-6.954
2500	20.826	197.504	179.194	45.777	481.311	312.770	-6.535
2600	20.843	198.322	179.914	47.860	481.561	306.024	-6.148
2700	20.864	199.109	180.610	49.945	481.809	299.268	-5.790
2800	20.891	199.868	181.285	52.033	482.054	292.502	-5.457
2900	20.924	200.601	181.938	54.124	482.299	285.728	-5.147
3000	20.963	201.311	182.572	56.218	482.543	278.946	-4.857
3100	21.010	202.000	183.188	58.317	482.789	272.155	-4.586
3200	21.064	202.667	183.786	60.420	483.036	265.357	-4.332
3300	21.126	203.317	184.368	62.530	483.286	258.550	-4.093
3400	21.197	203.948	184.935	64.646	483.540	251.736	-3.867
3500	21.277	204.564	185.487	66.769	483.799	244.915	-3.655
3600	21.365	205.164	186.025	68.902	484.064	238.086	-3.455
3700	21.463	205.751	186.550	71.043	484.335	231.249	-3.265
3800	21.569	206.325	187.063	73.194	484.614	224.405	-3.085
3900	21.685	206.887	187.564	75.357	484.903	217.554	-2.914
4000	21.809	207.437	188.054	77.532	485.201	210.695	-2.751
4100	21.941	207.977	188.534	79.719	485.510	203.829	-2.597
4200	22.082	208.508	189.003	81.920	485.830	196.955	-2.449
4300	22.231	209.029	189.463	84.136	486.164	190.073	-2.309
4400	22.388	209.542	189.913	86.367	486.510	183.183	-2.175
4500	22.551	210.047	190.355	88.614	486.871	176.285	-2.046
4600	22.722	210.544	190.788	90.877	487.247	169.379	-1.923
4700	22.899	211.035	191.214	93.158	487.638	162.465	-1.806
4800	23.081	211.519	191.632	95.457	488.046	155.542	-1.693
4900	23.269	211.997	192.043	97.775	488.471	148.610	-1.584
5000	23.461	212.469	192.447	100.111	488.912	141.670	-1.480
5100	23.658	212.935	192.844	102.467	489.372	134.721	-1.380
5200	23.858	213.397	193.235	104.843	489.849	127.762	-1.283
5300	24.061	213.853	193.619	107.238	490.345	120.794	-1.190
5400	24.266	214.305	193.998	109.655	490.860	113.817	-1.101
5500	24.474	214.752	194.371	112.092	491.394	106.829	-1.015
5600	24.682	215.195	194.739	114.550	491.947	99.832	-0.931
5700	24.892	215.633	195.102	117.028	492.519	92.825	-0.851
5800	25.102	216.068	195.460	119.528	493.110	85.808	-0.773
5900	25.312	216.499	195.813	122.049	493.720	78.780	-0.697
6000	25.521	216.926	196.161	124.590	494.349	71.742	-0.625

PREVIOUS: March 1977 (1 atm)   CURRENT: December 1982 (1 bar)

Nitrogen, Ion (N⁺)   IDEAL GAS M_r = 14.00615 Nitrogen, Ion (N⁺)   N†(g)

IP(N⁺, g) = 238750.50 ± 13 cm⁻¹
S°(298.15 K) = 159.797 ± 0.02 J·K⁻¹·mol⁻¹

$\Delta_f H°$(0 K) = 1873.152 ± 0.42 kJ·mol⁻¹
$\Delta_f H°$(298.15 K) = [1882.130] kJ·mol⁻¹

Electronic Levels and Quantum Weights

State	ϵ_i, cm⁻¹	g_i
$^3P_0$	0.0	1
$^3P_1$	48.7	3
$^3P_2$	130.8	5
$^1D_2$	15316.2	5
$^1S_0$	32688.8	1
$^5S_2$	46784.6	5

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	-7.116	1873.152		
100	24.729	135.201	179.245	-4.404			
200	21.896	151.192	161.758	-2.113			
250	21.497	156.030	160.148	-1.030			
298.15	21.284	159.797	159.797	0.	1882.130	1856.796	-325.303
300	21.278	159.929	159.797	0.039	1882.181	1856.639	-323.270
350	21.146	163.198	160.056	1.100	1883.552	1852.273	-276.437
400	21.060	166.016	160.629	2.155	1884.917	1847.712	-241.286
450	21.002	168.492	161.368	3.206	1886.274	1842.979	-213.927
500	20.960	170.703	162.193	4.255	1887.626	1838.096	-192.025
600	20.906	174.519	163.939	6.348	1890.306	1827.938	-159.136
700	20.874	177.739	165.686	8.437	1892.952	1817.334	-135.611
800	20.853	180.525	167.371	10.523	1895.562	1806.353	-117.943
900	20.839	182.980	168.972	12.608	1898.137	1795.047	-104.182
1000	20.829	185.175	170.484	14.691	1900.679	1783.456	-93.158
1100	20.821	187.160	171.911	16.774	1903.191	1771.612	-84.127
1200	20.815	188.972	173.259	18.855	1905.677	1759.540	-76.591
1300	20.811	190.638	174.532	20.937	1908.140	1747.262	-70.206
1400	20.808	192.180	175.738	23.018	1910.583	1734.795	-64.726
1500	20.805	193.615	176.883	25.098	1913.008	1722.154	-59.971
1600	20.803	194.958	177.971	27.179	1915.418	1709.351	-55.805
1700	20.802	196.219	179.008	29.259	1917.814	1696.399	-52.124
1800	20.803	197.408	179.997	31.339	1920.198	1683.306	-48.848
1900	20.804	198.533	180.943	33.420	1922.572	1670.080	-45.914
2000	20.806	199.600	181.850	35.500	1924.937	1656.730	-43.269
2100	20.810	200.615	182.719	37.581	1927.294	1643.261	-40.874
2200	20.816	201.583	183.555	39.662	1929.644	1629.681	-38.694
2300	20.824	202.509	184.359	41.744	1931.988	1615.994	-36.700
2400	20.835	203.395	185.134	43.827	1934.327	1602.205	-34.871
2500	20.848	204.246	185.882	45.911	1936.661	1588.318	-33.186
2600	20.864	205.064	186.604	47.997	1938.992	1574.339	-31.629
2700	20.883	205.852	187.302	50.084	1941.320	1560.269	-30.185
2800	20.904	206.612	187.978	52.174	1943.646	1546.114	-28.843
2900	20.929	207.346	188.634	54.265	1945.970	1531.875	-27.592
3000	20.956	208.056	189.269	56.359	1948.293	1517.556	-26.423
3100	20.987	208.743	189.886	58.457	1950.616	1503.160	-25.328
3200	21.020	209.410	190.486	60.557	1952.938	1488.689	-24.300
3300	21.056	210.058	191.069	62.661	1955.261	1474.145	-23.334
3400	21.094	210.687	191.637	64.768	1957.585	1459.531	-22.423
3500	21.135	211.299	192.190	66.880	1959.910	1444.849	-21.563
3600	21.178	211.895	192.729	68.995	1962.237	1430.100	-20.750
3700	21.223	212.476	193.255	71.115	1964.566	1415.286	-19.980
3800	21.269	213.042	193.768	73.240	1966.897	1400.410	-19.250
3900	21.317	213.595	194.270	75.369	1969.231	1385.472	-18.556
4000	21.366	214.136	194.760	77.503	1971.567	1370.474	-17.897
4100	21.417	214.664	195.239	79.642	1973.906	1355.417	-17.268
4200	21.468	215.180	195.707	81.787	1976.248	1340.304	-16.659
4300	21.520	215.686	196.166	83.936	1978.594	1325.135	-16.097
4400	21.573	216.182	196.615	86.091	1980.943	1309.911	-15.551
4500	21.625	216.667	197.056	88.251	1983.296	1294.634	-15.028
4600	21.679	217.143	197.487	90.416	1985.652	1279.304	-14.527
4700	21.732	217.610	197.910	92.586	1988.011	1263.923	-14.047
4800	21.784	218.068	198.326	94.762	1990.374	1248.492	-13.586
4900	21.837	218.517	198.733	96.943	1992.741	1233.012	-13.144
5000	21.889	218.959	199.133	99.129	1995.111	1217.483	-12.719
5100	21.941	219.393	199.526	101.321	1997.485	1201.907	-12.310
5200	21.992	219.820	199.912	103.518	1999.862	1186.284	-11.916
5300	22.042	220.239	200.292	105.719	2002.242	1170.616	-11.537
5400	22.092	220.652	200.665	107.926	2004.626	1154.902	-11.171
5500	22.141	221.057	201.032	110.138	2007.013	1139.145	-10.819
5600	22.189	221.457	201.393	112.354	2009.404	1123.344	-10.478
5700	22.236	221.850	201.749	114.575	2011.797	1107.500	-10.149
5800	22.281	222.237	202.099	116.801	2014.192	1091.614	-9.831
5900	22.326	222.618	202.443	119.032	2016.591	1075.687	-9.523
6000	22.370	222.994	202.783	121.267	2018.991	1059.719	-9.226

Enthalpy of Formation

$\Delta_f H°$(N⁺, g, 0 K) is calculated from $\Delta_f H°$(N, g, 0 K)[1] using the spectroscopic value of IP(N) = 117225.7 ± 0.3 cm⁻¹ (1402.331 ± 0.004 kJ·mol⁻¹) from Moore.[2] The ionization limit is converted from cm⁻¹ to kJ·mol⁻¹ using the factor, 1 cm⁻¹ = 0.01196266 kJ·mol⁻¹, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock et al.[3] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°$(N⁺, g, 298.15 K) is calculated from $\Delta_f H°$(N, g, 0 K) by using IP(N) with JANAF[1] enthalpies, $H°$(0 K)-$H°$(298.15 K), for N(g), N⁺(g), and e⁻(ref). $\Delta_f H°$(N → N⁺ + e⁻, 298.15 K) differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al.[4] $\Delta_f H°$(298.15 K) should be changed by -6.197 kJ·mol⁻¹ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[6] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first five excited states; the next excited state is 92237.2 cm⁻¹ above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first five excited states. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[6]

References

[1]JANAF Thermochemical Tables: N(g), 12-31-82; e⁻(ref), 3-31-82.
[2]C. E. Moore, U. S. Nat. Bur. Stand., NSRDS–NBS–3, Section 5, (1975).
[3]E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data 2, 663 (1973).
[4]H. M. Rosenstock, K. Draxl et al., J. Phys. Chem. Ref. Data 6, Supp. 1 (1977).
[5]R. D. Levin and S. G. Lias, U. S. Nat. Bur. Stand., NSRDS–NBS–71, (1982).
[6]J. R. Downey, Jr., The Dow Chemical Company, AFOSR–TR–0960, Contract No. F44620–75–1–0048, (1978).

Nitrogen, Ion (N⁻) $M_r = 14.00725$ IDEAL GAS $N_1^-(g)$

$\Delta_f H°(0\ K) = 477.574 \pm 1.9\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_f H°(298.15\ K) = [473.540]\ \mathrm{kJ\cdot mol^{-1}}$

$EA(N, g) = -0.07 \pm 0.02\ \mathrm{eV}$
$S°(298.15\ K) = 159.927 \pm 0.001\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm⁻¹	g_i
$^3P_2$	0	5
$^3P_1$	[63]	3
$^3P_0$	[90]	1
$^1D_2$	[10800]	5
$^1S_0$	[22390]	1

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
		J·K⁻¹·mol⁻¹		kJ·mol⁻¹			
0	0.	0.	INFINITE	-6.498	477.574		
100	22.234	136.475	178.809	-4.233			
200	21.252	151.496	161.855	-2.072			
250	21.096	156.220	160.274	-1.014			
298.15	21.09	159.927	159.927	0.	473.540	460.677	-80.709
300	21.007	160.057	159.928	0.039	473.514	460.597	-80.197
350	20.951	163.291	160.183	1.088	472.795	458.501	-68.428
400	20.913	166.086	160.750	2.134	472.072	456.508	-59.614
450	20.888	168.548	161.483	3.179	471.345	454.606	-52.769
500	20.869	170.747	162.301	4.223	470.612	452.786	-47.302
600	20.844	174.550	164.035	6.309	469.128	449.360	-39.120
700	20.829	177.762	165.773	8.392	467.611	446.184	-33.295
800	20.819	180.542	167.449	10.475	466.060	443.229	-28.940
900	20.812	182.994	169.043	12.556	464.475	440.470	-25.564
1000	20.807	185.187	170.550	14.637	462.857	437.889	-22.873
1100	20.804	187.170	171.972	16.718	461.210	435.471	-20.679
1200	20.801	188.980	173.315	18.798	459.538	433.205	-18.857
1300	20.799	190.645	174.585	20.878	457.842	431.079	-17.321
1400	20.797	192.186	175.787	22.958	456.126	429.085	-16.009
1500	20.796	193.621	176.929	25.037	454.393	427.214	-14.877
1600	20.794	194.963	178.015	27.117	452.645	425.459	-13.890
1700	20.793	196.223	179.049	29.196	450.883	423.814	-13.022
1800	20.793	197.412	180.037	31.276	449.109	422.272	-12.254
1900	20.792	198.536	180.981	33.355	447.325	420.830	-11.569
2000	20.791	199.602	181.886	35.434	445.531	419.482	-10.956
2100	20.791	200.617	182.754	37.513	443.729	418.224	-10.403
2200	20.790	201.584	183.588	39.592	441.920	417.052	-9.902
2300	20.790	202.508	184.390	41.671	440.103	415.962	-9.447
2400	20.790	203.393	185.164	43.750	438.281	414.951	-9.031
2500	20.789	204.242	185.910	45.829	436.453	414.017	-8.650
2600	20.789	205.057	186.631	47.908	434.620	413.156	-8.300
2700	20.789	205.842	187.328	49.987	432.783	412.365	-7.978
2800	20.789	206.598	188.003	52.066	430.941	411.642	-7.679
2900	20.789	207.327	188.657	54.145	429.095	410.986	-7.403
3000	20.788	208.032	189.291	56.223	427.246	410.393	-7.146
3100	20.788	208.714	189.906	58.302	425.393	409.862	-6.906
3200	20.788	209.374	190.504	60.381	423.536	409.390	-6.683
3300	20.788	210.013	191.086	62.460	421.677	408.977	-6.474
3400	20.788	210.634	191.652	64.539	419.815	408.620	-6.278
3500	20.788	211.236	192.203	66.617	417.951	408.318	-6.094
3600	20.788	211.822	192.740	68.696	416.083	408.069	-5.921
3700	20.788	212.392	193.263	70.775	414.214	407.872	-5.758
3800	20.788	212.946	193.774	72.854	412.342	407.726	-5.605
3900	20.787	213.486	194.272	74.932	410.468	407.629	-5.460
4000	20.787	214.012	194.759	77.011	408.591	407.580	-5.322
4100	20.787	214.526	195.235	79.090	406.713	407.578	-5.193
4200	20.787	215.026	195.701	81.169	404.833	407.622	-5.070
4300	20.787	215.516	196.156	83.247	402.950	407.710	-4.953
4400	20.787	215.993	196.601	85.326	401.066	407.843	-4.842
4500	20.787	216.461	197.037	87.405	399.180	408.018	-4.736
4600	20.787	216.917	197.465	89.484	397.293	408.235	-4.636
4700	20.787	217.365	197.883	91.562	395.403	408.493	-4.540
4800	20.787	217.802	198.294	93.641	393.512	408.792	-4.449
4900	20.787	218.231	198.696	95.720	391.619	409.130	-4.361
5000	20.787	218.651	199.091	97.798	389.724	409.506	-4.278
5100	20.787	219.062	199.479	99.877	387.828	409.921	-4.198
5200	20.787	219.466	199.859	101.956	385.930	410.373	-4.122
5300	20.787	219.862	200.233	104.034	384.030	410.861	-4.049
5400	20.787	220.251	200.600	106.113	382.129	411.385	-3.979
5500	20.787	220.632	200.961	108.192	380.226	411.944	-3.912
5600	20.787	221.006	201.315	110.270	378.321	412.538	-3.848
5700	20.787	221.374	201.664	112.349	376.414	413.166	-3.786
5800	20.787	221.736	202.007	114.428	374.506	413.827	-3.727
5900	20.787	222.091	202.344	116.506	372.595	414.522	-3.670
6000	20.787	222.441	202.676	118.585	370.682	415.248	-3.615

Enthalpy of Formation

$\Delta_f H°(N^-, g, 0\ K)$ is calculated from $\Delta_f H°(N, g, 0\ K)$[1] using the adopted electron affinity of EA(N) = -0.07 ± 0.02 eV (-6.754 ± 1.930 kJ·mol⁻¹). This value, recommended by Hotop and Lineberger,[2] is based on a dissociative attachment of electrons study[3]. Additional information on N⁻(g) may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock et al.[5] and Massey.[6] $\Delta_f H°(N^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(N, g, 0\ K)$ by using EA(N) with JANAF enthalpies, H°(0 K)-H°(298.15 K), for N⁻(g), N(g), and e⁻(ref). $\Delta_f H°(N^- \rightarrow N + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al.[5] $\Delta_f H°(298.15\ K)$ should be changed by +6.197 kJ·mol⁻¹ if t is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state for N⁻(g) is reported to be $2p^4$ ^3P. We estimate the fine structure separations in the ground state by comparison of isoelectronic series based on N⁻(g) [N⁻, O, F⁺, Ne⁺⁺, Na⁺⁺⁺] and C(g) [C, N⁺, O⁺⁺, F⁺⁺⁺]. The uncertainty in S°(298.15 K) in part reflects this estimation. Massey[6] listed the hyperfine splitting of the ground state as 97 and 137 cm⁻¹ based on a quadratic isoelectronic extrapolation. This technique led to high values in the case of O⁻(g)[3] and is assumed to give high results for N⁻(g).

A comparison of the isoelectronic sequence – N⁻(g), O(g), F⁺(g) – would suggest that stable electronic states may exist at low wave numbers. These states would greatly affect the entropy. We estimate two of these levels.

References

[1]JANAF Thermochemical Tables: N(g), 12-31-82; e⁻(ref), 3-31-82; O⁻(g), 9-30-82.
[2]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, to be published, (1985).
[3]J. Mazeau, F. Gresteau, R. I. Hall and A. Huetz, J. Phys. B 11, L557 (1978).
[4]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 4, 539 (1975).
[5]H. M. Rosenstock, K. Draxl et al., J. Phys. Chem. Ref. Data 6, Supp. 1 (1977).
[6]H. S. W. Massey, "Negative Ions," 3rd ed, Cambridge University Press, Cambridge, (1976).

Nitrogen Oxide (NO)   IDEAL GAS M_r = 30.0061   N₁O₁(g)

$S°(298.15\ K) = 210.758\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 89.775 \pm 0.17\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 90.291 \pm 0.17\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight

State	ϵ, cm⁻¹	g_i
²Π	0	2
	121.1	2

$\omega_e = 1903.60\ cm^{-1}$ $\omega_e x_e = 13.97\ cm^{-1}$ $\sigma = 1$
$B_e = 1.7042\ cm^{-1}$ $\alpha_e = 0.0178\ cm^{-1}$ $r_e = 1.1508\ Å$

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	-9.192	89.775	89.775	INFINITE
100	32.302	177.031	237.757	-6.073	89.991	88.944	-46.460
200	30.420	198.747	213.501	-2.951	90.202	87.800	-22.931
250	30.025	205.488	211.251	-1.441	90.256	87.193	-18.218
298.15	29.845	210.758	210.758	0.	90.291	86.600	-15.172
300	29.841	210.943	210.759	0.055	90.292	86.577	-15.074
350	29.823	215.540	211.122	1.546	90.316	85.955	-12.828
400	29.944	219.529	211.199	3.040	90.332	85.331	-11.143
450	30.175	223.068	212.974	4.542	90.343	84.705	-9.832
500	30.486	226.263	214.145	6.059	90.352	84.079	-8.784
600	31.238	231.886	216.646	9.144	90.366	82.822	-7.210
700	32.028	236.761	219.179	12.307	90.381	81.564	-6.086
800	32.767	241.087	221.652	15.548	90.398	80.303	-5.243
900	33.422	244.945	224.031	18.858	90.417	79.041	-4.587
1000	33.987	248.536	226.307	22.229	90.437	77.775	-4.063
1100	34.468	251.799	228.478	25.653	90.457	76.508	-3.633
1200	34.877	254.816	230.549	29.120	90.476	75.239	-3.275
1300	35.226	257.621	232.525	32.626	90.493	73.969	-2.972
1400	35.524	260.243	234.412	36.164	90.508	72.697	-2.712
1500	35.780	262.703	236.217	39.729	90.518	71.425	-2.487
1600	36.002	265.019	237.945	43.319	90.525	70.151	-2.290
1700	36.195	267.208	239.603	46.929	90.526	68.878	-2.116
1800	36.364	269.282	241.195	50.557	90.522	67.605	-1.962
1900	36.514	271.252	242.725	54.201	90.511	66.332	-1.824
2000	36.647	273.128	244.199	57.859	90.494	65.060	-1.699
2100	36.767	274.919	245.619	61.530	90.469	63.788	-1.587
2200	36.874	276.632	246.990	65.212	90.438	62.519	-1.484
2300	36.971	278.273	248.315	68.904	90.398	61.251	-1.391
2400	37.060	279.849	249.596	72.606	90.350	59.984	-1.306
2500	37.141	281.363	250.837	76.316	90.295	58.720	-1.227
2600	37.216	282.822	252.039	80.034	90.231	57.458	-1.154
2700	37.285	284.227	253.205	83.759	90.160	56.199	-1.087
2800	37.350	285.585	254.338	87.491	90.081	54.943	-1.025
2900	37.410	286.896	255.438	91.229	89.994	53.689	-0.967
3000	37.466	288.165	256.508	94.973	89.899	52.439	-0.913
3100	37.519	289.395	257.549	98.722	89.798	51.192	-0.863
3200	37.570	290.587	258.563	102.477	89.689	49.948	-0.815
3300	37.617	291.744	259.551	106.236	89.574	48.708	-0.771
3400	37.663	292.867	260.514	110.000	89.451	47.472	-0.729
3500	37.706	293.960	261.454	113.768	89.323	46.239	-0.690
3600	37.747	295.022	262.372	117.541	89.189	45.010	-0.653
3700	37.787	296.057	263.269	121.318	89.049	43.784	-0.618
3800	37.825	297.065	264.145	125.098	88.903	42.563	-0.585
3900	37.862	298.048	265.002	128.883	88.752	41.346	-0.554
4000	37.898	299.008	265.840	132.671	88.596	40.132	-0.524
4100	37.933	299.944	266.660	136.462	88.434	38.922	-0.496
4200	37.966	300.858	267.464	140.257	88.268	37.717	-0.469
4300	37.999	301.752	268.251	144.056	88.097	36.515	-0.444
4400	38.031	302.626	269.022	147.857	87.922	35.318	-0.419
4500	38.062	303.481	269.778	151.662	87.741	34.124	-0.396
4600	38.092	304.318	270.520	155.469	87.556	32.934	-0.374
4700	38.122	305.137	271.248	159.280	87.366	31.749	-0.353
4800	38.151	305.940	271.962	163.094	87.171	30.568	-0.333
4900	38.180	306.727	272.664	166.910	86.970	29.391	-0.313
5000	38.208	307.499	273.353	170.730	86.765	28.218	-0.295
5100	38.235	308.256	274.030	174.552	86.553	27.049	-0.277
5200	38.262	308.998	274.695	178.377	86.336	25.884	-0.260
5300	38.289	309.728	275.349	182.204	86.112	24.724	-0.244
5400	38.316	310.443	275.993	186.034	85.881	23.568	-0.228
5500	38.342	311.147	276.625	189.867	85.644	22.416	-0.213
5600	38.367	311.838	277.248	193.703	85.399	21.269	-0.198
5700	38.393	312.517	277.861	197.541	85.146	20.125	-0.184
5800	38.418	313.185	278.464	201.381	84.884	18.987	-0.171
5900	38.443	313.842	279.058	205.224	84.613	17.853	-0.158
6000	38.468	314.488	279.643	209.070	84.331	16.724	-0.146

PREVIOUS June 1963 (1 atm) CURRENT June 1963 (1 bar)

Enthalpy of Formation

Herzberg,[1] lists two $D_0°(NO)$ values, 5.296 and 6.487 eV. Gaydon[2] lists $D_0°(NO) = 6.49 \pm 0.05$ eV. A Birge–Sponer extrapolation of the vibrational levels, up to $v = 18$, of the ground state leads to a $D_0°$ of about 6.5 eV. Gaydon's[2] analysis on the predissociation of NO also leads to the higher value for $D°(NO)$.

Tanaka,[3] has observed and analyzed the emission bands of NO in the vacuum ultraviolet region. Tanaka's,[3] observation and interpretation of the abrupt cutoff (predissociation) of certain v' values in the β, γ, and δ bands and of the complete non appearance of ε and β' bands strongly favors a $D°(NO) = 6.48$ eV. $\Delta_f H°(NO, g, 298.15\ K)$ was calculated on this basis to be $22.033 \pm 1\ kcal \cdot mol^{-1}$.

More recently Frisch,[4] has calorimetrically determined the enthalpy of reaction for:

$$NO(g) + CO(g) \rightarrow CO_2(g) + 1/2N_2(g)$$

at 298.15 K, from which the author derives a $\Delta_f H°(NO, g, 298.15\ K) = 21.58 \pm 0.04\ kcal \cdot mol^{-1}$. The auxiliary values used by Frisch to calculate the enthalpy of formation of nitric oxide were based upon the 1961 atomic weight scale. Recalculating $\Delta_f H°(NO, g, 298.15\ K)$ using auxiliary functions based on the 1956 atomic weight scale had a negligible effect on the final result.

The calorimetrically determined heat of formation for nitric oxide, $21.58 \pm 0.04\ kcal \cdot mol^{-1}$, was selected as the best value.

Heat Capacity and Entropy

The spectroscopic constants were taken from Gillette and Eyster,[5] who measured and analyzed the fundamental rotation–vibration band of nitric oxide using a grating spectrometer. The constants used in this calculation were adjusted to correspond to the naturally occurring isotopic mixture.

References

[1]G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, (1950).
[2]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall, Ltd., London, (1953).
[3]Y. Tanaka, J. Chem. Phys. 22, 2045 (1954).
[4]M. A. Frisch, Thesis, University of Wisconsin, Madison, Wisconsin, 1962, Diss. Absts. 23, 1940 (1961).
[5]R. H. Gillette and E. H. Eyster, Phys. Revs. 56, 1113 (1939).

Nitrogen Oxide, Ion (NO⁺) IDEAL GAS $M_r = 30.00555$

Nitrogen Oxide, Ion (NO₁) N₁O†(g)

$\Delta_f H°(0\ K) = 983.995 \pm 0.8\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 990.185 \pm 0.8\ kJ\cdot mol^{-1}$

$(298.15\ K) = 198.219\ J\cdot K^{-1}\cdot mol^{-1}$

| Electronic Level and Quantum Weight | | |
State	ϵ_i, cm⁻¹	g_i
$^1\Sigma^+$	0	1

$\omega_e = 2377.1\ cm^{-1}$ $\omega_e x_e = 16.35\ cm^{-1}$ $\sigma = 1$
$B_e = 2.002\ cm^{-1}$ $\alpha_e = 0.0202\ cm^{-1}$ $r_e = 1.0619\ Å$

Enthalpy of Formation

Watanabe[1] and Walker and Weissler[2] have measured the ionization potential of NO(g) by photoionization, yielding IP = 9.25 ± 0.02 and 9.20 ± 0.03 eV, respectively. Hagstrum[3] reported IP = 9.4 ± 0.2 eV by electron impact. Huber[4] determined spectroscopically the ionization potential for NO(g), IP = 9.267 ± 0.005 eV (213.72 ± 0.1 kcal·mol⁻¹). The last value has been selected, and yields the enthalpy of formation of NO⁺(g), $\Delta_f H°(NO^+, g, 0\ K) = 235.18\ kcal\cdot mol^{-1}$, using $\Delta_f H°(NO, g, 0\ K) = 21.46 \pm 0.04\ kcal\cdot mol^{-1}$.

Heat Capacity and Entropy

The selected molecular constants were obtained from the ultraviolet spectra by Miescher.[5] The tabulated thermodynamic functions are in reasonable agreement with those calculated by Hilsenrath and Messina,[6] who have used slightly different molecular constants.

References

[1] K. Watanabe, J. Chem. Phys. 22, 1564 (1954).
[2] W. C. Walker and G. L. Weissler, J. Chem. Phys. 23, 1962 (1955).
[3] H. D. Hagstrum, J. Chem. Phys. 23, 1178 (1955).
[4] K. P. Huber, Helv. Phys. Acta 34, 929 (1961).
[5] E. Miescher, Can. J. Phys. 33, 355 (1955), Helv. Phys. Acta 29, 135 (1956).
[6] J. Hilsenrath and C. G. Messina, U. S. Nat. Bur. Stand. Report 8504, (1964).

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure $p° = 0.1\ MPa$

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
	J·K⁻¹·mol⁻¹	J·K⁻¹·mol⁻¹	J·K⁻¹·mol⁻¹	kJ·mol⁻¹	kJ·mol⁻¹	kJ·mol⁻¹	
0	0.	0.	INFINITE	-8.670	983.995		
100	29.104	166.421	224.100	-5.768			
200	29.107	186.595	200.882	-2.857			
250	29.111	193.091	198.698	-1.402			
298.15	29.123	198.219	198.219	0.	990.185	983.978	-172.389
300	29.124	198.399	198.219	0.054	990.224	983.939	-171.319
350	29.163	202.891	198.574	1.511	991.253	982.811	-146.676
400	29.244	206.790	199.363	2.971	992.275	981.535	-128.175
450	29.378	210.242	200.383	4.436	993.288	980.131	-113.771
500	29.568	213.346	201.527	5.910	994.293	978.615	-102.235
600	30.089	218.781	203.962	8.891	996.282	975.293	-84.907
700	30.728	223.466	206.421	11.931	998.252	971.659	-72.505
800	31.403	227.613	208.816	15.038	1000.214	967.703	-63.185
900	32.059	231.350	211.115	18.211	1002.175	963.521	-55.921
1000	32.666	234.760	213.312	21.448	1004.139	959.121	-50.099
1100	33.213	237.899	215.406	24.742	1006.109	954.524	-45.327
1200	33.697	240.810	217.403	28.088	1008.085	949.747	-41.341
1300	34.124	243.525	219.309	31.480	1010.066	944.805	-37.963
1400	34.497	246.067	221.131	34.911	1012.053	939.711	-35.061
1500	34.825	248.459	222.874	38.378	1014.043	934.474	-32.541
1600	35.112	250.716	224.544	41.875	1016.036	929.104	-30.332
1700	35.365	252.852	226.147	45.399	1018.030	923.610	-28.379
1800	35.588	254.880	227.687	48.947	1020.024	917.998	-26.640
1900	35.786	256.810	229.170	52.516	1022.017	912.276	-25.080
2000	35.963	258.650	230.598	56.103	1024.008	906.449	-23.674
2100	36.121	260.408	231.976	59.708	1025.995	900.522	-22.399
2200	36.263	262.092	233.307	63.327	1027.979	894.501	-21.238
2300	36.391	263.707	234.594	66.960	1029.959	888.389	-20.176
2400	36.507	265.258	235.839	70.605	1031.933	882.191	-19.200
2500	36.612	266.750	237.046	74.261	1033.902	875.911	-18.301
2600	36.709	268.188	238.216	77.927	1035.865	869.553	-17.470
2700	36.798	269.575	239.352	81.602	1037.823	863.119	-16.698
2800	36.880	270.915	240.456	85.286	1039.774	856.613	-15.980
2900	36.955	272.211	241.529	88.978	1041.720	850.047	-15.311
3000	37.025	273.465	242.572	92.677	1043.659	843.395	-14.685
3100	37.091	274.680	243.589	96.383	1045.593	836.687	-14.098
3200	37.152	275.858	244.579	100.095	1047.520	829.917	-13.547
3300	37.209	277.003	245.544	103.813	1049.442	823.087	-13.028
3400	37.263	278.114	246.486	107.537	1051.358	816.200	-12.539
3500	37.313	279.195	247.405	111.266	1053.269	809.255	-12.077
3600	37.361	280.247	248.303	114.999	1055.174	802.257	-11.640
3700	37.407	281.271	249.180	118.738	1057.074	795.205	-11.226
3800	37.450	282.269	250.038	122.481	1058.969	788.102	-10.833
3900	37.491	283.243	250.877	126.228	1060.860	780.950	-10.460
4000	37.531	284.192	251.698	129.979	1062.745	773.748	-10.104
4100	37.569	285.120	252.502	133.734	1064.626	766.500	-9.765
4200	37.605	286.025	253.289	137.492	1066.502	759.206	-9.442
4300	37.640	286.911	254.061	141.255	1068.374	751.867	-9.133
4400	37.673	287.776	254.817	145.020	1070.241	744.485	-8.838
4500	37.705	288.623	255.559	148.789	1072.103	737.060	-8.556
4600	37.737	289.452	256.287	152.561	1073.961	729.594	-8.285
4700	37.767	290.264	257.001	156.337	1075.814	722.088	-8.025
4800	37.796	291.060	257.702	160.115	1077.662	714.542	-7.776
4900	37.825	291.839	258.391	163.896	1079.505	706.959	-7.536
5000	37.853	292.604	259.068	167.680	1081.342	699.337	-7.306
5100	37.880	293.354	259.733	171.466	1083.174	691.679	-7.084
5200	37.906	294.089	260.386	175.256	1084.999	683.984	-6.871
5300	37.932	294.812	261.029	179.048	1086.819	676.255	-6.665
5400	37.957	295.521	261.661	182.842	1088.631	668.492	-6.466
5500	37.982	296.218	262.283	186.639	1090.436	660.694	-6.275
5600	38.006	296.902	262.895	190.438	1092.234	652.865	-6.090
5700	38.030	297.575	263.498	194.240	1094.023	645.003	-5.911
5800	38.053	298.237	264.091	198.044	1095.803	637.110	-5.738
5900	38.076	298.887	264.675	201.851	1097.574	629.186	-5.570
6000	38.098	299.528	265.251	205.660	1099.334	621.233	-5.408

PREVIOUS June 1966 (1 atm) CURRENT June 1966 (1 bar)

Nitrogen Oxide (NO₂) $N_1O_2(g)$

IDEAL GAS $M_r = 46.0055$ Nitrogen Oxide (NO₂)

$S°(298.15\ K) = 240.034 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 35.93 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 33.10 \pm 0.8\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies
ν, cm⁻¹

1357.8(1)
756.8(1)
1665.5(1)

Ground State Quantum Weight: 2
Point Group: C_{2v} $\sigma = 2$
Bond Distance: N–O = 1.197 Å
Bond Angle: O–N–O = 134° 15'
Product of the Moments of Inertia: $I_A I_B I_C = 1.54229 \times 10^{-116}\ g^3 \cdot cm^6$

Enthalpy of Formation

The equilibrium constants for NO(g) + 1/2 O₂ → NO₂(g) of Bodenstein and Lindner,[1] as given by Giauque and Kemp[2] were subjected to 2nd and 3rd law analysis. 3rd law analysis gave $\Delta_f H°(298.15\ K) = -13.67$ kcal·mol⁻¹ and 2nd law $\Delta_f H°(298.15\ K) = -13.52 \pm 0.01$ kcal·mol⁻¹. The 3rd law value had a very slight trend with temperature which was consistent with an entropy error of 0.25 cal·K⁻¹·mol⁻¹, the 2nd law entropy was also consistent with an entropy error of 0.25 cal·K⁻¹·mol⁻¹. However the functions for all three gases are well established to about 0.03 cal·K⁻¹·mol⁻¹ or better and so this must be interpreted as due to errors in the data. On this basis the 3rd law value was chosen and combined with JANAF auxiliary data to give $\Delta_f H°(298.15\ K) = 7.91 \pm 0.2$ kcal·mol⁻¹, where the uncertainty includes that due to the possible error in the equilibrium constants.

Heat Capacity and Entropy

Bird et al. have given a complete review of the microwave spectrum of NO₂. They also give a corrected infra-red vibrational assignment, adopted here, which is in excellent agreement with calculations from the microwave data. They report $I_A = 0.34981 \times 10^{-39}$, $I_B = 6.45446 \times 10^{-39}$, and $I_C = 6.81994 \times 10^{-39}$ g·cm². The bond length and angle were chosen to give the best fit of the moments of inertia.

References

[1] M. Bodenstein and Lindner, Z. physik. Chem. 100, 82 (1922).
[2] W. F. Giauque and J. D. Kemp, J. Chem. Phys. 6, 40 (1938).
[3] G. R. Bird, J. C. Baird, A. W. Jache, J. A. Hodgeson, R. F. Curl Jr., A. C. Kunkle, J. W. Bransford, J. Rastrup–Andersen and J. Rosenthal, J. Chem. Phys. 40, 3378 (1964).

T/K	C°p	S°	-[G°-H°(Tr)]/T	H°-H°(Tr)	Δf H°	Δf G°	log Kf
		J·K⁻¹·mol⁻¹		kJ·mol⁻¹	kJ·mol⁻¹		
0	0.	0.	INFINITE	-10.186	35.927	35.927	INFINITE
100	33.276	202.563	271.168	-6.861	34.898	39.963	-20.874
200	34.385	225.852	243.325	-3.495	33.897	45.422	-11.863
250	35.593	233.649	240.634	-1.746	33.460	48.355	-10.103
298.15	36.974	240.034	240.034	0.	33.095	51.258	-8.980
300	37.029	240.262	240.034	0.068	33.083	51.371	-8.944
350	38.583	246.086	240.491	1.958	32.768	54.445	-8.125
400	40.171	251.342	241.524	3.927	32.512	57.560	-7.517
450	41.728	256.164	242.886	5.575	32.310	60.703	-7.046
500	43.206	260.638	244.440	8.099	32.154	63.867	-6.672
600	45.834	268.755	247.830	12.555	31.959	70.230	-6.114
700	47.986	275.988	251.345	17.250	31.878	76.616	-5.717
800	49.708	282.512	254.840	22.138	31.874	83.008	-5.420
900	51.076	288.449	258.250	27.179	31.923	89.397	-5.188
1000	52.166	293.889	261.545	32.344	32.005	95.779	-5.003
1100	53.041	298.903	264.717	37.605	32.109	102.152	-4.851
1200	53.748	303.550	267.761	42.946	32.226	108.514	-4.724
1300	54.326	307.876	270.683	48.351	32.351	114.867	-4.615
1400	54.803	311.920	273.485	53.808	32.478	121.209	-4.522
1500	55.200	315.715	276.175	59.309	32.603	127.543	-4.441
1600	55.533	319.288	278.759	64.846	32.724	133.868	-4.370
1700	55.815	322.663	281.244	70.414	32.837	140.186	-4.307
1800	56.055	325.861	283.634	76.007	32.940	146.497	-4.251
1900	56.262	328.897	285.937	81.624	33.032	152.804	-4.201
2000	56.441	331.788	288.158	87.259	33.111	159.106	-4.155
2100	56.596	334.545	290.302	92.911	33.175	165.404	-4.114
2200	56.732	337.181	292.373	98.577	33.223	171.700	-4.077
2300	56.852	339.706	294.377	104.257	33.255	177.993	-4.042
2400	56.958	342.128	296.316	109.947	33.270	184.285	-4.011
2500	57.052	344.455	298.196	115.648	33.268	190.577	-3.982
2600	57.136	346.694	300.018	121.357	33.248	196.870	-3.955
2700	57.211	348.852	301.787	127.075	33.210	203.164	-3.930
2800	57.278	350.934	303.505	132.799	33.155	209.460	-3.908
2900	57.339	352.945	305.176	138.530	33.082	215.757	-3.886
3000	57.394	354.889	306.800	144.267	32.992	222.058	-3.866
3100	57.444	356.772	308.382	150.009	32.885	228.363	-3.848
3200	57.490	358.597	309.923	155.756	32.761	234.670	-3.831
3300	57.531	360.366	311.425	161.507	32.622	240.981	-3.814
3400	57.569	362.084	312.890	167.262	32.467	247.298	-3.799
3500	57.604	363.754	314.319	173.020	32.297	253.618	-3.785
3600	57.636	365.377	315.715	178.783	32.113	259.945	-3.772
3700	57.666	366.957	317.079	184.548	31.914	266.276	-3.759
3800	57.693	368.495	318.412	190.316	31.701	272.613	-3.747
3900	57.719	369.994	319.715	196.086	31.475	278.956	-3.736
4000	57.742	371.455	320.991	201.859	31.236	285.305	-3.726
4100	57.764	372.881	322.239	207.635	30.985	291.659	-3.716
4200	57.784	374.274	323.461	213.412	30.720	298.020	-3.706
4300	57.803	375.634	324.659	219.191	30.444	304.388	-3.698
4400	57.821	376.963	325.833	224.973	30.155	310.762	-3.689
4500	57.837	378.262	326.983	230.756	29.854	317.142	-3.681
4600	57.853	379.534	328.112	236.540	29.540	323.530	-3.674
4700	57.867	380.778	329.219	242.326	29.214	329.925	-3.667
4800	57.881	381.996	330.306	248.114	28.875	336.326	-3.660
4900	57.894	383.190	331.373	253.902	28.523	342.736	-3.654
5000	57.906	384.360	332.421	259.692	28.158	349.152	-3.648
5100	57.917	385.507	333.451	265.483	27.778	355.576	-3.642
5200	57.928	386.631	334.463	271.276	27.384	362.006	-3.636
5300	57.938	387.735	335.458	277.069	26.974	368.446	-3.631
5400	57.948	388.818	336.436	282.863	26.548	374.892	-3.626
5500	57.957	389.881	337.398	288.658	26.106	381.347	-3.622
5600	57.965	390.926	338.344	294.455	25.646	387.811	-3.617
5700	57.973	391.952	339.276	300.251	25.167	394.281	-3.613
5800	57.981	392.960	340.193	306.049	24.669	400.762	-3.609
5900	57.988	393.951	341.096	311.848	24.150	407.249	-3.606
6000	57.995	394.926	341.985	317.647	23.608	413.748	-3.602

PREVIOUS: September 1964 (1 atm)   CURRENT: September 1964 (1 bar)

Nitrogen Oxide (NO₂) $N_1O_2(g)$

Nitrogen Oxide, Ion (NO₂⁻)   **IDEAL GAS** $M_r = 46.006048$ **Nitrogen Oxide, Ion (ONO⁻)** $N_1O_2^-(g)$

$S°(298.15\ \text{K}) = 236.598 \pm 2.1\ \text{J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0\ \text{K}) = -193.73 \pm 5.8\ \text{kJ·mol}^{-1}$
$\Delta_f H°(298.15\ \text{K}) = -202.72 \pm 5.8\ \text{kJ·mol}^{-1}$

T/K	$C°_p$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
		J·K⁻¹·mol⁻¹			kJ·mol⁻¹		
0	0.	0.	INFINITE	-10.227	-193.726		
100	33.278	198.965	267.973	-6.901			
200	34.509	222.275	239.931	-3.531			
250	35.955	230.122	237.208	-1.771			
298.15	37.663	236.598	236.598	0.	-202.715	-177.273	31.057
300	37.733	236.831	236.599	0.070	-202.765	-177.115	30.838
350	39.645	242.791	237.065	2.004	-204.075	-172.735	25.779
400	41.538	248.209	238.124	4.034	-205.309	-168.173	21.961
450	43.317	253.206	239.526	6.156	-206.476	-163.460	18.974
500	44.933	257.855	241.129	8.363	-207.587	-158.621	16.571
600	47.641	266.297	244.635	12.997	-209.683	-148.628	12.939
700	49.714	273.804	248.275	17.870	-211.665	-138.295	10.320
800	51.291	280.550	251.895	22.924	-213.581	-127.682	8.337
900	52.496	286.664	255.424	28.116	-215.462	-116.831	6.781
1000	53.429	292.245	258.831	33.414	-217.324	-105.773	5.525
1100	54.160	297.373	262.105	38.795	-219.179	-94.527	4.489
1200	54.741	302.111	265.244	44.241	-221.035	-83.113	3.618
1300	55.208	306.512	268.251	49.739	-222.896	-71.545	2.875
1400	55.590	310.618	271.132	55.279	-224.764	-59.832	2.232
1500	55.904	314.464	273.894	60.855	-226.643	-47.986	1.671
1600	56.166	318.081	276.544	66.459	-228.534	-36.014	1.176
1700	56.387	321.493	279.089	72.087	-230.439	-23.923	0.735
1800	56.574	324.721	281.535	77.735	-232.360	-11.720	0.340
1900	56.734	327.784	283.889	83.400	-234.307	0.591	-0.016
2000	56.872	330.698	286.157	89.081	-236.252	13.004	-0.340
2100	56.992	333.476	288.345	94.774	-238.226	25.515	-0.635
2200	57.098	336.129	290.457	100.479	-240.218	38.121	-0.905
2300	57.191	338.670	292.498	106.193	-242.229	50.817	-1.154
2400	57.275	341.105	294.473	111.917	-244.260	63.602	-1.384
2500	57.351	343.445	296.386	117.648	-246.310	76.471	-1.598
2600	57.421	345.696	298.239	123.387	-248.380	89.424	-1.797
2700	57.487	347.864	300.037	129.132	-250.468	102.456	-1.982
2800	57.550	349.955	301.783	134.884	-252.574	115.566	-2.156
2900	57.612	351.977	303.479	140.642	-254.699	128.750	-2.319
3000	57.673	353.931	305.129	146.407	-256.840	142.010	-2.473
3100	57.735	355.823	306.733	152.177	-258.997	155.341	-2.617
3200	57.799	357.657	308.296	157.954	-261.169	168.740	-2.754
3300	57.866	359.436	309.819	163.737	-263.354	182.208	-2.884
3400	57.937	361.165	311.304	169.527	-265.553	195.744	-3.007
3500	58.012	362.845	312.753	175.324	-267.763	209.343	-3.124
3600	58.092	364.481	314.167	181.130	-269.983	223.006	-3.236
3700	58.178	366.074	315.548	186.943	-272.212	236.731	-3.342
3800	58.271	367.626	316.899	192.765	-274.449	250.577	-3.444
3900	58.370	369.141	318.219	198.597	-276.692	264.361	-3.541
4000	58.476	370.620	319.510	204.440	-278.940	278.262	-3.634
4100	58.590	372.066	320.775	210.293	-281.193	292.220	-3.723
4200	58.711	373.479	322.013	216.158	-283.448	306.233	-3.809
4300	58.840	374.862	323.226	222.035	-285.705	320.300	-3.891
4400	58.977	376.216	324.415	227.926	-287.963	334.419	-3.970
4500	59.121	377.543	325.581	233.831	-290.221	348.589	-4.046
4600	59.273	378.844	326.725	239.751	-292.478	362.809	-4.120
4700	59.432	380.121	327.847	245.686	-294.733	377.079	-4.191
4800	59.598	381.374	328.949	251.637	-296.987	391.397	-4.259
4900	59.771	382.604	330.032	257.606	-299.238	405.762	-4.325
5000	59.951	383.814	331.095	263.592	-301.486	420.173	-4.390
5100	60.136	385.003	332.141	269.596	-303.731	434.629	-4.452
5200	60.327	386.172	333.169	275.619	-305.973	449.127	-4.512
5300	60.523	387.323	334.179	281.662	-308.212	463.671	-4.570
5400	60.724	388.456	335.174	287.724	-310.448	478.255	-4.626
5500	60.930	389.573	336.153	293.807	-312.681	492.881	-4.681
5600	61.139	390.672	337.117	299.910	-314.913	507.548	-4.734
5700	61.351	391.756	338.066	306.035	-317.142	522.254	-4.785
5800	61.566	392.825	339.001	312.181	-319.371	537.001	-4.836
5900	61.783	393.879	339.922	318.348	-321.600	551.783	-4.885
6000	62.002	394.920	340.830	324.537	-323.831	566.606	-4.933

Electronic Levels and Quantum Weights

State	ϵ_i, cm⁻¹	g_i
[¹A₁]	[0]	[1]
[³B₁]	[22000]	[3]
[¹B₁]	[27000]	[1]

Vibrational Frequencies and Degeneracies
ν_i, cm⁻¹
[1320](1)
[750](1)
1244 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: N–O = [1.23 ± 0.04] Å
Bond Angle: O–N–O = 115° ± 3°
Product of the Moments of Inertia: $I_A I_B I_C = [2.59592 \times 10^{-115}]\ \text{g}^3\text{·cm}^6$

Enthalpy of Formation

The recent literature concerning the electron affinity of NO₂(g) is summarized in the following table.

Source	Technique	electron affinity NO₂(g), eV
1	magnetron technique, direct electron-capture process	3.99 ± 0.16
2	endothermic charge transfer reaction	>2.04, >3.063
3	endothermic charge transfer reaction	2.30 ± 0.15
4	photodetachment of e⁻ from NO₂⁻ in argon matrix	<3.9
5	reaction of NO₂⁻ with HCl and HBr in flowing after glow system	<2.6
6	correlation between heats of hydration and heterolytic bond dissociation energies	2.5
7	charge transfer reactions, flowing after glow system	2.38 ± 0.06

The early literature on the electron affinity of NO₂(g) is best summarized and referenced by Berkowitz et al.,[2] Ferguson, et al.[5] and Dunkin, et al.[7] Much of these early data are not only widely scattered but also conflicting.

The value chosen for the electron affinity of NO₂(g) is 2 38 ± 0.06 eV, based on the work of Dunkin et al.[7] This leads to $\Delta_f H°$(NO₂; g, 298.15 K) = -48.45 ± 1.38 kcal·mol⁻¹, using JANAF auxiliary data.

Heat Capacity and Entropy

The infrared spectrum of the NO₂⁻ ion isolated in an argon matrix was studied by Milligan et al.[4] and Milligan and Jacox.[8] They reported that the antisymmetric stretching fundamental was $\nu_3 = 1244$ cm⁻¹.

Hochstrasser and Marchetti,[9] in combination with data from Sidman,[10] reported $\nu_1 = 1325$ cm⁻¹, $\nu_2 = 831$ cm⁻¹ and $\nu_3 = 1243$ cm⁻¹ as the vibrational frequencies of the nitrite ion in solution. These frequencies are also very similar to the values reported for NO₂(g) by Herzberg.[12]

The ν_1 and ν_2 vibrational frequencies of NO₂⁻(g) were assumed to be the same as those for nitrite ion in solution. The value adopted for ν_3 was that of Milligan, et al.[4,8]

Milligan, et al.,[4,8] via studies of the infrared spectrum of NO₂⁻ ion isolated in an argon matrix, concluded that the isotopic data were consistent with a O–N–O angle of 115°. Hochstrasser and Marchetti,[9] relying on crystallographic data for NaNO₂(cr) collected by other investigators, reported the N–O bond distance as 1.23 ± 0.04 Å and the O–N–O bond angle as 115° ± 3°. The N–O bond distance in NO₂⁻(cr) is assumed to be the same as that reported for NaNO₂(cr).

The electronic states are estimated by analogy with the electronic levels of the isoelectronic molecule SO₂.[12]

References

1. A. L. Farragher, F. M. Page and R. C Wheeler, Disc Faraday Soc. 37, 203 (1964).
2. J. Berkowitz, W. A. Chupka and D. Gutman, J. Chem. Phys 55, 2733 (1971).
3. C. Lifshitz, B M. Hughes, and T. O. Tiernan, Chem. Phys. Letters 7, 469 (1970).
4. D. E. Milligan, H. E. Jacox and W. A. Guillory, J. Chem Phys. 52, 3864 (1970).

Nitrogen Oxide (NO₃) IDEAL GAS M_r = 62.0049 Nitrogen Oxide (NO₃) N₂O₃(g)

$S°(298.15 \text{ K}) = [252.619] \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = 77.53 \pm 20.9 \text{ kJ·mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = 71.13 \pm 20.9 \text{ kJ·mol}^{-1}$

Vibrational Frequencies and Degeneracies
ν, cm⁻¹

[1158](2)
[940](1)
[704](2)
[765](1)

Ground State Quantum Weight: 2 σ = [6]
Point Group: [D₃ₕ]
Bond Distance: O–N – [1.2] Å
Bond Angle: O–N–O – [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [5.311350 \times 10^{-115}] \text{ g}^3\text{·cm}^6$

Enthalpy of Formation

The enthalpy of formation is based on equilibrium constants for the reaction N₂O₅(g) → NO₃(g) + NO₂(g) obtained from shock wave studies by Schott and Davidson.[1] These equilibria give a 2nd law value of $\Delta_f H°(495 \text{ K}) = 21.5 \pm 1.4$ kcal·mol⁻¹, corresponding to $\Delta_f H°(298.15 \text{ K}) = 22.2$ kcal·mol⁻¹, and a 3rd law value of $\Delta_f H°(298.15 \text{ K}) = 22.2$ kcal·mol⁻¹. The resulting enthalpy of formation is 17.0 kcal·mol⁻¹.

Guillory and Johnston[2] report an equilibrium constant based on estimated Beer's law constants for NO₃ and attributed to the reaction O₂ + NO → NO₃. This gives a 3rd law heat of formation of 12 ± 2 kcal·mol⁻¹ which was not considered. A tentative value of 23 kcal·mol⁻¹ (or greater) may be derived from the $D°$ given by Ramsay.[3]

Heat Capacity and Entropy

The structure and frequencies are those estimated by Hisatsune.[4] A symmetry of D₃ₕ was chosen on the basis of Walsh's[5] correlation, and the bond distance was taken as 2% longer than in the nitrate ion. The planar mode frequencies were calculated from estimated Urey–Bradley force constants, while the out-of-plane wagging frequency (765 cm⁻¹) was assumed the same as in HNO₃(g).

There are several conflicting bits of information concerning NO₃ radicals. Chantry et al.[6] studied the electron resonance and optical absorption spectra of what appears to be NO₃ radicals trapped in crystals of urea nitrate. The authors suggest a planar structure without a threefold axis (thus C₂ or C₂ᵥ symmetry), at least for the trapped radicals. Guillory and Johnston[2] report for gaseous NO₃ radicals an infrared frequency at 1840 cm⁻¹ which they assign as the N–O stretch. The similarity of this frequency to those in N–O and X–N–O molecules led the authors to suggest an OONO structure (thus C₅ symmetry) rather than the nitrate structure. The remaining frequencies for such a structure may be crudely estimated by analogy with those measured for (NO)₂ by Smith et al.[7] Based on such frequencies and assumed bond distances, the room temperature entropy for the OONO structure would be 68–72 cal·K⁻¹·mol⁻¹. Such an entropy is quite inconsistent with the 2nd law $\Delta_5 S°(495 \text{ K}) = 33.2 \pm 3$ cal·K⁻¹·mol⁻¹ for N₂O₅(g) → NO₃(g) + NO₂(g) obtained from the shock wave studies of Schott and Davidson. The Hisatsune functions based on the nitrate structure were selected because they are consistent with the experimental entropy. The principal moments of inertia for this structure are $I_A = I_B = 6.4277 \times 10^{-39}$ and $I_C = 12.8555 \times 10^{-39}$ g·cm². A structure of C₅ symmetry would result if the nitrate structure were distorted to give one non-equivalent oxygen. Ramsay[3] suggests that such distortion can only be small, based on the high dispersion optical spectra of the gas phase.

References

[1]G. Schott and N. Davidson, J. Amer. Chem. Soc. 80, 1841 (1958).
[2]W. Guillory and H. S. Johnston, J. Amer. Chem. Soc. 85, 1695 (1963).
[3]D. A. Ramsay, Proc. 10th Colloq. Spect. Intnl. (1962), Univ. Maryland, pp. 583–596, (1963).
[4]I. C. Hisatsune, J. Phys. Chem. 65, 2249 (1961).
[5]A. D. Walsh, J. Chem. Soc. 1953, 2301 (1953).
[6]G. W. Chantry, A. Horsfield, J. R. Morton and D. H. Whiffen, Mol. Phys. 5, 589 (1962).
[7]A. L. Smith, W. E. Keller and H. L. Johnston, J. Chem. Phys. 19, 189 (1951).

Enthalpy Reference Temperature = T_r = 298.15 K · Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	-10.959	77.529	77.529	INFINITE
100	33.345	211.871	288.193	-7.632	75.048	87.847	-45.887
200	37.739	235.888	256.603	-4.143	72.715	101.581	-26.530
250	42.240	244.778	253.366	-2.147	71.797	108.909	-22.755
298.15	46.934	252.619	252.619	0.	71.128	116.121	-20.344
300	47.113	252.910	252.620	0.087	71.106	116.400	-20.267
350	51.765	260.527	253.211	2.561	70.637	123.989	-18.504
400	55.929	267.717	254.579	5.255	70.359	131.631	-17.189
450	59.533	274.519	256.420	8.144	70.240	139.299	-16.169
500	62.601	280.954	258.555	11.200	70.246	146.973	-15.354
600	67.380	292.815	263.295	17.712	70.527	162.297	-14.129
700	70.793	303.472	268.286	24.630	71.042	177.554	-13.249
800	73.266	313.095	273.296	31.840	71.691	192.726	-12.584
900	75.095	321.836	278.211	39.262	72.417	207.813	-12.061
1000	76.476	329.822	282.979	46.844	73.186	222.816	-11.639
1100	77.539	337.163	287.576	54.547	73.977	237.741	-11.289
1200	78.373	343.947	291.994	62.344	74.776	252.593	-10.995
1300	79.037	350.248	296.236	70.216	75.576	267.379	-10.743
1400	79.573	356.125	300.306	78.147	76.371	282.103	-10.525
1500	80.013	361.631	304.213	86.127	77.155	296.771	-10.334
1600	80.377	366.807	307.965	94.147	77.925	311.387	-10.166
1700	80.682	371.689	311.571	102.200	78.678	325.955	-10.015
1800	80.939	376.308	315.040	110.282	79.411	340.479	-9.880
1900	81.159	380.690	318.381	118.387	80.122	354.963	-9.759
2000	81.348	384.858	321.602	126.513	80.809	369.411	-9.648
2100	81.511	388.831	324.709	134.656	81.472	383.825	-9.547
2200	81.653	392.626	327.711	142.814	82.108	398.208	-9.455
2300	81.777	396.259	330.613	150.986	82.717	412.562	-9.370
2400	81.887	399.741	333.421	159.169	83.298	426.890	-9.291
2500	81.984	403.086	336.141	167.363	83.851	441.195	-9.218
2600	82.070	406.303	338.778	175.565	84.376	455.478	-9.151
2700	82.147	409.402	341.337	183.776	84.873	469.743	-9.088
2800	82.216	412.391	343.822	191.994	85.343	483.989	-9.029
2900	82.278	415.277	346.236	200.219	85.785	498.217	-8.974
3000	82.334	418.067	348.584	208.450	86.200	512.432	-8.922
3100	82.385	420.768	350.869	216.686	86.590	526.634	-8.874
3200	82.431	423.384	353.095	224.927	86.954	540.822	-8.828
3300	82.473	425.922	355.263	233.172	87.293	555.000	-8.785
3400	82.512	428.384	357.378	241.421	87.608	569.169	-8.744
3500	82.547	430.777	359.441	249.674	87.901	583.327	-8.706
3600	82.580	433.102	361.455	257.931	88.171	597.479	-8.669
3700	82.609	435.365	363.422	266.190	88.419	611.622	-8.635
3800	82.637	437.569	365.345	274.452	88.647	625.761	-8.602
3900	82.663	439.716	367.224	282.717	88.854	639.893	-8.570
4000	82.686	441.809	369.063	290.985	89.042	654.019	-8.541
4100	82.708	443.851	370.862	299.255	89.210	668.142	-8.512
4200	82.728	445.844	372.624	307.526	89.360	682.260	-8.485
4300	82.747	447.791	374.349	315.800	89.491	696.376	-8.459
4400	82.765	449.694	376.040	324.076	89.603	710.487	-8.435
4500	82.782	451.554	377.697	332.353	89.698	724.597	-8.411
4600	82.797	453.373	379.323	340.632	89.774	738.704	-8.388
4700	82.812	455.154	380.917	348.913	89.831	752.811	-8.367
4800	82.825	456.898	382.482	357.194	89.869	766.917	-8.346
4900	82.838	458.606	384.018	365.478	89.887	781.023	-8.326
5000	82.850	460.279	385.527	373.762	89.886	795.127	-8.307
5100	82.862	461.920	387.009	382.048	89.863	809.233	-8.288
5200	82.872	463.529	388.465	390.334	89.819	823.337	-8.271
5300	82.883	465.108	389.896	398.622	89.753	837.445	-8.254
5400	82.892	466.657	391.303	406.911	89.662	851.552	-8.237
5500	82.901	468.178	392.687	415.201	89.547	865.662	-8.221
5600	82.910	469.672	394.049	423.491	89.406	879.776	-8.206
5700	82.918	471.140	395.388	431.782	89.237	893.890	-8.192
5800	82.926	472.582	396.707	440.075	89.040	908.010	-8.178
5900	82.933	474.000	398.005	448.368	88.811	922.129	-8.164
6000	82.940	475.393	399.283	456.661	88.550	936.257	-8.151

Nitrogen Oxide (NO₃)

Phosphorus Nitride (PN)

IDEAL GAS $M_r = 44.98046$ $N_1P_1(g)$

$S°(298.15\ K) = 211.137\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 105\ 77 \pm 5.0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 104.78 \pm 5\ 0\ kJ·mol^{-1}$

Electronic Level and Multiplicity

State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 1337.24$ cm^{-1} $\omega_e x_e = 6.983$ cm^{-1} $\sigma = 1$
$B_e = 0.7862$ cm^{-1} $\alpha_e = 0.00557$ cm^{-1} $r_e = 1.4910$ Å

Enthalpy of Formation

The selected $\Delta_f H°(298.15\ K)$ was calculated from the $D_0° = 165\ 8 \pm 1.2$ kcal·mol^{-1} reported by Potter and DiStefano.[1] $D_0° = 163.7 \pm 1.2$ kcal·mol^{-1} was experimentally determined by Huffman et al.[2] The $D_0°$ reported by Huffman et al.[2] was derived using a pressure–composition method, i.e., measurement of equilibrium vapor pressure, at 1173 K for the reaction [PN(g) → P$_2$(g) + N$_2$(g)]. Potter and DiStefano[1] recalculated Huffman's results to obtain their $D_0°$ value. Gaydon[3] lists a $D_0° = 138.4 \pm 19$ kcal·mol^{-1} The corresponding enthalpy of formation are:

Source	$\Delta_f H°$(298.15 K), kcal·mol^{-1}
Potter and DiStefano[1]	25.0 ± 1.2
Huffman et al.[2]	27.1 ± 1.2
Gaydon[3]	53 ± 19

Heat Capacity and Entropy

The molecular constants are taken from Herzburg.[4]

References

[1] R. L. Potter and V. N. DiStefano, J. Phys. Chem. 65, 849 (1961).
[2] E. O. Huffman, G. Tarbutton, K. L. Elmore, W. E. Cate, H K Walters, Jr., and G. V Elmore, J. Amer. Chem. Soc. 76, 6329 (1954).
[3] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall (1953).
[4] G Herzburg, "Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., 2nd Ed. (1960).

Phosphorus Nitride (PN) $N_1P_1(g)$ Standard State Pressure = $p° = 0.1$ MPa

Enthalpy Reference Temperature = T_r = 298.15 K

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
	(J·K^{-1}·mol^{-1})			(kJ·mol^{-1})			
0	0.	0.	INFINITE	-8.703	105.772	105.772	INFINITE
100	29.105	179.230	237.189	-5.796	106.341	98.177	-51.282
200	29.168	199.412	213.832	-2.884	105.534	90.075	-23.525
250	29.361	205.938	211.624	-1.422	105.177	86.251	-18.021
298.15	29.710	211.137	211.137	0.	104.780	82.641	-14.478
300	29.726	211.321	211.138	0.055	104.764	82.503	-14.365
350	30.230	215.940	211.501	1.553	103.598	78.899	-11.775
400	30.809	220.013	212.315	3.079	103.077	75.407	-9.847
450	31.409	223.677	213.378	4.635	102.584	71.978	-8.355
500	31.991	227.017	214.577	6.220	102.116	68.603	-7.167
600	33.033	232.944	217.157	9.473	101.244	61.983	-5.396
700	33.879	238.102	219.788	12.820	100.437	55.504	-4.142
800	34.548	242.672	222.369	16.242	99.673	49.138	-3.208
900	35.075	246.772	224.856	19.725	98.934	42.866	-2.488
1000	35.494	250.490	227.237	23.254	98.211	36.675	-1.916
1100	35.830	253.890	229.507	26.821	97.496	30.556	-1.451
1200	36.103	257.019	231.671	30.418	33.214	25.580	-1.113
1300	36.328	259.918	233.734	34.040	33.281	24.941	-1.002
1400	36.516	262.618	235.702	37.682	33.344	24.297	-0.907
1500	36.675	265.143	237.581	41.342	33.403	23.649	-0.824
1600	36.812	267.514	239.379	45.016	33.458	22.996	-0.751
1700	36.930	269.749	241.100	48.704	33.509	22.341	-0.686
1800	37.033	271.863	242.751	52.402	33.556	21.683	-0.629
1900	37.124	273.868	244.336	56.110	33.600	21.022	-0.578
2000	37.206	275.774	245.861	59.826	33.642	20.359	-0.532
2100	37.279	277.591	247.329	63.551	33.680	19.694	-0.490
2200	37.346	279.327	248.744	67.282	33.716	19.027	-0.452
2300	37.407	280.988	250.110	71.020	33.750	18.358	-0.417
2400	37.463	282.582	251.430	74.763	33.781	17.688	-0.385
2500	37.515	284.112	252.707	78.512	33.811	17.017	-0.356
2600	37.563	285.584	253.944	82.266	33.839	16.345	-0.328
2700	37.608	287.003	255.142	86.024	33.866	15.672	-0.303
2800	37.651	288.371	256.304	89.787	33.891	14.997	-0.280
2900	37.692	289.693	257.433	93.555	33.915	14.322	-0.258
3000	37.730	290.972	258.530	97.326	33.937	13.646	-0.238
3100	37.767	292.210	259.596	101.101	33.959	12.969	-0.219
3200	37.802	293.409	260.634	104.879	33.979	12.292	-0.201
3300	37.836	294.573	261.645	108.661	33.999	11.614	-0.184
3400	37.869	295.703	262.630	112.446	34.018	10.935	-0.168
3500	37.900	296.801	263.591	116.235	34.036	10.256	-0.153
3600	37.931	297.869	264.529	120.026	34.053	9.577	-0.139
3700	37.961	298.909	265.444	123.821	34.069	8.896	-0.126
3800	37.990	299.922	266.338	127.618	34.085	8.216	-0.113
3900	38.018	300.909	267.212	131.419	34.100	7.535	-0.101
4000	38.046	301.872	268.066	135.222	34.115	6.854	-0.089
4100	38.073	302.811	268.902	139.028	34.129	6.172	-0.079
4200	38.099	303.729	269.721	142.836	34.143	5.490	-0.068
4300	38.125	304.626	270.522	146.648	34.156	4.807	-0.058
4400	38.151	305.503	271.307	150.461	34.168	4.125	-0.049
4500	38.176	306.360	272.076	154.278	34.180	3.442	-0.040
4600	38.201	307.200	272.831	158.097	34.192	2.759	-0.031
4700	38.226	308.022	273.571	161.918	34.203	2.075	-0.023
4800	38.250	308.827	274.297	165.742	34.214	1.391	-0.015
4900	38.274	309.616	275.010	169.568	34.224	0.708	-0.008
5000	38.298	310.389	275.710	173.397	34.234	0.023	-0.000
5100	38.321	311.148	276.397	177.228	34.243	-0.661	0.007
5200	38.345	311.892	277.073	181.061	34.251	-1.345	0.014
5300	38.368	312.623	277.737	184.897	34.259	-2.030	0.020
5400	38.391	313.340	278.389	188.735	34.267	-2.715	0.026
5500	38.414	314.045	279.031	192.575	34.274	-3.400	0.032
5600	38.436	314.737	279.663	196.417	34.280	-4.085	0.038
5700	38.459	315.418	280.284	200.262	34.285	-4.770	0.044
5800	38.481	316.087	280.895	204.109	34.290	-5.455	0.049
5900	38.503	316.745	281.497	207.958	34.294	-6.140	0.054
6000	38.525	317.392	282.090	211.810	34.296	-6.826	0.059

PREVIOUS: September 1962 (1 atm)   CURRENT September 1962 (1 bar)

Nitrogen Sulfide (SN) IDEAL GAS M_r = 46.0667 Nitrogen Sulfide (NS) NS(g)

$S°(298.15 K) = 222.087$ J·K⁻¹·mol⁻¹

$\Delta_f H°(0\ K) = 262.9 \pm 105$ kJ·mol⁻¹
$\Delta_f H°(298.15\ K) = 263.6 \pm 105$ kJ·mol⁻¹

Electronic Levels and Multiplicities

State	ϵ_i, cm⁻¹	g_i
$^2\Pi_r$	0	2
	223	2

$\omega_e = 1220.0$ cm⁻¹ $\omega_e x_e = 7.75$ cm⁻¹ $\sigma = 1$
$B_e = [0.7762]$ cm⁻¹ $\alpha_e = [0.0064]$ cm⁻¹ $r_e = 1.495(7)$ Å

Enthalpy of Formation

The dissociation energy is listed by Gaydon.[1]

Heat Capacity and Entropy

The spectroscopic constants other than B_e and α_e are from Herzberg,[2] r_e is from Bowen[3] and has been used, together with the equation
$\alpha_e = 6(\sqrt{\omega_e x_e B_e^3} - 6B_e^2)/\omega_e^2$ to calculate B_e and α_e.

References

[1] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Ed., Chapman and Hall, London (1953).
[2] G. Herzberg, "Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Company, New York (1950).
[3] H. J. M. Bowen, Tables of Interatomic Distances and Configuration in Molecules and Ions, The Chemical Society, London (1958).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C°_p$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	-9.397	262.942	262.942	INFINITE
100	32.301	186.768	250.632	-6.386	263.812	254.378	-132.873
200	32.201	209.348	224.999	-3.130	263.971	244.827	-63.942
250	31.833	216.488	222.611	-1.531	263.823	240.056	-50.157
298.15	31.793	222.087	222.087	0.	263.592	235.498	-41.258
300	31.797	222.284	222.088	0.059	263.582	235.324	-40.974
350	32.020	227.200	222.476	1.653	263.282	230.637	-34.421
400	32.391	231.498	223.340	3.263	260.731	226.084	-29.524
450	32.824	235.338	224.464	4.894	259.703	221.806	-25.747
500	33.267	238.820	225.728	6.546	258.615	217.656	-22.738
600	34.081	244.959	228.435	9.914	256.907	209.632	-18.250
700	34.751	250.265	231.183	13.357	255.482	201.868	-15.064
800	35.284	254.941	233.866	16.860	254.219	194.297	-12.686
900	35.704	259.122	236.444	20.410	199.924	187.958	-10.909
1000	36.039	262.902	238.904	23.998	200.036	186.622	-9.748
1100	36.308	266.350	241.245	27.616	200.133	185.276	-8.798
1200	36.529	269.519	243.471	31.258	200.214	183.922	-8.006
1300	36.713	272.450	245.589	34.920	200.277	182.562	-7.335
1400	36.867	275.177	247.606	38.600	200.322	181.197	-6.761
1500	36.999	277.725	249.530	42.293	200.348	179.830	-6.262
1600	37.114	280.117	251.367	45.999	200.356	178.462	-5.826
1700	37.214	282.370	253.125	49.715	200.347	177.094	-5.441
1800	37.303	284.499	254.810	53.441	200.322	175.726	-5.099
1900	37.383	286.519	256.426	57.176	200.282	174.361	-4.794
2000	37.455	288.438	257.979	60.918	200.228	172.998	-4.518
2100	37.521	290.267	259.473	64.667	200.162	171.638	-4.269
2200	37.582	292.014	260.913	68.422	200.085	170.282	-4.043
2300	37.639	293.686	262.302	72.183	199.997	168.929	-3.836
2400	37.691	295.289	263.643	75.949	199.900	167.580	-3.647
2500	37.741	296.828	264.940	79.721	199.795	166.236	-3.473
2600	37.788	298.310	266.195	83.498	199.683	164.895	-3.313
2700	37.833	299.737	267.411	87.279	199.564	163.560	-3.164
2800	37.875	301.113	268.590	91.064	199.439	162.228	-3.026
2900	37.916	302.443	269.735	94.854	199.309	160.902	-2.898
3000	37.955	303.729	270.847	98.647	199.174	159.580	-2.779
3100	37.993	304.974	271.928	102.445	199.035	158.262	-2.667
3200	38.030	306.181	272.979	106.246	198.892	156.949	-2.562
3300	38.066	307.352	274.003	110.051	198.746	155.641	-2.464
3400	38.101	308.489	275.001	113.859	198.596	154.337	-2.371
3500	38.135	309.594	275.974	117.671	198.442	153.037	-2.284
3600	38.168	310.669	276.922	121.486	198.286	151.742	-2.202
3700	38.201	311.715	277.849	125.304	198.126	150.451	-2.124
3800	38.233	312.734	278.753	129.126	197.963	149.165	-2.050
3900	38.265	313.727	279.637	132.951	197.796	147.883	-1.981
4000	38.296	314.697	280.502	136.779	197.626	146.605	-1.914
4100	38.326	315.643	281.347	140.610	197.452	145.332	-1.852
4200	38.357	316.567	282.175	144.444	197.275	144.063	-1.792
4300	38.386	317.469	282.985	148.281	197.093	142.798	-1.735
4400	38.416	318.352	283.779	152.122	196.907	141.538	-1.680
4500	38.445	319.216	284.557	155.965	196.717	140.281	-1.628
4600	38.474	320.061	285.320	159.811	196.523	139.029	-1.579
4700	38.503	320.889	286.068	163.660	196.323	137.782	-1.531
4800	38.532	321.700	286.802	167.511	196.119	136.538	-1.486
4900	38.560	322.495	287.522	171.366	195.909	135.299	-1.442
5000	38.588	323.274	288.229	175.223	195.694	134.064	-1.401
5100	38.616	324.038	288.924	179.083	195.474	132.834	-1.360
5200	38.644	324.789	289.607	182.946	195.247	131.608	-1.322
5300	38.671	325.525	290.277	186.812	195.015	130.386	-1.285
5400	38.699	326.248	290.937	190.681	194.776	129.169	-1.249
5500	38.726	326.958	291.585	194.552	194.532	127.956	-1.215
5600	38.753	327.656	292.223	198.426	194.281	126.748	-1.182
5700	38.780	328.343	292.851	202.303	194.023	125.544	-1.150
5800	38.807	329.017	293.469	206.182	193.759	124.345	-1.120
5900	38.834	329.681	294.077	210.064	193.488	123.151	-1.090
6000	38.861	330.334	294.676	213.949	193.211	121.961	-1.062

PREVIOUS: June 1961 (1 atm) CURRENT: June 1961 (1 bar)

Nitrogen Sulfide (NS) NS(g)

Silicon Nitride (SiN)   IDEAL GAS $M_r = 42.0922$

N₁Si₁(g)

$S^\circ(298.15\ K) = 216.812\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$

$\Delta_f H^\circ(0\ K) = 371.20 \pm 62.8\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_f H^\circ(298.15\ K) = 372.38 \pm 62.8\ \mathrm{kJ\cdot mol^{-1}}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm⁻¹	g_i
²Σ⁺	0	2
	[6000]	4
	24299.4	2
	[31000]	4

$\omega_e = 1150.8\ \mathrm{cm^{-1}}$ $\omega_e x_e = 6.55\ \mathrm{cm^{-1}}$ $\sigma = 1$
$B_e = 0.7299\ \mathrm{cm^{-1}}$ $\alpha_e = 0.00567\ \mathrm{cm^{-1}}$ $r_e = 1.5718\ \mathrm{Å}$

Enthalpy of Formation

A linear Birge–Sponer extrapolation of the ground state gives a dissociation energy of 142.9 kcal·mol⁻¹. The ground state can correlate with normal atoms Si(³P) + N(⁴S) or with Si(³P) + N(²D), in this latter case D_0° would be 88 kcal·mol⁻¹. The uncertainty in the extrapolation is quite large, ± 30 kcal·mol⁻¹, since only 6 levels, of the estimated total of 87 levels, are observed.

A dissociation energy can also be calculated from the B²Σ state by a much shorter extrapolation. This extrapolation is done graphically since some curvature is evident in the first six levels. A value of D_0° (B²Σ) = 50.4 kcal·mol⁻¹ is obtained. This corresponds to D_0°(X²Σ) = 119.9 kcal·mol⁻¹ for normal products or D_0° (X²Σ) = 65 kcal·mol⁻¹ for excited nitrogen as a product. The uncertainty in this extrapolation is less than the ground state and is probably ± 20 kcal·mol⁻¹.

An estimate of D_0° (SiN) may be obtained by equating D_0° (SiN)/D_0° (SiO) = D_0° (CN)/D_0° (CO): this yields D_0° (SiN) = 135 kcal·mol⁻¹.

A comparison of the isoelectronic molecules CP, BS and BeCl and the related molecules CN, BO, BeF indicates D_0° (SiN) > 115 kcal·mol⁻¹.

A value of D_0° (SiN) = 130 ± 15 kcal·mol⁻¹ is in agreement within the uncertainties of both ground state and B state extrapolations assuming normal atoms as products, and is in agreement with the other estimates. This value is adopted and yields $\Delta_f H^\circ$(SiN, g, 298.15 K) = 89 kcal·mol⁻¹.

Heat Capacity and Entropy

The B–X transition has been reported by Jenkins and de Laszlo.[1] The rotational and vibrational constants are derived from their work and adjusted to normal isotopic abundance. The A²Π–C²Π transition has been observed by Shetlar.[2] The height of the A state is estimated by correlation with CP(g). The level of the B state is taken from Herzberg.[3]

References

[1] F. A. Jenkins and H. de Laszlo, Proc. Roy. Soc. (London) 122, 103 (1929).
[2] M. D. Shetlar, Ph.D. Thesis, Univ. of California, Berkeley (1965).
[3] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., 2nd Edition, New York, (1950).

Silicon Nitride (SiN)

	Enthalpy Reference Temperature = T_r = 298.15 K (J·K⁻¹·mol⁻¹)				Standard State Pressure = p° = 0.1 MPa (kJ·mol⁻¹)		
T/K	C_p°	S°	$-(G^\circ-H^\circ(T_r))/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log K_f$
0	0.	0.	INFINITE	-8.733	371.197	371.197	INFINITE
100	29.106	184.787	243.038	-5.825	372.387	362.282	-189.237
200	29.267	204.984	219.537	-2.910	372.667	352.002	-91.934
250	29.630	211.550	217.306	-1.439	372.561	346.845	-72.469
298.15	30.168	216.812	216.812	0.	372.376	341.909	-59.901
300	30.191	216.999	216.813	0.056	372.368	341.720	-59.499
350	30.859	221.703	217.183	1.582	372.130	336.630	-50.239
400	31.551	225.868	218.013	3.142	371.874	331.576	-43.299
450	32.213	229.623	219.098	4.736	371.611	326.554	-37.905
500	32.818	233.049	220.324	6.362	371.347	321.562	-33.593
600	33.832	239.126	222.964	9.697	370.814	311.655	-27.132
700	34.616	244.403	225.658	13.121	370.269	301.838	-22.523
800	35.234	249.067	228.298	16.615	369.698	292.101	-19.072
900	35.752	253.248	230.842	20.165	369.098	282.437	-16.392
1000	36.222	257.039	233.275	23.764	368.466	272.841	-14.252
1100	36.683	260.513	235.596	27.409	367.807	263.311	-12.504
1200	37.156	263.725	237.808	31.101	367.125	253.841	-11.049
1300	37.652	266.718	239.918	34.841	366.428	244.429	-9.821
1400	38.173	269.528	241.933	38.632	365.720	235.071	-8.771
1500	38.713	272.180	243.862	42.476	365.006	225.764	-7.862
1600	39.264	274.696	245.711	46.375	364.289	216.504	-7.068
1700	39.814	277.093	247.487	50.329	313.395	207.736	-6.383
1800	40.355	279.384	249.196	54.338	312.910	201.535	-5.848
1900	40.877	281.580	250.843	58.399	312.467	195.360	-5.371
2000	41.372	283.689	252.433	62.512	312.066	189.207	-4.942
2100	41.834	285.719	253.970	66.673	311.705	183.073	-4.554
2200	42.258	287.675	255.458	70.878	311.380	176.956	-4.201
2300	42.642	289.562	256.900	75.123	311.089	170.852	-3.880
2400	42.984	291.384	258.299	79.405	310.829	164.760	-3.586
2500	43.285	293.145	259.658	83.719	310.595	158.679	-3.315
2600	43.544	294.848	260.979	88.060	310.384	152.607	-3.066
2700	43.765	296.496	262.264	92.426	310.192	146.542	-2.835
2800	43.948	298.091	263.515	96.812	310.016	140.484	-2.621
2900	44.097	299.636	264.734	101.215	309.853	134.433	-2.421
3000	44.215	301.133	265.923	105.630	309.699	128.386	-2.235
3100	44.304	302.584	267.082	110.057	309.553	122.345	-2.061
3200	44.368	303.992	268.214	114.490	309.411	116.308	-1.899
3300	44.409	305.358	269.319	118.929	309.271	110.276	-1.746
3400	44.430	306.684	270.398	123.372	309.131	104.248	-1.602
3500	44.435	307.972	271.453	127.815	308.990	98.224	-1.466
3600	44.425	309.224	272.485	132.258	-75.306	102.665	-1.490
3700	44.402	310.440	273.495	136.699	-75.040	107.605	-1.519
3800	44.370	311.624	274.483	141.138	-74.781	112.538	-1.547
3900	44.330	312.776	275.450	145.573	-74.529	117.464	-1.573
4000	44.283	313.898	276.397	150.004	-74.284	122.383	-1.598
4100	44.231	314.991	277.325	154.430	-74.047	127.297	-1.622
4200	44.176	316.056	278.235	158.850	-73.819	132.205	-1.644
4300	44.118	317.095	279.126	163.265	-73.598	137.108	-1.666
4400	44.059	318.108	280.001	167.673	-73.414	142.006	-1.686
4500	44.000	319.098	280.859	172.076	-73.178	146.898	-1.705
4600	43.941	320.064	281.700	176.473	-72.980	151.787	-1.724
4700	43.883	321.009	282.527	180.865	-72.789	156.671	-1.741
4800	43.827	321.932	283.338	185.250	-72.605	161.551	-1.758
4900	43.772	322.835	284.135	189.630	-72.428	166.428	-1.774
5000	43.721	323.719	284.918	194.005	-72.257	171.300	-1.790
5100	43.672	324.584	285.687	198.374	-72.093	176.170	-1.804
5200	43.626	325.432	286.443	202.739	-71.935	181.036	-1.819
5300	43.584	326.262	287.187	207.100	-71.783	185.900	-1.832
5400	43.544	327.077	287.918	211.456	-71.637	190.760	-1.845
5500	43.508	327.875	288.637	215.808	-71.496	195.618	-1.858
5600	43.476	328.659	289.345	220.158	-71.360	200.474	-1.870
5700	43.447	329.428	290.042	224.504	-71.230	205.327	-1.882
5800	43.422	330.184	290.727	228.847	-71.106	210.177	-1.893
5900	43.400	330.926	291.402	233.188	-70.986	215.026	-1.904
6000	43.382	331.655	292.067	237.528	-70.872	219.873	-1.914

PREVIOUS: March 1967 (1 atm)   CURRENT March 1967 (1 bar)

Silicon Nitride (Si₂N)   IDEAL GAS $M_r = 70.1777$ Silicon Nitride (Si₂N)   N₁Si₂(g)

$S°(298.15\ \text{K}) = [256.487 \pm 8.4]\ \text{J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0\ \text{K}) = 396.43 \pm 20.9\ \text{kJ·mol}^{-1}$
$\Delta_f H°(298.15\ \text{K}) = 397.48 \pm 20.9\ \text{kJ·mol}^{-1}$

Electronic Levels and Quantum Weights

ε, cm⁻¹	g_i
0	[4]
[24000]	[4]
[28000]	[2]

Vibrational Frequencies and Degeneracies
ν, cm⁻¹
[600](1)
[240](2)
[1000](1)

Point Group [D∞h] $\sigma = 2$
Bond Distance: Si–N = [170] Å
Bond Angle: Si–N–Si = [180]°
Rotational Constant: $B_0 = [0.103845]$ cm⁻¹

Enthalpy of Formation

Zmbov and Margrave[1] have identified Si₂N(g) in a mass spectrometer. They also determined partial pressures of Si₂N(g) in equilibrium with Si(g) and N₂(g). From four of these measurements, in the temperature range 1742–1846 K, we obtain a 2nd law $\Delta_f H°(298.15\ \text{K}) = 99.6 \pm 6$ kcal·mol⁻¹ for the reaction Si₂N(g) = 2 Si(g) + 0.5 N₂(g), and a 3rd law $\Delta_f H°(298.15\ \text{K}) = 120.2$ kcal·mol⁻¹ with a drift of -11.4 ± 3.4 cal·K⁻¹·mol⁻¹. Considering the small temperature range and the uncertainties in the free energy functions, the data appear consistent. We adopt the 3rd law enthalpy of reaction which yields $\Delta_f H°(\text{Si}_2\text{N, g}, 298.15\ \text{K}) = 95$ kcal·mol⁻¹.

Heat Capacity and Entropy

Si₂N(g) is considered to be closely related to C₂N(g), and its structure and electronic configuration are adopted by analogy to this species. The bond length was obtained by adding the difference between the bond distances of SiN(g) and CN(g) to the bond length in CNC(g). The vibrational frequencies were estimated by comparson with several molecules, CNC(g); state of C₃ (g), NCN(g); and Si₂C(g). It should be noted that there is a wide variation in observed frequencies for these molecules and ν_1 and ν_3 may be significantly different from the chosen values.

The electronic ground state is considered to be $^2\pi_g$ with excited states of $^2\Delta_u$ and $^2\Sigma_u^-$ as in the case of CNC(g). The levels are obtained from those in CNC(g) by use of the shift between C₃(g) and SiCSi(g).

Reference

[1]K. F. Zmbov and J. L. Margrave, Rice University, personal communication, (March 1967).

Standard State Pressure = $p° = 0.1$ MPa

Enthalpy Reference Temperature = $T_r = 298.15$ K

T/K	C°p	S°	-(G°-H°(Tr))/T	H°-H°(Tr)	ΔfH°	ΔfG°	log Kf
		J·K⁻¹·mol⁻¹		kJ·mol⁻¹			
0	0.	0.	INFINITE	-11.822	396.430	396.430	INFINITE
100	35.904	209.763	296.993	-8.723	397.545	385.325	-201.273
200	44.596	237.627	260.893	-4.653	397.802	372.941	-97.402
250	47.543	247.906	257.295	-2.347	397.680	366.736	-76.625
298.15	49.884	256.487	256.487	0.	397.480	360.795	-63.210
300	49.965	256.795	256.488	0.092	397.471	360.567	-62.780
350	51.951	264.652	257.104	2.642	397.223	354.436	-52.897
400	53.570	271.699	258.495	5.281	396.959	348.341	-45.489
450	54.886	278.087	260.323	7.994	396.690	342.280	-39.731
500	55.958	283.927	262.395	10.766	396.418	336.249	-35.128
600	57.554	294.280	266.869	16.447	395.855	324.268	-28.230
700	58.648	303.239	271.439	22.260	395.251	312.384	-23.310
800	59.420	311.124	275.917	28.166	394.584	300.590	-19.627
900	59.981	318.156	280.226	34.137	393.843	288.883	-16.766
1000	60.399	324.499	284.342	40.157	393.021	277.266	-14.483
1100	60.718	330.271	288.259	46.214	392.117	265.734	-12.619
1200	60.966	335.565	291.983	52.298	391.130	254.287	-11.069
1300	61.163	340.453	295.526	58.405	390.059	242.926	-9.761
1400	61.321	344.992	298.899	64.529	388.902	231.651	-8.643
1500	61.450	349.227	302.115	70.668	387.658	220.462	-7.677
1600	61.557	353.196	305.185	76.819	386.327	209.359	-6.835
1700	61.646	356.931	308.120	82.979	284.554	199.235	-6.122
1800	61.721	360.457	310.930	89.147	283.509	194.246	-5.637
1900	61.785	363.795	313.626	95.323	282.460	189.316	-5.205
2000	61.840	366.966	316.214	101.504	281.408	184.440	-4.817
2100	61.887	369.984	318.703	107.690	280.353	179.618	-4.468
2200	61.928	372.864	321.100	113.881	279.295	174.846	-4.151
2300	61.965	375.618	323.411	120.076	278.233	170.122	-3.864
2400	61.997	378.256	325.642	126.274	277.170	165.444	-3.601
2500	62.025	380.787	327.797	132.475	276.103	160.811	-3.360
2600	62.051	383.220	329.882	138.679	275.035	156.220	-3.139
2700	62.075	385.563	331.902	144.883	273.964	151.671	-2.934
2800	62.097	387.821	333.859	151.094	272.891	147.161	-2.745
2900	62.118	390.000	335.757	157.305	271.817	142.690	-2.570
3000	62.137	392.106	337.601	163.517	270.741	138.255	-2.407
3100	62.156	394.144	339.392	169.732	269.663	133.857	-2.255
3200	62.175	396.118	341.134	175.949	268.584	129.493	-2.114
3300	62.194	398.031	342.829	182.167	267.504	125.163	-1.981
3400	62.214	399.888	344.480	188.388	266.423	120.866	-1.857
3500	62.234	401.692	346.089	194.610	265.341	116.601	-1.740
3600	62.255	403.445	347.658	200.834	-504.045	133.288	-1.934
3700	62.278	405.151	349.189	207.061	-504.299	150.995	-2.132
3800	62.302	406.813	350.684	213.290	-504.557	168.709	-2.319
3900	62.327	408.431	352.144	219.521	-504.817	186.430	-2.497
4000	62.355	410.010	353.571	225.755	-505.079	204.158	-2.666
4100	62.384	411.550	354.966	231.992	-505.342	221.892	-2.827
4200	62.416	413.053	356.331	238.232	-505.604	239.633	-2.980
4300	62.450	414.522	357.668	244.476	-505.866	257.379	-3.127
4400	62.486	415.959	358.976	250.722	-506.126	275.132	-3.266
4500	62.524	417.363	360.258	256.973	-506.384	292.891	-3.400
4600	62.566	418.738	361.515	263.227	-506.639	310.656	-3.528
4700	62.609	420.084	362.746	269.486	-506.891	328.426	-3.650
4800	62.655	421.402	363.955	275.749	-507.139	346.201	-3.767
4900	62.704	422.695	365.140	282.017	-507.384	363.981	-3.880
5000	62.755	423.962	366.304	288.290	-507.625	381.767	-3.988
5100	62.809	425.205	367.447	294.568	-507.861	399.557	-4.092
5200	62.865	426.426	368.569	300.852	-508.093	417.352	-4.192
5300	62.923	427.624	369.672	307.141	-508.321	435.151	-4.289
5400	62.984	428.800	370.756	313.437	-508.544	452.954	-4.381
5500	63.047	429.957	371.822	319.738	-508.761	470.762	-4.471
5600	63.112	431.093	372.871	326.046	-508.976	488.573	-4.557
5700	63.179	432.211	373.902	332.361	-509.187	506.388	-4.641
5800	63.248	433.310	374.917	338.682	-509.395	524.207	-4.721
5900	63.318	434.392	375.916	345.010	-509.600	542.030	-4.799
6000	63.391	435.457	376.899	351.346	-509.801	559.856	-4.874

Titanium Nitride (TiN)   CRYSTAL $M_r = 61.8867$ Titanium Nitride (TiN) $N_1Ti_1(cr)$

T/K	Enthalpy Reference Temperature = T_r = 298.15 K J·K⁻¹·mol⁻¹				Standard State Pressure = $p°$ = 0.1 MPa kJ·mol⁻¹		
	$C°_p$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
0	0.	0.	INFINITE	-5.487	-333.971	-333.971	INFINITE
100	10.761	4.422	56.044	-5.162	-335.658	-327.283	170.955
200	27.330	17.338	33.350	-3.202	-337.070	-318.294	83.130
298.15	37.079	30.235	30.235	0.	-337.649	-308.929	54.123
300	37.238	30.465	30.236	0.069	-337.654	-308.750	53.758
400	43.811	42.171	31.787	4.154	-337.641	-299.104	39.059
500	47.057	52.338	34.906	8.716	-337.289	-289.506	30.245
600	48.723	61.074	38.557	13.510	-336.812	-279.993	24.376
700	49.781	68.667	42.328	18.437	-336.294	-270.564	20.190
800	50.618	75.370	46.048	23.458	-335.753	-261.211	17.055
900	51.384	81.376	49.645	28.558	-335.232	-251.925	14.621
1000	52.145	86.829	53.095	33.734	-334.797	-242.693	12.677
1100	52.919	91.835	56.392	38.987	-334.508	-233.498	11.088
1200	53.718	96.474	59.542	44.319	-338.345	-224.203	9.759
1300	54.538	100.806	62.551	49.731	-337.610	-214.721	8.628
1400	55.384	104.878	65.430	55.227	-336.890	-205.295	7.660
1500	56.246	108.729	68.190	60.809	-336.193	-195.920	6.823
1600	57.128	112.387	70.839	66.477	-335.528	-186.591	6.092
1700	58.020	115.877	73.386	72.235	-334.906	-177.301	5.448
1800	58.927	119.219	75.840	78.082	-334.337	-168.047	4.877
1900	59.848	122.430	78.208	84.020	-333.831	-158.823	4.366
2000	60.777	125.523	80.497	90.052	-348.087	-149.170	3.896
2100	61.710	128.511	82.713	96.176	-348.489	-139.214	3.463
2200	62.655	131.403	84.861	102.394	-348.804	-129.240	3.069
2300	63.605	134.209	86.946	108.707	-349.031	-119.255	2.708
2400	64.559	136.937	88.972	115.115	-349.170	-109.261	2.378
2500	65.517	139.591	90.944	121.619	-349.218	-99.264	2.074
2600	66.480	142.180	92.865	128.219	-349.175	-89.266	1.793
2700	67.446	144.707	94.738	134.915	-349.040	-79.272	1.534
2800	68.413	147.177	96.567	141.708	-348.813	-69.284	1.293
2900	69.387	149.595	98.354	148.598	-348.493	-59.307	1.068
3000	70.362	151.964	100.102	155.586	-348.079	-49.341	0.859
3100	71.337	154.287	101.812	162.670	-347.571	-39.392	0.664
3200	72.316	156.567	103.488	169.853	-346.969	-29.460	0.481
3220.000	72.513	157.018	103.819	171.301	--- CRYSTAL <---> LIQUID ---		
3300	73.295	158.807	105.130	177.134	-346.271	-19.548	0.309
3400	74.279	161.010	106.742	184.512	-345.478	-9.659	0.148
3500	75.262	163.177	108.323	191.989	-344.590	0.205	-0.003
3600	76.244	165.311	109.877	199.565	-343.606	10.043	-0.145
3700	77.228	167.414	111.403	207.238	-751.624	27.640	-0.390
3800	78.215	169.486	112.905	215.010	-749.214	48.669	-0.669
3900	79.203	171.531	114.382	222.881	-746.762	69.634	-0.933
4000	80.193	173.549	115.836	230.851	-744.267	90.556	-1.182
4100	81.182	175.541	117.268	238.920	-741.729	111.375	-1.419
4200	82.171	177.509	118.679	247.087	-739.144	132.151	-1.644
4300	83.161	179.454	120.069	255.354	-736.511	152.863	-1.857
4400	84.152	181.377	121.441	263.720	-733.829	173.517	-2.060
4500	85.144	183.280	122.794	272.185	-731.095	194.108	-2.253

Titanium Nitride (TiN) $N_1Ti_1(cr)$

$S°(298.15 K) = 30.235 ± 0.21$ J·K⁻¹·mol⁻¹
$T_m = 3220 ± 50$ K

$\Delta_f H°(0 K) = -333\ 971 ± 4.2$ kJ·mol⁻¹
$\Delta_f H°(298.15 K) = -337.649 ± 4.2$ kJ·mol⁻¹
$\Delta_{fus} H° = [66.944]$ kJ·mol⁻¹

Enthalpy of Formation

Humphrey[1] and Neumann et al.[2] determined the enthalpy of combustion of titanium nitride by burning the material in an oxygen bomb calorimeter. For reaction (a) Humphrey obtained $\Delta_f H°(298.15 K) = -145.05 ± 0.14$ kcal·mol⁻¹ and Neumann et al., $\Delta_f H°(298.15 K) = -145.0$ kcal·mol⁻¹. From an examination of the combustion products Humphrey reported that the TiO_2 was >95 percent rutile and <5 percent anatase, but made no correction for the anatase. The adopted $\Delta_f H°(298.15 K) = -80.7$ kcal·mol⁻¹ is the average of three values, two from Humphrey (-80.75, -80.61) one as reported and one corrected for anatase and one from Neumann et al. (-80 8). The uncertainty in the adopted enthalpy is due mainly to the uncertainty in the enthalpy of formation of rutile. Hoch et al.[3] determined the vapor pressure of reaction (b), in the temperature range 1987-2241 K, using a Knudsen effusion method. 3rd law analysis of the data yields $\Delta_f H°(298.15 K) = -79.5$ kcal·mol⁻¹. Linevsky[4] obtained the titanium partial pressures of reaction (C) at fixed nitrogen pressures using atomic absorption spectroscopy. 3rd law analysis of the data gives a $\Delta_f H°(298.15 K) = -81 ± 18$ kcal·mol⁻¹ These equilibrium measurements were not considered in deriving the heat of formation due to their large uncertainties in comparison to the calorimetric data.

Source	Method	Reaction	T/K	$\Delta_f H°(298.15 K)$ kcal·mol⁻¹ 2nd law	3rd law	Drift cal·K⁻¹·mol⁻¹	$\Delta_f H°(298.15 K)$ kcal·mol⁻¹
1	Calorimeter	(a) TiN(cr) + O₂(g) → TiO₂(rutile) + 1/2 N₂(g)	298				-145.05 ± .14
2	Calorimeter	(a) TiN(cr) + O₂(g) → TiO₂(rutile) + 1/2 N₂(g)	298				-14505 ± .14 *
3	Calorimeter	(a) TiN(cr) + O₂(g) → TiO₂(rutile) + 1/2 N₂(g)	298				-145.0
	Equilibrium	(b) TiN(cr) → Ti(g) + 1/2 N₂(g)	1987-2241				-79.5
4	Equilibrium	(c) TiN(cr) → Ti(g) + 1/2 N₂(g)	2088-2141	212 ± 9	192.5	-9.3 ± 4.3	-81.2
				230 ± 17	194.2	-17 ± 8	

*Assumes that the product TiO_2 is 95 percent rutile and 5 percent anatase.

Heat Capacity and Entropy

Low temperature heat capacities are from the data (52-296 K) of Shomate.[5] Naylor[6] measured high temperature heat contents (388–1738 K). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. Above 1738 K the heat capacity is graphically extrapolated. The entropy is based on $S°(50.0) = 0.138$ cal·K⁻¹·mol⁻¹.

Fusion Data

Refer to the liquid table for details.

References

[1] G. L. Humphrey, J. Amer. Chem. Soc. 73, 2261 (1951).
[2] B. Neumann, C. Kroger and H. Kunz, Z anorg. allg. Chem. 218, 379–401 (1934).
[3] M. Hoch, D. P. Dingledy and H. L. Johnston, J. Amer. Chem. Soc. 77, 304–6 (1955).
[4] M. J. Linevsky, General Electric Co., AFML–TR–64–420, (February 1965).
[5] C. H. Shomate, J. Amer. Chem. Soc. 68, 310 (1946).
[6] B. F. Naylor, J. Amer. Chem. Soc. 68, 370 (1946).

Titanium Nitride (TiN) LIQUID $M_r = 61.8867$ Titanium Nitride (TiN) N₁Ti₁(l)

$S°(298.15 \text{ K}) = [52.733] \text{ J·K}^{-1}\text{·mol}^{-1}$
$T_{fus} = 3220 \pm 50 \text{ K}$

$\Delta_f H°(298.15 \text{ K}) = [-265.813] \text{ kJ·mol}^{-1}$
$\Delta_{fus} H° = [66.944] \text{ kJ·mol}^{-1}$

Enthalpy of Formation
$\Delta_f H°(\text{TiN, l, } 298.15 \text{ K})$ is calculated from $\Delta_f H°(\text{TiN, cr, } 298.15 \text{ K})$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(3220 \text{ K}) - H°(298.15 \text{ K})$, between the crystal and liquid.

Heat Capacity and Entropy
A glass transition is assumed at 2200 K. Below 2200 K the heat capacity is obtained from the heat capacity of the crystal. Above 2200 K it is assumed constant and estimated as 15 cal·K⁻¹·mol⁻¹ or 7.5 cal·K⁻¹ g-atom. $S°(\text{l, } 298.15 \text{ K})$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data
T_{fus} is taken from Agte and Moers.[1] $\Delta_{fus} H°$ is derived from an estimated $\Delta_m S° = 2.5$ cal·K⁻¹ g-atom as suggested by Kubaschewski et al.[2]

References
[1] C Agte and K Moers, Z. Anorg Allg. Chem. 198, 233–43 (1931).
[2] O. Kubaschewski, E. Ll. Evans and C. B Alcock, "Metallurgical Thermochemistry," Pergamon Press, New York, (1967).

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
	(J·K⁻¹·mol⁻¹)				(kJ·mol⁻¹)		
0	0						
100							
200							
298.15	37.079	52.733	52.733	0.	-265.813	-243.800	42.713
300	37.238	52.963	52.734	0.069	-265.818	-243.664	42.426
400	43.811	64.670	54.285	4.154	-265.805	-236.267	30.853
500	47.057	74.836	57.404	8.716	-265.453	-228.919	23.915
600	48.723	83.572	61.056	13.510	-264.658	-221.656	19.297
700	49.781	91.165	64.827	18.437	-264.458	-214.477	16.004
800	50.618	97.868	68.546	23.458	-263.917	-207.374	13.540
900	51.384	103.874	72.143	28.558	-263.396	-200.337	11.627
1000	52.145	109.337	75.593	33.734	-262.961	-193.355	10.100
1100	52.919	114.333	78.891	38.987	-262.672	-186.410	8.852
1200	53.718	118.972	82.040	44.319	-266.509	-179.365	7.808
1300	54.538	123.394	85.049	49.731	-265.774	-172.133	6.916
1400	55.384	127.377	87.929	55.227	-265.054	-164.957	6.155
1500	56.246	131.227	90.688	60.809	-264.357	-157.831	5.496
1600	57.128	134.885	93.337	66.477	-263.692	-150.751	4.922
1700	58.020	138.375	95.884	72.235	-263.070	-143.712	4.416
1800	58.927	141.717	98.338	78.082	-262.501	-136.708	3.967
1900	59.848	144.928	100.706	84.020	-261.995	-129.733	3.567
2000	60.777	148.021	102.995	90.052	-276.251	-122.330	3.195
2100	61.710	151.009	105.211	96.176	-276.653	-114.624	2.851
2200	62.655	153.901	107.359	102.394	-276.968	-106.900	2.538
2200.000	62.655	153.901	107.359	102.394	-277.232	GLASS <--> LIQUID	
2200.000	62.760	153.901	107.359	102.394	-277.503	TRANSITION	
2300	62.760	156.691	109.443	108.670	-277.779	-99.164	2.252
2400	62.760	159.362	111.468	114.945	-278.060	-91.416	1.990
2500	62.760	161.924	113.436	121.222	-278.345	-83.657	1.748
2600	62.760	164.386	115.348	127.498	-278.635	-75.886	1.525
2700	62.760	166.754	117.208	133.774	-278.929	-68.105	1.318
2800	62.760	169.037	119.019	140.050	-279.227	-60.313	1.125
2900	62.760	171.239	120.782	146.326	-279.527	-52.511	0.946
3000	62.760	173.367	122.499	152.602	-279.832	-44.698	0.778
3100	62.760	175.425	124.174	158.878	-280.139	-36.876	0.621
3200	62.760	177.417	125.807	165.154	-280.449	-29.043	0.474
3220.000	62.760	177.808	126.128	166.409	-280.761	CRYSTAL <--> LIQUID	
3300	62.760	179.348	127.400	171.430	-281.076	-21.201	0.336
3400	62.760	181.222	128.956	177.706		-13.350	0.205
3500	62.760	183.041	130.475	183.982		-5.490	0.082
3600	62.760	184.809	131.960	190.258		2.379	-0.035
3700	62.760	186.529	133.412	196.534	-690.492	18.046	-0.255
3800	62.760	188.203	134.832	202.810	-689.578	37.183	-0.511
3900	62.760	189.833	136.221	209.086	-688.721	56.297	-0.754
4000	62.760	191.422	137.581	215.362	-687.920	75.390	-0.984
4100	62.760	192.971	138.913	221.638	-687.174	94.463	-1.203
4200	62.760	194.484	140.219	227.914	-686.481	113.519	-1.412
4300	62.760	195.961	141.498	234.190	-685.839	132.559	-1.610
4400	62.760	197.403	142.752	240.466	-685.247	151.585	-1.800
4500	62.760	198.814	143.982	246.742	-684.701	170.597	-1.980

Titanium Nitride (TiN)

$M_r = 61.8867$ Titanium Nitride (TiN) N_1Ti_1(cr,l)

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
	J·K⁻¹·mol⁻¹	J·K⁻¹·mol⁻¹	J·K⁻¹·mol⁻¹	kJ·mol⁻¹	kJ·mol⁻¹	kJ·mol⁻¹	
0	0.	0.	INFINITE	-5.487	-333.971	-333.971	INFINITE
100	10.761	4.422	56.044	-5.162	-335.658	-327.283	170.955
200	27.330	17.338	33.350	-3.202	-337.070	-318.294	83.130
298.15	37.079	30.235	30.235	0.	-337.649	-308.929	54.123
300	37.238	30.465	30.236	0.069	-337.654	-308.750	53.758
400	43.811	42.171	31.787	4.154	-337.641	-299.104	39.059
500	47.057	52.338	34.906	8.716	-337.289	-289.506	30.245
600	48.723	61.074	38.557	13.510	-336.812	-279.993	24.376
700	49.781	68.667	42.328	18.437	-336.294	-270.564	20.190
800	50.618	75.370	46.048	23.458	-335.753	-261.211	17.035
900	51.384	81.376	49.645	28.558	-335.232	-251.925	14.621
1000	52.145	86.829	53.095	33.734	-334.797	-242.693	12.677
1100	52.919	91.835	56.392	38.987	-334.508	-233.498	11.088
1200	53.718	96.474	59.542	44.319	-338.345	-224.203	9.759
1300	54.538	100.806	62.551	49.731	-337.610	-214.721	8.628
1400	55.384	104.878	65.430	55.227	-336.890	-205.295	7.660
1500	56.246	108.729	68.190	60.809	-336.193	-195.920	6.823
1600	57.128	112.387	70.839	66.477	-335.528	-186.591	6.092
1700	58.020	115.877	73.386	72.235	-334.906	-177.301	5.448
1800	58.927	119.219	75.840	78.082	-334.337	-168.047	4.877
1900	59.848	122.430	78.208	84.020	-333.831	-158.823	4.366
2000	60.777	125.523	80.497	90.052	-348.087	-149.170	3.896
2100	61.710	128.511	82.713	96.176	-348.489	-139.214	3.463
2200	62.655	131.403	84.861	102.394	-348.804	-129.240	3.069
2300	63.605	134.209	86.946	108.707	-349.031	-119.255	2.708
2400	64.559	136.937	88.972	115.115	-349.170	-109.261	2.378
2500	65.517	139.591	90.944	121.619	-349.218	-99.264	2.074
2600	66.480	142.180	92.865	128.219	-349.175	-89.266	1.793
2700	67.446	144.707	94.738	134.915	-349.040	-79.272	1.534
2800	68.413	147.177	96.567	141.708	-348.813	-69.284	1.293
2900	69.387	149.595	98.354	148.598	-348.493	-59.307	1.058
3000	70.362	151.964	100.102	155.586	-348.079	-49.341	0.859
3100	71.337	154.287	101.812	162.670	-347.571	-39.392	0.664
3200	72.316	156.567	103.488	169.853	-346.969	-29.460	0.481
						CRYSTAL ←→ LIQUID TRANSITION	
3220.000	72.513	157.018	103.819	171.301	-280.139	-21.201	0.336
3220.000	62.760	177.808	103.819	238.245	-280.449	-13.350	0.205
3300	62.760	179.348	105.631	243.266	-280.761	-5.490	0.082
3400	62.760	181.222	107.827	249.542	-281.076	2.379	-0.035
3500	62.760	183.041	109.950	255.818	-690.492	18.046	-0.255
3600	62.760	184.809	112.005	262.094	-689.578	37.183	-0.511
3700	62.760	186.529	113.996	268.370	-688.721	56.297	-0.754
3800	62.760	188.203	115.927	274.646	-687.920	75.390	-0.984
3900	62.760	189.833	117.801	280.922	-687.174	94.463	-1.203
4000	62.760	191.422	119.622	287.198	-686.481	113.519	-1.412
4100	62.760	192.971	121.392	293.474	-685.839	132.559	-1.610
4200	62.760	194.484	123.115	299.750	-685.247	151.585	-1.800
4300	62.760	195.961	124.792	306.026	-684.701	170.597	-1.980
4400	62.760	197.403	126.426	312.302			
4500	62.760	198.814	128.019	318.578			

Titanium Nitride (TiN) N_1Ti_1(cr,l)

CRYSTAL-LIQUID

0 to 3220 K   crystal
above   3220 K   liquid

Refer to the individual tables for details.

Titanium Nitride (TiN)

Vanadium Nitride (VN) CRYSTAL M_r = 64.9482 Vanadium Nitride (VN) N₁V₁(cr)

$S°(298.15 K) = 37.264 \pm 0.42$ J·K⁻¹·mol⁻¹
$\Delta_f H°(0 K) = -214.403 \pm 5.0$ kJ·mol⁻¹
$\Delta_f H°(298.15 K) = -217.150 \pm 5.0$ kJ·mol⁻¹

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	-6.228	-214.403	-214.403	INFINITE
100	15.111	8.354	64.935	-5.658	-215.773	-207.899	108.595
200	29.675	23.719	40.504	-3.357	-216.763	-199.597	52.129
298.15	37.981	37.264	37.264	0.	-217.150	-191.068	33.474
300	38.200	37.499	37.264	0.070	-217.152	-190.907	33.240
400	43.296	49.239	38.830	4.164	-217.082	-182.158	23.787
500	46.183	59.227	41.937	8.645	-216.731	-173.464	18.122
600	48.208	67.832	45.553	13.368	-216.221	-164.856	14.352
700	49.819	75.387	49.286	18.271	-215.615	-156.342	11.666
800	51.212	82.132	52.978	23.324	-214.951	-147.919	9.658
900	52.480	88.238	56.561	28.509	-214.256	-139.582	8.101
1000	53.668	93.829	60.013	33.817	-213.540	-131.323	6.860
1100	54.806	98.998	63.325	39.241	-212.812	-123.137	5.847
1200	55.907	103.814	66.500	44.777	-212.084	-115.017	5.007
1300	56.986	108.332	69.546	50.421	-211.362	-106.957	4.298
1400	58.045	112.594	72.470	56.173	-210.655	-98.952	3.692
1500	59.091	116.634	75.281	62.030	-209.963	-90.998	3.169
1600	60.124	120.481	77.987	67.990	-209.284	-83.089	2.713
1700	61.170	124.158	80.595	74.057	-208.625	-75.222	2.311
1800	62.049	127.679	83.114	80.217	-207.999	-67.393	1.956
1900	62.969	131.058	85.549	86.468	-207.420	-59.598	1.638
2000	63.932	134.313	87.906	92.813	-206.890	-51.832	1.354
2100	64.852	137.454	90.191	99.252	-206.420	-44.091	1.097
2200	65.772	140.493	92.409	105.784	-228.900	-36.266	0.861
2300	66.651	143.436	94.564	112.405	-228.716	-27.514	0.625
2400	67.530	145.291	96.660	119.114	-228.450	-18.771	0.409
2500	68.408	149.065	98.701	125.911	-228.102	-10.041	0.210
2600	69.287	151.766	100.690	132.796	-227.671	-1.327	0.027
2700	70.166	154.397	102.631	139.768	-227.156	7.369	-0.143
2800	71.044	156.965	104.526	146.829	-226.558	16.044	-0.299
2900	71.923	159.473	106.377	153.977	-225.877	24.697	-0.445
3000	72.802	161.926	108.188	161.214	-225.110	33.325	-0.580
3100	73.638	164.327	109.961	168.536	-224.262	41.925	-0.706
3200	74.475	166.678	111.696	175.941	-223.333	50.497	-0.824
3300	75.312	168.983	113.398	183.430	-222.323	59.039	-0.935
3400	76.191	171.244	115.066	191.006	-221.231	67.549	-1.038
3500	77.027	173.465	116.703	198.667	-220.055	76.026	-1.135

Enthalpy of Formation

Mah[1] measured the enthalpy of combustion of vanadium mononitride at 303.15 K. The composition of the sample was VN₁.₀₀ which corresponds to the nitrogen-rich boundary of the mononitride phase (see Phase Data section). Chemical analysis also showed that the sample contained 0.07 weight percent of unreacted vanadium. The composition of the combustion products ranged from VO₂.₂₃₁ to VO₂.₂₉₆. X-ray diffraction patterns showed the solid combustion products to be a mixture of V_2O_4 and V_2O_5. JANAF enthalpy of formation data[2] for these two oxides are used to correct Mah's combustion values to correspond to the formation of the pentoxide as the final state. Our values for this correction agree with those of Mah[1] to within 0.1 cal·K⁻¹·mol⁻¹ mononitride. For the process VN(cr) + 1.25 O₂(g) - 0.5 V_2O_5(cr) + 0.5 N₂(g), we obtain $\Delta_f H°$ = -133 41 ± 0.43 kcal·mol⁻¹ at unit fugacities of oxygen and nitrogen. When this value is combined with the enthalpy of formation of V_2O_5,[2] that for vanadium mononitride is $\Delta_f H°$(VN, cr, 298.15 K) = -51.9 ± 1.2 kcal·mol⁻¹. We adopt this value and include in the overall uncertainty (±1.2 kcal·mol⁻¹) the error associated with correcting the combustion values for the V_2O_4(cr) formed to V_2O_5(cr) as the final state.

Other values for $\Delta_f H°$ can be derived from the results of dissociation pressure measurements,[3] emf data,[4] and equilibrium data[5] obtained by an effusion-mass spectrometric technique. Analyses of these data are summarized below.

Source	Method	Reaction	Data Points	T/K	$\Delta_f H°$(298 15 K), kcal·mol⁻¹ 2nd law	3rd law	Drift	$-\Delta_f H°$(298.15 K) kcal·mol⁻¹
Slade and Higson[3]	Static	A	2	1476-1544	-68.8	-41.1 ± 1.8	-18.3	41.1
Voleinik and Shabdenov[4]	emf	A	Equation	363-403	-54.4	-55.5 ± 0.1	-2.7	55.5 ± 0.1
Farber and Srivastava[5]	Mass Spec.	B	13	1900-2412	173.5	181.7 ± 1.6	3.8 ± 0.8	58.5 ± 3.6

Reactions: A) V(cr) + 0.5·N₂(g) = VN(cr) B) VN(cr) = V(g) + 0.5 N₂(g)

Results obtained from the dissociation pressures of Slade and Higson[3] are obviously not reliable. Two other more extensive sets of dissociation pressure data[6,7] have been reported for the mononitride phase Brauer and Schnell[6] measured the nitrogen dissociation pressures for VN₀.₇₂ between 1573 and 1873 K, while Kozheurov et al.[7] determined equilibrium pressures for VNₓ (x = 0.55-0.9) at temperatures in the range 1573-1923 K. Unfortunately, these compositions are significantly different from VN₁.₀₀, and thus the data are probably of no use in defining the enthalpy of formation of the mononitride at its nitrogen-rich phase boundary. The 3rd law values of $\Delta_f H°$ obtained from the emf[4] and mass spectral[5] data are 3.6 and 6.6 kcal mol⁻¹, respectively, more negative than our adopted value. However, since the thermal functions used in the analysis of the mass spectral data[5] are based on extrapolated data, the 2nd law value, $\Delta_f H°$(298.15 K) = -50.3 kcal·mol⁻¹, is probably more reliable. This value is in much better agreement with that obtained by combustion calorimetry.

Heat Capacity and Entropy

Shomate and Kelley.[8] (52.6-296.3 K) measured the low temperature heat capacities for VN. The purity of the mononitride sample based on an analysis for vanadium by permanganate titration was found to be 99.76 weight percent. Their $C_p°$ data corrected to 1969 Atomic Weight Scale are adopted. S°(298 15 K) is obtained from the adopted $C_p°$ data and is based on S°(52 K) = 0.47 cal·K⁻¹·mol⁻¹. This latter value is calculated from the Debye function D(35/T) which was suggested by Shomate and Kelley.[8]

High temperature enthalpies for VN have been reported by King[9] for the temperature range 408-1611 K. The sample was identical to that employed by Shomate and Kelley[8] and was contained in platinum-rhodium alloy capsules for the "drop" experiments. His experimental enthalpies are corrected to refer to the 1969 Atomic Weight Scale. Also, his reported temperatures are corrected to the IPTS-68 scale. A technique based on orthogonal polynomials is used to fit the corrected enthalpies by computer. The curve is constrained to join smoothly with the low temperature $C_p°$ data[8] near 298 K. Our smoothed enthalpies show an average deviation of ±0.4% from the experimental values.[9] The maximum deviation is +2.1% at 408 K. No anomalies are observed in either the low temperature $C_p°$ data[8] or the high temperature enthalpies.[9] $C_p°$ data above 1613 K are obtained by graphical extrapolation. Satoh[10] has measured the mean specific heats of VN over three temperature intervals by means of an ice calorimeter. However, the sample used in his study was impure (97.93% VN), and we believe the results are probably not reliable. They do show considerable scatter from our adopted results; deviations are in the range of ±1-5%.

Phase Data

The mononitride phase has been prepared by several workers[1,5-8,10,11-13] at temperatures as high as 1600 K. X-ray data[6,11] and dissociation pressure measurements[7] have shown that the phase has an extensive homogeneity range. Although Kozeurov et al.[7] were unable to obtain VN₁.₀₀ at 1273 K, Brauer and Schnell[6] and Hahn[11] reported that the composition of the mononitride phase extends from VN₀.₇₂ to VN₁.₀₀ (42 to 50 atomic percent nitrogen) at 1273-1873 K. The dissociation pressure data of Kozheurov et al.[7] indicate that the vanadium-rich phase boundary decreases from VN₀.₇₂ at 1573 K to VN₀.₅₆ at 1923 K The structure of the mononitride is face-centered cubic.[6,11] Further information on the vanadium-vanadium nitride system has been reviewed by Storms.[14]

Vanadium Nitride (VN)

Vanadium Nitride (VN)

IDEAL GAS $M_r = 64.9482$

$S°(298.15\ K) = [233.384 \pm 8.4]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 523.18 \pm 20.9\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 523\ 00 \pm 20.9\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights

ε_i, cm⁻¹	g_i	ε_i, cm⁻¹	g_i	ε_i, cm⁻¹	g_i
0	[6]	[12000]	[2]	[21000]	[2]
[1000]	[2]	[13000]	[3]	[22000]	[6]
[3000]	[1]	[14000]	[6]	[24000]	[2]
[10000]	[6]	[15000]	[1]	[25000]	[6]
		[16000]	[6]	[28000]	[6]
		[18000]	[2]		
		[19000]	[2]		
		[20000]	[1]		

Ground State Configuration: $[^4\Delta]$

$\omega_e = [1025]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.5905]\ cm^{-1}$ $r_e = [1.612]\ Å$
$\omega_e x_e = [4.41]\ cm^{-1}$
$\alpha_e = [0.00354]\ cm^{-1}$

Enthalpy of Formation

Dissociation energies for the diatomic group III-VI transition–metal nitrides have been estimated by Gingerich[1] and provide support for the existence of these gaseous molecules. Very recently, mass-spectrometric evidence[2] has been presented which verifies the existence of VN(g). Using an effusion-mass spectrometric technique, Farber and Srivastava[2] observed the VN⁺ion as one of the vapor species in equilibrium with solid VN in the temperature range 1900–2412 K. The molecular precursor of this ion is assumed to be VN(g). Results of effusion weight loss and mass spectrometric experiments[2] were combined to yield partial pressures for the species involved in the following two reactions: (A) VN(cr) − VN(g) and (B) VN(g) − V(g) + 0.5 N₂(g). During the course of these experiments, the ion intensities for each species did not show any variation with time. This implies that the mononitride phase remained at near unit activity during their measurements.

Source	Reaction	T/K	Data Points	$\Delta_f H°(298.15\ K)$, kcal·mol⁻¹ 2nd law	3rd law	Diff cal·K⁻¹·mol⁻¹	$\Delta_f H°(298.15\ K)$ kcal mol⁻¹
[2]	A	1900–2412	13	174.3	185.4 ± 2.4	5.2 ± 1.4	133.5 ± 3.6
[2]	B	1900–2412	12*	−1.9	−3.6 ± 1.6	−0.8 ± 1.4	126.8 ± 3.6

*One point rejected due to failure of a statistical test.

The 3rd law value of 126.8 ± 3.6 kcal·mol⁻¹ for $\Delta_f H°$ is considered to be more reliable than that (133.5 kcal·mol⁻¹) derived from the sublimation data, since the results for the gas phase reaction (B) show the least drift. Also, Farber and Srivastava[2] reported a 2nd law value determined from ion intensity plots of $\Delta_f H° = 3 \pm 5$ kcal·mol⁻¹ for reaction (B) at 2162 K. Using auxiliary data,[3] this value leads to $\Delta_f H°$(VN, g, 298.15 K) = 122.0 ± 7.0 kcal·mol⁻¹. We adopt $\Delta_f H°$(VN, g, 298.15 K) = 125.0 ± 5.0 kcal·mol⁻¹ which is a weighted average of the 3rd law value derived from reaction (B) and the 2nd law value based on ion intensity plots. The adopted $\Delta_f H°$ value corresponds to a bond dissociation energy, $D°$(298.5 K), of 111.2 kcal·mol⁻¹. This compares favorably with the value (116 kcal·mol⁻¹) estimated by Gingerich.[1]

Heat Capacity and Entropy

The value of r_e(VN) is obtained from the expression r_e(MO)−r_e(MN) = −0.023 A with r_e(VO) = 1.589 A.[3] Differences in the bond lengths[4] for the oxides and nitrides of As, B, P, Si, and Ti are used to establish the value −0.023. B_e is calculated from the estimated value for r_e. The value of α_e is obtained from the other constants assuming a Morse potential function. The values of ω_e and $\omega_e x_e$ are assumed to lie between those for TiO(g) and TiO₂(g). VN is isoelectronic with TiO. Farber and Srivastava[2] have estimated a somewhat higher value (1065 cm⁻¹) for ω_e. However, their estimate is based partially on estimated JANAF data[3] for ZrN(g).

The ground state electronic configuration ($^4\Delta$), upper electronic levels and quantum weights are estimated by analogy with those for TiO.[3,5] It is possible, however, that the ground state for VN is $^4\Delta$. VN is also isoelectronic with ScF and ZrO which both have singlet ground states.[5] If the adopted ground state and first excited state are interchanged, then the value of $S°$(298.15 K) is reduced by 1.94 cal·K⁻¹·mol⁻¹. Our adopted upper levels and quantum weights contribute 0.61 and 1.11 cal·K⁻¹·mol⁻¹ to the entropy of VN(g) at 2000 and 4000 K, respectively.

References

[1] K. A. Gingerich, J. Chem. Phys. 49, 19 (1968).
[2] M. Farber and R. D. Srivastava, J. Chem. Soc. Faraday Trans. 1, 69, 390 (1973).
[3] JANAF Thermochemical Tables. VN(cr), VO(g) and TiO₂(g), 12-31-73; V(g), 6-30-73; N₂(g), 9-30-65; ZrN(g), 6-30-63.
[4] B. Rosen, Ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, (1970).
[5] L. Brewer and D. W. Green, High Temp. Sci. 1, 26 (1969).

Vanadium Nitride (VN) N_1V_1(g)

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C°_p$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−8.800	523.175	523.175	INFINITE
100	29.107	201.085	260.002	−5.892	524.143	512.744	−267.830
200	29.518	221.325	236.173	−2.970	523.774	501.419	−130.957
250	30.234	227.982	233.891	−1.477	523.395	495.873	−103.607
298.15	31.147	233.384	233.384	0.	523.000	490.608	−85.952
300	31.184	233.577	233.384	0.058	522.983	490.407	−85.387
350	32.193	238.460	233.768	1.642	522.574	485.010	−72.384
400	33.143	242.821	234.632	3.276	522.180	479.671	−62.639
450	33.983	246.775	235.765	4.955	521.804	474.380	−55.065
500	34.699	250.393	237.049	6.672	521.446	469.130	−49.010
600	35.799	256.823	239.823	10.200	520.761	458.732	−39.936
700	36.560	262.402	242.659	13.821	520.084	448.447	−33.464
800	37.092	267.321	245.440	17.505	519.380	438.260	−28.615
900	37.472	271.713	248.120	21.234	518.619	428.165	−24.850
1000	37.750	275.676	250.680	24.996	517.789	418.159	−21.842
1100	37.959	279.284	253.119	28.782	516.879	408.239	−19.386
1200	38.118	282.594	255.439	32.586	515.875	398.406	−17.342
1300	38.245	285.651	257.647	36.404	514.771	388.661	−15.617
1400	38.349	288.489	259.750	40.234	513.556	379.005	−14.141
1500	38.441	291.138	261.755	44.074	512.231	369.440	−12.865
1600	38.527	293.622	263.670	47.922	510.798	359.967	−11.752
1700	38.614	295.960	265.501	51.779	509.248	350.587	−10.772
1800	38.706	298.169	267.256	55.645	507.579	341.301	−9.904
1900	38.807	300.265	268.938	59.521	505.783	332.112	−9.130
2000	38.921	302.258	270.555	63.407	503.853	323.021	−8.436
2100	39.048	304.160	272.110	67.305	501.783	314.029	−7.811
2200	39.192	305.980	273.609	71.217	476.683	305.245	−7.247
2300	39.353	307.726	275.054	75.144	474.173	297.508	−6.757
2400	39.531	309.404	276.451	79.088	471.574	289.881	−6.309
2500	39.727	311.022	277.801	83.051	469.188	282.357	−5.900
2600	39.940	312.584	279.109	87.034	466.717	274.933	−5.523
2700	40.171	314.096	280.377	91.040	464.265	267.603	−5.177
2800	40.441	315.565	281.608	95.069	461.831	260.364	−4.857
2900	40.678	316.984	282.803	99.124	459.419	253.211	−4.561
3000	40.954	318.367	283.966	103.205	457.031	246.142	−4.286
3100	41.242	319.715	285.097	107.315	454.667	239.151	−4.030
3200	41.541	321.029	286.200	111.454	452.329	232.236	−3.791
3300	41.850	322.312	287.275	115.623	450.019	225.394	−3.568
3400	42.167	323.566	288.324	119.824	447.731	218.622	−3.359
3500	42.492	324.793	289.348	124.057	445.485	211.916	−3.163
3600	42.821	325.995	290.350	128.323	443.263	205.274	−2.978
3700	43.154	327.173	291.329	132.621	−5.736	199.894	−2.822
3800	43.490	328.328	292.287	136.954	−6.210	205.458	−2.824
3900	43.827	329.462	293.226	141.320	−6.703	211.035	−2.826
4000	44.163	330.576	294.145	145.719	−7.216	216.624	−2.829
4100	44.498	331.670	295.018	150.152	−7.752	222.227	−2.831
4200	44.829	332.747	295.933	154.618	−8.339	227.843	−2.834
4300	45.157	333.805	296.801	159.118	−8.891	233.472	−2.836
4400	45.479	334.847	297.654	163.650	−9.497	239.115	−2.839
4500	45.795	335.873	298.492	168.213	−10.129	244.773	−2.841
4600	46.104	336.883	299.316	172.808	−10.788	250.445	−2.844
4700	46.405	337.877	300.126	177.434	−11.475	256.131	−2.847
4800	46.698	338.858	300.922	182.089	−12.192	261.832	−2.849
4900	46.981	339.823	301.706	186.773	−12.939	267.549	−2.852
5000	47.254	340.775	302.478	191.485	−13.718	273.281	−2.855
5100	47.517	341.714	303.238	196.224	−14.531	279.029	−2.858
5200	47.770	342.639	303.987	200.988	−15.378	284.793	−2.861
5300	48.011	343.551	304.725	205.777	−16.262	290.574	−2.864
5400	48.241	344.451	305.452	210.590	−17.184	296.372	−2.867
5500	48.459	345.338	306.170	215.425	−18.145	302.187	−2.870
5600	48.665	346.213	306.877	220.281	−19.148	308.020	−2.873
5700	48.860	347.076	307.575	225.158	−20.194	313.872	−2.876
5800	49.043	347.927	308.263	230.053	−21.285	319.742	−2.880
5900	49.214	348.767	308.942	234.966	−22.422	325.631	−2.883
6000	49.374	349.596	309.613	239.895	−23.608	331.541	−2.886

N₁Zr₁(cr)

Zirconium Nitride (ZrN)

CRYSTAL $\quad$ M_f = 105.2267 $\quad$ Zirconium Nitride (ZrN)

$S°(298.15\ K) = 38.861 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = [3225\ K]$

$\Delta_f H°(0\ K) = -362.020 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -365.263 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [67.362]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of reaction I, $-174.25 \pm 0.30\ kcal \cdot mol^{-1}$, was measured by Mah and Gelbert.[7] The $\Delta_f H°(298.15\ K)$ of ZrN was obtained using $261.5 \pm 0.2\ kcal \cdot mol^{-1}$ for $\Delta_f H°(298.15\ K)$ of ZrO₂. For the same reaction, Neumann et al.[1] obtain $-176\ 0\ kcal \cdot mol^{-1}$ on a sample of unspecified purity. Vapor pressure measurements of Hoch et al.[2] lead to 81 kcal·mol⁻¹ for the $\Delta_f H°(298\ 15\ K)$ of ZrN. However, this value is uncertain by 10% as evidenced by the work on ZrO₂ by Chupka et al.[3]

$$(I)\ ZrN(cr) + O_2(g) = ZrO_2(cr) + 1/2\ N_2(g)$$
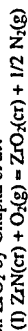
Heat Capacity and Entropy

Low temperature measurements, 53 297 K, of Todd[4] were smoothly joined to those of Coughlin and King,[5] 298 1073 K.

Fusion Data

Estimated by Henderson and Scheffee.[6]

References

[1]B. Neumann, C. Kroger and H Kunz, Z. Anorg Chem. 218, 379 (1934).
[2]M. Hoch, D. P. Dingledy and H. L Johnston, J. Amer. Chem. Soc. 77, 304 (1955).
[3]W A. Chupka. J. Berkowitz and M G. Inghram, J. Chem. Phys. 26, 1207 (1957).
[4]S. S. Todd, J. Amer. Chem. Soc. 72, 2914 (1950).
[5]J. P. Coughlin and E. G. King, J. Amer. Chem. Soc. 72, 2262 (1950).
[6]C. B. Henderson and R S. Scheffee, Alexandria, Va., "Survey of Thermochemical Data," Atlantic Research Corp., (January 1960).
[7]A. D. Mah and N. L. Gelbert, J. Am. Chem. Soc. 78, 3261 (1956).

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
		J·K⁻¹·mol⁻¹			kJ·mol⁻¹		
0	0.	0.	INFINITE	-6.590	-362.020	-362.020	INFINITE
100	15.548	8.134	68.383	-6.025	-363.793	-355.210	185.543
200	31.765	24.376	42.325	-3.590	-365.006	-346.073	90.385
298.15	40.443	38.861	38.861	0.	-365.263	-336.697	58.988
300	40.556	39.112	38.862	0.075	-365.262	-336.519	58.593
400	44.756	51.399	40.508	4.356	-364.999	-326.969	42.698
500	47.078	61.649	43.741	8.954	-364.495	-317.516	33.171
600	48.660	70.378	47.471	13.744	-363.888	-308.176	26.829
700	49.894	77.974	51.298	18.673	-363.247	-298.942	22.307
800	50.940	84.706	55.061	23.716	-362.609	-289.799	18.922
900	51.882	90.760	58.697	28.857	-362.003	-280.734	16.293
1000	52.752	96.272	62.183	34.089	-361.447	-271.735	14.194
1100	53.580	101.339	65.515	39.406	-360.950	-262.788	12.479
1200	54.379	106.036	68.698	44.804	-364.228	-253.662	11.042
1300	55.153	110.419	71.741	50.281	-363.317	-244.485	9.824
1400	55.915	114.534	74.652	55.835	-362.391	-235.379	8.782
1500	56.668	118.418	77.442	61.464	-361.459	-226.339	7.882
1600	57.409	122.099	80.119	67.168	-360.532	-217.362	7.096
1700	58.141	125.601	82.692	72.945	-359.618	-208.442	6.405
1800	58.873	128.945	85.169	78.796	-358.727	-199.575	5.792
1900	59.597	132.147	87.558	84.720	-357.869	-190.757	5.244
2000	60.321	135.223	89.865	90.716	-357.054	-181.983	4.753
2100	60.973	138.181	92.096	96.780	-356.296	-173.248	4.309
2200	61.756	141.036	94.256	102.937	-376.922	-163.802	3.889
2300	62.471	143.797	96.350	109.128	-376.712	-154.119	3.500
2400	63.187	146.471	98.383	115.411	-376.435	-144.447	3.144
2500	63.898	149.065	100.359	121.765	-376.093	-134.788	2.816
2600	64.614	151.585	102.281	128.191	-375.685	-125.143	2.514
2700	65.321	154.037	104.152	134.688	-375.210	-115.516	2.235
2800	66.032	156.425	105.977	141.255	-374.669	-105.907	1.976
2900	66.743	158.755	107.757	147.894	-374.060	-96.319	1.735
3000	67.450	161.029	109.495	154.604	-373.384	-86.754	1.511
3100	68.157	163.252	111.193	161.384	-372.641	-77.211	1.301
3200	68.864	165.428	112.854	168.235	-371.830	-67.694	1.105
3225.000	69.041	165.964	113.264	169.959	--- CRYSTAL <--> LIQUID ---		
3300	69.572	167.557	114.480	175.157	-370.952	-58.203	0.921
3400	70.279	169.645	116.072	182.149	-370.005	-48.740	0.749
3500	70.986	171.692	117.632	189.213	-368.991	-39.306	0.587
3600	71.693	173.702	119.161	196.347	-367.908	-29.901	0.434
3700	72.396	175.676	120.662	203.551	-366.758	-20.528	0.290
3800	73.103	177.616	122.135	210.826	-365.539	-11.186	0.154
3900	73.810	179.524	123.582	218.172	-364.252	-1.878	0.025
4000	74.517	181.402	125.005	225.588	-362.896	7.397	-0.097

Standard State Pressure = $p°$ = 0.1 MPa

Enthalpy Reference Temperature = T_r = 298.15 K

CURRENT: June 1961

PREVIOUS:

Zirconium Nitride (ZrN) $\qquad$ N₁Zr₁(cr)

Zirconium Nitride (ZrN) **LIQUID** $M_r = 105.2267$ **Zirconium Nitride (ZrN)** $N_1Zr_1(l)$

$S°(298.15\ K) = [62.342]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-290.749]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [67.362]\ kJ·mol^{-1}$

$T_{fus} = [3225]\ K$

Enthalpy of Formation
$\Delta_f H°(ZrN, l, 298.15\ K)$ is calculated from that of the crystal by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy,
$H°(3225\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy
Calculated from the solid. The heat capacity function of the solid was assumed to approximate those of the liquid up to the estimated glass point of 2150 K. Above the glass point the heat capacity was estimated.
$S°(ZrN, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

| | | | Enthalpy Reference Temperature = T_r = 298.15 K | | Standard State Pressure = $p°$ = 0.1 MPa | | |
| | | | J·K⁻¹·mol⁻¹ | | kJ·mol⁻¹ | | |
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0	0					
298.15	40.443	62.342	62.342	0.	-290.749	-269.183	47.160
300	40.556	62.592	62.342	0.075	-290.747	-269.049	46.846
400	44.756	74.880	63.989	4.356	-290.484	-261.846	34.194
500	47.078	85.130	67.222	8.954	-289.981	-254.742	26.613
600	48.660	93.858	70.952	13.744	-289.374	-247.750	21.569
700	49.894	101.454	74.778	18.673	-288.732	-240.864	17.973
800	50.940	108.186	78.542	23.716	-288.094	-234.069	15.283
900	51.882	114.241	82.177	28.857	-287.489	-227.353	13.195
1000	52.752	119.753	85.663	34.089	-286.932	-220.701	11.528
1100	53.580	124.820	88.996	39.406	-286.436	-214.103	10.167
1200	54.379	129.516	92.179	44.804	-289.714	-207.325	9.025
1300	55.153	133.900	95.222	50.281	-288.802	-200.496	8.056
1400	55.915	138.015	98.153	55.835	-287.876	-193.738	7.228
1500	56.668	141.898	100.922	61.464	-286.945	-187.046	6.514
1600	57.409	145.579	103.599	67.168	-286.017	-180.416	5.890
1700	58.141	149.082	106.173	72.945	-285.103	-173.844	5.342
1800	58.873	152.426	108.650	78.796	-284.213	-167.326	4.856
1900	59.597	155.628	111.039	84.720	-283.355	-160.856	4.422
2000	60.321	158.704	113.346	90.716	-282.539	-154.430	4.033
2100	60.973	161.663	115.577	96.781	-281.780	-148.043	3.682
2150.000	61.273	163.101	116.665	99.838		GLASS <--> LIQUID	
2150.000	58.576	163.101	116.665	99.838		TRANSITION	
2200	58.576	164.448	117.736	102.766	-302.558	-140.944	3.346
2300	58.576	167.052	119.824	108.624	-302.701	-133.594	3.034
2400	58.576	169.545	121.844	114.482	-302.850	-126.239	2.748
2500	58.576	171.936	123.800	120.339	-303.005	-118.877	2.484
2600	58.576	174.233	125.696	126.197	-303.164	-111.509	2.240
2700	58.576	176.444	127.535	132.054	-303.329	-104.134	2.015
2800	58.576	178.574	129.320	137.912	-303.497	-96.753	1.805
2900	58.576	180.630	131.054	143.770	-303.670	-89.367	1.610
3000	58.576	182.615	132.740	149.627	-303.846	-81.974	1.427
3100	58.576	184.536	134.380	155.485	-304.025	-74.575	1.257
3200	58.576	186.396	135.976	161.342	-304.208	-67.171	1.096
3225.000	58.576	186.852	136.369	162.807		CRYSTAL <--> LIQUID	
3300	58.576	188.198	137.532	167.200	-304.394	-59.760	0.946
3400	58.576	189.947	139.048	173.058	-304.583	-52.345	0.804
3500	58.576	191.645	140.526	178.915	-304.774	-44.923	0.670
3600	58.576	193.295	141.969	184.773	-304.968	-37.496	0.544
3700	58.576	194.900	143.378	190.630	-305.164	-30.063	0.424
3800	58.576	196.462	144.755	196.488	-305.362	-22.626	0.311
3900	58.576	197.984	146.100	202.346	-305.563	-15.183	0.203
4000	58.576	199.467	147.416	208.203	-305.766	-7.734	0.101
4100	58.576	200.913	148.703	214.061	-305.971	-0.281	0.004
4200	58.576	202.325	149.963	219.918	-306.178	7.177	-0.089
4300	58.576	203.703	151.197	225.776	-306.387	14.641	-0.178
4400	58.576	205.050	152.406	231.634	-306.597	22.109	-0.262
4500	58.576	206.366	153.590	237.491	-306.810	29.582	-0.343
4600	58.576	207.653	154.752	243.349	-307.024	37.059	-0.421
4700	58.576	208.913	155.891	249.206	-307.240	44.542	-0.495
4800	58.576	210.146	157.008	255.064	-858.394	63.646	-0.693
4900	58.576	211.354	158.105	260.922	-858.265	83.062	-0.885
5000	58.576	212.538	159.182	266.779	-858.155	102.476	-1.071
5100	58.576	213.698	160.239	272.637	-868.062	121.888	-1.248
5200	58.576	214.835	161.278	278.494	-867.986	141.298	-1.419
5300	58.576	215.951	162.299	284.352	-867.923	160.706	-1.584
5400	58.576	217.046	163.303	290.210	-867.875	180.114	-1.742
5500	58.576	218.120	164.290	296.067	-867.838	199.521	-1.895
5600	58.576	219.176	165.261	301.925	-867.811	218.927	-2.042
5700	58.576	220.213	166.216	307.782	-867.795	238.333	-2.184
5800	58.576	221.231	167.156	313.640	-867.787	257.739	-2.321
5900	58.576	222.233	168.081	319.498	-867.786	277.144	-2.454
6000	58.576	223.217	168.991	325.355	-867.792	296.550	-2.582

PREVIOUS: CURRENT: June 1961

Zirconium Nitride (ZrN) $N_1Zr_1(l)$

Zirconium Nitride (ZrN)

$M_r = 105.2267$ Zirconium Nitride (ZrN) $N_1Zr_1(cr,l)$

Standard State Pressure = $p° = 0.1$ MPa

Enthalpy Reference Temperature = $T_r = 298.15$ K

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J K⁻¹ mol⁻¹	J K⁻¹ mol⁻¹	J K⁻¹ mol⁻¹	kJ mol⁻¹	kJ mol⁻¹	kJ mol⁻¹	
0	0.	0.	INFINITE	-6.590	-362.020	-362.020	INFINITE
100	15.548	8.134	68.383	-6.025	-363.793	-355.210	185.543
200	31.765	24.376	42.325	-3.590	-365.006	-346.073	90.385
298.15	40.443	38.861	38.861	0.	-365.263	-336.697	58.988
300	40.556	39.112	38.862	0.075	-365.262	-336.519	58.593
400	44.756	51.399	40.508	4.356	-364.999	-326.969	42.698
500	47.078	61.649	43.741	8.954	-364.495	-317.516	33.171
600	48.660	70.378	47.471	13.744	-363.888	-308.176	26.829
700	49.894	77.974	51.298	18.673	-363.247	-298.942	22.307
800	50.940	84.706	55.061	23.716	-362.609	-289.799	18.922
900	51.882	90.760	58.697	28.857	-362.003	-280.734	16.293
1000	52.752	96.272	62.183	34.089	-361.447	-271.735	14.194
1100	53.580	101.339	65.515	39.406	-360.950	-262.788	12.479
1200	54.379	106.036	68.698	44.804	-364.228	-253.662	11.042
1300	55.153	110.419	71.741	50.281	-363.317	-244.485	9.824
1400	55.915	114.534	74.652	55.835	-362.391	-235.379	8.782
1500	56.668	118.418	77.442	61.464	-361.459	-226.339	7.882
1600	57.409	122.099	80.119	67.168	-360.532	-217.362	7.096
1700	58.141	125.601	82.692	72.945	-359.618	-208.442	6.405
1800	58.873	128.945	85.169	78.796	-358.727	-199.575	5.792
1900	59.597	132.147	87.558	84.720	-357.869	-190.757	5.244
2000	60.321	135.223	89.865	90.716	-357.054	-181.983	4.753
2100	60.973	138.181	92.096	96.780	-356.296	-173.248	4.309
2200	61.756	141.036	94.255	102.917	-376.922	-163.802	3.889
2300	62.471	143.797	96.350	109.128	-376.712	-154.119	3.500
2400	63.187	146.471	98.383	115.411	-376.435	-144.447	3.144
2500	63.898	149.065	100.359	121.765	-376.093	-134.788	2.816
2600	64.614	151.585	102.281	128.191	-375.685	-125.143	2.514
2700	65.321	154.037	104.152	134.688	-375.210	-115.516	2.235
2800	66.032	156.425	105.977	141.255	-374.669	-105.907	1.976
2900	66.743	158.755	107.757	147.894	-374.060	-96.319	1.735
3000	67.450	161.029	109.495	154.604	-373.384	-86.754	1.511
3100	68.157	163.252	111.193	161.384	-372.641	-77.211	1.301
3200	68.864	165.428	112.854	168.235	-371.830	-67.694	1.105
3225.000	69.041	165.954	113.264	169.959		CRYSTAL <--> LIQUID	
3225.000	58.576	185.852	113.264	237.321		TRANSITION	
3300	58.576	188.198	114.952	241.715	-304.394	-59.760	0.946
3400	58.576	189.947	117.132	247.572	-304.583	-52.345	0.804
3500	58.576	191.645	119.236	253.430	-304.774	-44.923	0.670
3600	58.576	193.295	121.271	259.287	-304.968	-37.496	0.544
3700	58.576	194.900	123.239	265.145	-305.164	-30.063	0.424
3800	58.576	196.462	125.146	271.003	-305.362	-22.626	0.311
3900	58.576	197.984	126.994	276.860	-305.563	-15.183	0.203
4000	58.576	199.467	128.787	282.718	-305.766	-7.734	0.101
4100	58.576	200.913	130.529	288.575	-305.971	-0.281	0.004
4200	58.576	202.325	132.222	294.433	-306.178	7.177	-0.089
4300	58.576	203.703	133.868	300.291	-306.387	14.641	-0.178
4400	58.576	205.050	135.470	306.148	-306.597	22.109	-0.262
4500	58.576	206.366	137.031	312.006	-306.810	29.582	-0.343
4600	58.576	207.653	138.553	317.863	-307.024	37.059	-0.421
4700	58.576	208.913	140.036	323.721	-307.240	44.542	-0.495
4800	58.576	210.145	141.484	329.579	-868.394	63.646	-0.693
4900	58.576	211.354	142.898	335.436	-868.265	83.062	-0.885
5000	58.576	212.538	144.279	341.294	-868.155	102.476	-1.071
5100	58.576	213.698	145.629	347.151	-868.062	121.888	-1.248
5200	58.576	214.835	146.949	353.009	-867.986	141.298	-1.419
5300	58.576	215.951	148.240	358.867	-867.923	160.706	-1.584
5400	58.576	217.046	149.504	364.724	-867.875	180.114	-1.742
5500	58.576	218.120	150.742	370.582	-867.838	199.521	-1.895
5600	58.576	219.176	151.955	376.439	-867.811	218.927	-2.042
5700	58.576	220.213	153.143	382.297	-867.795	238.333	-2.184
5800	58.576	221.231	154.308	388.155	-867.787	257.739	-2.321
5900	58.576	222.233	155.451	394.012	-867.786	277.144	-2.454
6000	58.576	223.217	156.572	399.870	-867.792	296.550	-2.582

$N_1Zr_1(cr,l)$

Zirconium Nitride (ZrN)

CRYSTAL-LIQUID

0 to 3225 K crystal
above 3225 K liquid

Refer to the individual tables for details.

Zirconium Nitride (ZrN)   IDEAL GAS $M_r = 105.2267$ $N_1Zr_1(g)$

$S°(298.15 \text{ K}) = [233.487] \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = [714.342] \text{ kJ·mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = [713.372] \text{ kJ·mol}^{-1}$

Electronic Level and Quantum Weight		
State	ϵ, cm^{-1}	g_i
[$^2\Sigma$]	0	[2]

$\omega_e = [840] \text{ cm}^{-1}$ $\omega_e x_e = [5] \text{ cm}^{-1}$ $\sigma = 1$
$B_e = [0.4146] \text{ cm}^{-1}$ $\alpha_e = [0.0025] \text{ cm}^{-1}$ $r_e = [1.83]$ Å

Enthalpy of Formation
$\Delta_f H°(0 \text{ K})$ was estimated as 170.7 kcal·mol^{-1} by Gordon.[1] $\Delta_f H°(298.15 \text{ K})$ was then calculated.

Heat Capacity and Entropy
Molecular constants were estimated by Gordon.[1] r_e was calculated from the relationship $r_e = (16.858778/\mu B_e)^{1/2}$ Å.

Reference
[1] J. S Gordon, Astrosystems International, Livingston, New Jersey, personal communication, (January 10, 1963).

Zirconium Nitride (ZrN)

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta H°$	$\Delta G°$	$\log K_f$
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	-8.863	714.342	714.342	INFINITE
100	29.114	200.910	260.451	-5.954	714.913	704.218	-367.846
200	29.877	221.235	236.323	-3.018	714.201	693.763	-181.192
250	30.752	227.993	234.003	-1.503	713.772	688.703	-143.897
298.15	31.661	233.487	233.487	0.	713.372	683.911	-119.818
300	31.695	233.683	233.488	0.059	713.357	683.728	-119.048
350	32.569	238.636	233.877	1.666	712.965	678.821	-101.309
400	33.326	243.036	234.752	3.314	712.594	673.969	-88.011
450	33.961	246.999	235.896	4.996	712.239	669.162	-77.674
500	34.488	250.605	237.189	6.708	711.893	664.395	-69.409
600	35.286	256.968	239.970	10.199	711.202	654.960	-57.019
700	35.845	262.452	242.799	13.757	710.472	645.643	-48.178
800	36.248	267.266	245.562	17.363	709.673	636.435	-41.555
900	36.549	271.554	248.217	21.003	708.778	627.333	-36.409
1000	36.781	275.417	250.747	24.670	707.769	618.336	-32.299
1100	36.964	278.931	253.151	28.358	706.637	609.447	-28.940
1200	37.114	282.154	255.436	32.062	701.665	600.888	-26.156
1300	37.239	285.130	257.607	35.780	700.817	592.524	-23.808
1400	37.345	287.894	259.673	39.509	699.919	584.227	-21.798
1500	37.437	290.474	261.641	43.248	698.960	575.996	-20.058
1600	37.519	292.892	263.520	46.996	697.932	567.832	-18.538
1700	37.592	295.169	265.315	50.752	696.824	559.734	-17.199
1800	37.659	297.320	267.034	54.515	695.626	551.704	-16.010
1900	37.720	299.358	268.682	58.283	694.330	543.743	-14.949
2000	37.776	301.294	270.265	62.058	692.923	535.853	-13.995
2100	37.829	303.138	271.786	65.839	691.398	528.037	-13.134
2200	37.880	304.899	273.252	69.624	668.420	521.042	-12.371
2300	37.927	306.584	274.665	73.414	666.210	514.392	-11.682
2400	37.973	308.199	276.029	77.209	663.998	507.839	-11.053
2500	38.017	309.750	277.347	81.009	661.786	501.378	-10.476
2600	38.059	311.242	278.622	84.813	659.572	495.005	-9.945
2700	38.100	312.679	279.857	88.621	657.358	488.717	-9.455
2800	38.140	314.066	281.054	92.433	655.144	482.512	-9.001
2900	38.179	315.405	282.215	96.249	652.930	476.386	-8.581
3000	38.218	316.700	283.343	100.069	650.716	470.336	-8.189
3100	38.255	317.953	284.440	103.892	648.503	464.359	-7.824
3200	38.292	319.169	285.506	107.720	646.290	458.455	-7.484
3300	38.328	320.347	286.544	111.551	644.077	452.619	-7.164
3400	38.364	321.492	287.555	115.385	641.866	446.850	-6.865
3500	38.399	322.605	288.541	119.224	639.655	441.147	-6.584
3600	38.434	323.687	289.502	123.065	637.445	435.507	-6.319
3700	38.469	324.740	290.440	126.910	635.237	429.927	-6.069
3800	38.503	325.767	291.357	130.759	633.029	424.408	-5.834
3900	38.537	326.767	292.252	134.611	630.823	418.947	-5.611
4000	38.571	327.744	293.127	138.466	628.618	413.542	-5.400
4100	38.604	328.696	293.983	142.323	626.414	408.193	-5.200
4200	38.638	329.627	294.821	146.187	624.212	402.897	-5.011
4300	38.671	330.537	295.641	150.053	622.011	397.653	-4.831
4400	38.704	331.426	296.444	153.921	619.811	392.461	-4.659
4500	38.736	332.296	297.231	157.793	617.613	387.319	-4.496
4600	38.769	333.148	298.003	161.669	615.417	382.226	-4.340
4700	38.801	333.982	298.759	165.547	613.222	377.180	-4.192
4800	38.834	334.799	299.502	169.429	50.092	383.798	-4.177
4900	38.866	335.600	300.230	173.314	48.248	390.769	-4.166
5000	38.898	336.386	300.945	177.202	46.389	397.778	-4.156
5100	38.930	337.156	301.648	181.093	44.515	404.825	-4.146
5200	38.962	337.913	302.338	184.988	42.629	411.908	-4.138
5300	38.994	338.655	303.016	188.886	40.731	419.028	-4.130
5400	39.026	339.384	303.683	192.787	38.823	426.183	-4.123
5500	39.057	340.101	304.339	196.691	36.907	433.374	-4.116
5600	39.089	340.805	304.984	200.598	34.983	440.600	-4.110
5700	39.121	341.497	305.618	204.509	33.052	447.860	-4.104
5800	39.152	342.178	306.243	208.423	31.116	455.155	-4.099
5900	39.184	342.847	306.857	212.339	29.176	462.482	-4.095
6000	39.215	343.506	307.463	216.259	27.233	469.843	-4.090

PREVIOUS: June 1963 (1 atm)   CURRENT June 1963 (1 bar)

$N_1Zr_1(g)$ Zirconium Nitride (ZrN)

Nitrogen (N₂)   REFERENCE STATE – IDEAL GAS $M_r = 28.0134$ Nitrogen (N₂)   N₂(ref)

$\Delta_f H°(0\ K) = 0\ \text{kJ·mol}^{-1}$
$\Delta_f H°(298.15\ K) = 0\ \text{kJ·mol}^{-1}$

$S°(298.15\ K) = 191.609 \pm 0.020\ \text{J·K}^{-1}\text{·mol}^{-1}$

Vibrational and Rotational Levels (cm⁻¹)

Direct Summation of Electronic Ground State:

$E = G - G_0 + F = G - G_0 + BZ - DZ^2 + \dots \approx G - G_0 + B^2Z/(B + DZ),$

where $Z = J(J + 1)$, $Y = v + 1/2$, and we omit subscript v on G, F, B, and D

$G = 2358.583Y - 14.33594Y^2 - 3.76755 \times 10^{-3}Y^3 + 2.753652 \times 10^{-4}Y^4 - 2.701198 \times 10^{-5}Y^5 + 1.749062 \times 10^{-7}Y^6$

$B = 1.998197 - 0.017279Y - 3.283 \times 10^{-5}Y^2, D = 5.74 \times 10^{-6}$

Ground State Configuration, $^1\Sigma_g^+$

$v_{max} = 58, J_{max} = 260 - 250v/v_{max}$

$\sigma = 2$

Excited Electronic States – Contributions at 4800 – 6000 K Calculated
Using First-Order Corrections:

State	$\epsilon_i/\text{cm}^{-1}$	g_i	B_e/cm^{-1}	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$
$A^3\Sigma_u^+$	49754.78	3	1.4546	1460.638	13.8723
$B^3\Pi_g$	59306.81	6	1.63745	1733.391	14.1221
$W^3\Delta_u$	59380.	6	[1.47327]	1501.4	11.6

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

These are calculated by combining direct summation of vibrational-rotational energy levels of the electronic ground state with an approximate correction for the contribution of three excited states. All spectroscopic constants are from Lofthus and Krupenie[1] except the vibrational polynomial G used in direct summation of the ground state. We revise the G equation[1] so that is converges near $D_0^0 = 78715$ cm⁻¹.[21] Experimental data are limited to $v \le 27$ and there is uncertainty in the extrapolation to high v values. Methods proposed by Khachkuruzov[3] are used to approximate the infinite-series (F) equation for rotational levels and the limiting values (J_{max}) of rotational quantum number. Values in the J_{max} equation are estimated by comparison with Khachkuruzov[3] and Gurvich et al.[4]

Contributions of excited states begin to appear in C_p^0 at ~4800 K. We obtain these contributions using the difference between approximate calculations for four states (X, A, B, and W) and one state (ground state). These approximate calculations used first-order corrections for anharmonicity and vibrational-rotational interaction. The excited state contribution to C_p^0 is 0.019 cal⁻¹ K⁻¹·mol⁻¹ at 5000 K.

Values and uncertainties at 298.15 K are the same as those selected by CODATA.[2] Uncertainties at 6000 K are considerably larger due to uncertainty in the extrapolation of G and F. Comparing our approximate calculation (a) with our adopted values (b) and those (c) of Gurvich et al.[4], we have $S°(600\ K) = 69.981, 69.999$ and $70.005\ \text{cal}^{-1}\text{·mol}^{-1}$ and $H(T) - H(0\ K) = 51.196, 51.271$, and $51.289\ \text{J·K·mol}^{-1}$.

References

[1] A. Lofthus and P. H. Krupenie, J. Phys. Chem. Ref. Data 6, 113 (1977).
[2] ICSU–CODATA Task Group, J. Chem. Thermodynamics 4, 331 (1972).
[3] G. A. Khachkuruzov, Opt. Spectrosc. 30, 455 (1971).
[4] L. V. Gurvich, G. A. Khachkuruzov et al., "Thermodynamic Properties of Individual Substances. Volume I. Calculation of the Thermodynamic Properties," English Translation, Reports AD-659660, AD-659659, AD-659679 (avail. NTIS), 1967; Volume II, Russian Edition, Moscow, (1962).

Nitrogen (N₂)   N₂(ref)

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	-8.670	0.	0.	0.
100	29.104	159.811	217.490	-5.768	0.	0.	0.
200	29.107	179.985	194.272	-2.857	0.	0.	0.
250	29.111	186.481	192.088	-1.402	0.	0.	0.
298.15	29.124	191.609	191.609	0.	0.	0.	0.
300	29.125	191.789	191.610	0.054	0.	0.	0.
350	29.165	196.281	191.964	1.511	0.	0.	0.
400	29.249	200.181	192.753	2.971	0.	0.	0.
450	29.387	203.633	193.774	4.437	0.	0.	0.
500	29.580	206.739	194.917	5.911	0.	0.	0.
600	30.110	212.176	197.353	8.894	0.	0.	0.
700	30.754	216.866	199.813	11.937	0.	0.	0.
800	31.433	221.017	202.209	15.046	0.	0.	0.
900	32.090	224.757	204.510	18.223	0.	0.	0.
1000	32.697	228.170	206.708	21.463	0.	0.	0.
1100	33.241	231.313	208.804	24.760	0.	0.	0.
1200	33.723	234.226	210.802	28.109	0.	0.	0.
1300	34.147	236.943	212.710	31.503	0.	0.	0.
1400	34.518	239.487	214.533	34.936	0.	0.	0.
1500	34.843	241.880	216.277	38.405	0.	0.	0.
1600	35.128	244.138	217.948	41.904	0.	0.	0.
1700	35.378	246.275	219.552	45.429	0.	0.	0.
1800	35.600	248.304	221.094	48.978	0.	0.	0.
1900	35.796	250.234	222.577	52.548	0.	0.	0.
2000	35.971	252.074	224.006	56.137	0.	0.	0.
2100	36.126	253.833	225.385	59.742	0.	0.	0.
2200	36.268	255.517	226.717	63.361	0.	0.	0.
2300	36.395	257.132	228.004	66.995	0.	0.	0.
2400	36.511	258.684	229.250	70.640	0.	0.	0.
2500	36.616	260.176	230.458	74.296	0.	0.	0.
2600	36.713	261.614	231.629	77.963	0.	0.	0.
2700	36.801	263.001	232.765	81.639	0.	0.	0.
2800	36.883	264.341	233.869	85.323	0.	0.	0.
2900	36.959	265.637	234.942	89.015	0.	0.	0.
3000	37.030	266.891	235.986	92.715	0.	0.	0.
3100	37.096	268.106	237.003	96.421	0.	0.	0.
3200	37.158	269.285	237.993	100.134	0.	0.	0.
3300	37.216	270.429	238.959	103.852	0.	0.	0.
3400	37.271	271.541	239.901	107.577	0.	0.	0.
3500	37.323	272.622	240.821	111.306	0.	0.	0.
3600	37.373	273.675	241.719	115.041	0.	0.	0.
3700	37.420	274.699	242.596	118.781	0.	0.	0.
3800	37.465	275.698	243.454	122.525	0.	0.	0.
3900	37.508	276.671	244.294	126.274	0.	0.	0.
4000	37.550	277.622	245.115	130.027	0.	0.	0.
4100	37.590	278.549	245.919	133.784	0.	0.	0.
4200	37.629	279.456	246.707	137.545	0.	0.	0.
4300	37.666	280.341	247.479	141.309	0.	0.	0.
4400	37.702	281.208	248.236	145.078	0.	0.	0.
4500	37.738	282.056	248.978	148.850	0.	0.	0.
4600	37.773	282.885	249.706	152.625	0.	0.	0.
4700	37.808	283.698	250.420	156.405	0.	0.	0.
4800	37.843	284.494	251.122	160.187	0.	0.	0.
4900	37.878	285.275	251.811	163.973	0.	0.	0.
5000	37.912	286.041	252.488	167.763	0.	0.	0.
5100	37.947	286.792	253.153	171.556	0.	0.	0.
5200	37.981	287.529	253.807	175.352	0.	0.	0.
5300	38.013	288.253	254.451	179.152	0.	0.	0.
5400	38.046	288.964	255.083	182.955	0.	0.	0.
5500	38.080	289.662	255.705	186.761	0.	0.	0.
5600	38.116	290.348	256.318	190.571	0.	0.	0.
5700	38.154	291.023	256.921	194.384	0.	0.	0.
5800	38.193	291.687	257.515	198.201	0.	0.	0.
5900	38.234	292.341	258.099	202.023	0.	0.	0.
6000	38.276	292.984	258.675	205.848	0.	0.	0.

PREVIOUS: March 1977 (1 atm)   CURRENT: March 1977 (1 bar)

Nitrogen, Ion (N₂⁺)   IDEAL GAS $M_r = 28.01285$ Nitrogen, Ion (N₂⁺)   N₂⁺(g)

$S°(298.15\ K) = 197.660 \pm 0.04\ \text{kJ·mol}^{-1}$

$\Delta_f H°(0\ K) = 1503.303 \pm 0.04\ \text{kJ·mol}^{-1}$
$\Delta_f H°(298.15\ K) = [1509\ 499]\ \text{kJ·mol}^{-1}$

Electronic and Molecular Constants (σ = 2)

State	g	T_o, cm⁻¹	ω_e, cm⁻¹	$\omega_e x_e$, cm⁻¹	$\omega_e y_e$, cm⁻¹	B_e, cm⁻¹	α_e, cm⁻¹	r_e, Å
X²Σ_g⁺	2	0.0	2207.00	16.10	−0.040	1.9319	0.0190	1.116384
A²Π_u	4	9016.4	1903.53	15.011		1.748	0.020	1.17364
B²Σ_u⁺	2	25566.0	2419.84	23.19		2.073	0.020	1.07772

Enthalpy of Formation

The adopted value for the enthalpy of formation of N₂⁺(g), $\Delta_f H°(0\ K) = 359.298 \pm 0.01\ \text{kcal·mol}^{-1}$ is recommended in a critical review on the energetics of gaseous ions by Rosenstock et al.[1] This value is derived from ionization potentials determined in the spectroscopic studies of Worley[2] and Ogawa and Tanaka.[3] The IP values are 125665.8 and 125666.8 cm⁻¹ respectively.

$\Delta_f H°(N_2^+, 298.15\ K)$ is obtained from $\Delta_f H°(N_2, g, 0\ K)$ by using IP (N₂, g, 0 K) with JANAF[7] enthalpies $H°(0\ K)-H°(298\ 15)$ for N₂(g). N₂(g), and e⁻ (ref) $\Delta_f H°(298\ 15)$ for the reaction N₂(g) = N₂⁺(g) + e⁻ (ref) differs from a room temperature threshold energy due to the inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al.[1] $\Delta_f H°(298.15)$ should be changed by −6 197 kJ·mol⁻¹ if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The thermal functions are calculated using the program of McBride and Gordon.[4] The contributions of vibrational anharmonicity and rotation–vibration interaction are calculated via the procedures given by Pennington and Kobe.[5] In this procedure the energy levels are calculated as follows: $\epsilon = T_o + G(v) - G(o) + B_v J(J+1) - D_v J^2(J+1)^2$ where $G(v) = \omega_e\ (v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3$ and $B_v = B_e - \alpha_e(v + 1/2)$. When a value of D_e is not available, it is calculated to be $D_e = 4B_e^3/\omega_e^2$. Molecular constant data in the table are from the critical review of Lofthus and Krupenie.[6] Electronic levels above 5000 cm⁻¹ given by Lofthus and Krupenie are not included since they make negligible contributions to the thermodynamic properties at 6000 K.

References

[1] H. M. Rosenstock, H. Draxl, B. W. Steiner, and J. T. Herron, J. Phys. Chem. Ref. Data 6, Supp. 1 (1977).
[2] R. E. Worley, Phys. Rev. 64, 207 (1943).
[3] M. Ogawa and Y. Tanaka, Can. J. Phys. 40, 1593 (1962).
[4] B. J. McBride and S. Gordon, NASA TN D-4097, (1967).
[5] R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954).
[6] A. Lofthus and P. H. Krupenie, J. Phys. Chem. Ref. Data 6, 113 (1977).
[7] JANAF Thermochemical Tables: N₂(g), 3-31-77, e⁻(ref), 3-31-77.

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p° = 0.1\ MPa$

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta H°$	$\Delta G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−8.669	1503.303		
100	29.104	165.859	223.544	−5.768			
200	29.137	197.660	211.948	−2.858			
298.15	29.137	197.660	197.660	0.	1509.499	1501.440	−263.046
300	29.139	197.840	197.660	0.054	1509.538	1501.390	−261.415
400	29.331	206.242	198.804	2.975	1511.620	1498.361	−193.666
500	29.752	212.827	200.973	5.927	1513.711	1494.804	−156.161
600	30.379	218.305	203.418	8.933	1515.812	1490.826	−129.788
700	31.097	223.042	205.890	12.006	1517.922	1486.495	−110.924
800	31.819	227.242	208.302	15.153	1520.037	1481.861	−96.756
900	32.495	231.030	210.620	18.369	1522.155	1476.962	−85.721
1000	33.108	234.486	212.836	21.650	1524.275	1471.826	−76.880
1100	33.657	237.668	214.951	24.988	1526.395	1466.479	−69.637
1200	34.148	240.617	216.968	28.379	1528.515	1460.939	−63.593
1300	34.597	243.369	218.894	31.816	1530.637	1455.221	−58.472
1400	35.018	245.948	220.736	35.297	1532.763	1449.340	−54.076
1500	35.422	248.378	222.498	38.819	1534.895	1443.307	−50.260
1600	35.822	250.677	224.188	42.381	1537.037	1437.131	−46.918
1700	36.225	252.860	225.811	45.984	1539.193	1430.821	−43.964
1800	36.636	254.943	227.372	49.627	1541.365	1424.384	−41.335
1900	37.059	256.935	228.876	53.311	1543.559	1417.825	−38.979
2000	37.496	258.847	230.327	57.039	1545.776	1411.150	−36.855
2100	37.944	260.687	231.729	60.811	1548.022	1404.364	−34.932
2200	38.403	262.463	233.086	64.628	1550.298	1397.470	−33.180
2300	38.869	264.180	234.401	68.492	1552.607	1390.472	−31.579
2400	39.339	265.844	235.676	72.402	1554.951	1383.372	−30.108
2500	39.809	267.459	236.916	76.360	1557.330	1376.174	−28.754
2600	40.275	269.030	238.121	80.364	1559.746	1368.880	−27.501
2700	40.733	270.559	239.294	84.414	1562.200	1361.493	−26.340
2800	41.181	272.048	240.437	88.510	1564.690	1354.014	−25.259
2900	41.615	273.501	241.552	92.650	1567.216	1346.445	−24.252
3000	42.032	274.919	242.641	96.833	1569.778	1338.789	−23.310
3100	42.433	276.304	243.705	101.056	1572.374	1331.047	−22.428
3200	42.811	277.657	244.745	105.318	1575.002	1323.220	−21.599
3300	43.165	278.980	245.762	109.617	1577.661	1315.311	−20.820
3400	43.496	280.273	246.758	113.951	1580.348	1307.321	−20.085
3500	43.804	281.538	247.734	118.316	1583.062	1299.251	−19.390
3600	44.084	282.776	248.690	122.710	1585.801	1291.103	−18.733
3700	44.343	283.988	249.628	127.132	1588.561	1282.879	−18.111
3800	44.581	285.174	250.548	131.578	1591.342	1274.580	−17.520
3900	44.794	286.335	251.451	136.048	1594.141	1266.208	−16.959
4000	44.994	287.471	252.337	140.537	1596.957	1257.764	−16.425
4100	45.158	288.584	253.207	145.045	1599.786	1249.249	−15.916
4200	45.307	289.674	254.063	149.568	1602.627	1240.665	−15.430
4300	45.439	290.742	254.903	154.106	1605.478	1232.013	−14.966
4400	45.556	291.788	255.730	158.656	1608.338	1223.295	−14.522
4500	45.656	292.813	256.543	163.216	1611.205	1214.512	−14.098
4600	45.730	293.817	257.342	167.786	1614.078	1205.665	−13.691
4700	45.794	294.801	258.129	172.362	1616.954	1196.755	−13.300
4800	45.846	295.766	258.903	176.944	1619.832	1187.784	−12.926
4900	45.889	296.712	259.665	181.531	1622.711	1178.753	−12.566
5000	45.920	297.639	260.415	186.122	1625.591	1169.664	−12.219
5100	45.933	298.549	261.154	190.714	1628.469	1160.517	−11.886
5200	45.939	299.441	261.881	195.308	1631.345	1151.313	−11.565
5300	45.939	300.316	262.598	199.902	1634.218	1142.054	−11.256
5400	45.932	301.174	263.305	204.495	1637.087	1132.741	−10.957
5500	45.919	302.017	264.001	209.088	1639.952	1123.375	−10.669
5600	45.900	302.844	264.687	213.679	1642.812	1113.957	−10.391
5700	45.875	303.657	265.364	218.268	1645.666	1104.488	−10.121
5800	45.843	304.454	266.031	222.854	1648.513	1094.969	−9.861
5900	45.805	305.237	266.689	227.436	1651.353	1085.400	−9.609
6000	45.761	306.007	267.338	232.015	1654.184	1075.784	−9.366

Nitrogen, Ion (N₂⁺)   N₂⁺(g)

N₂⁻(g)

Nitrogen, Ion (N₂⁻) IDEAL GAS $M_r = 28.01395$ Nitrogen, Ion (N₂⁻)

$S°(298.15\ K) = 204.54 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 155 \pm 96\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [148.615]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight

State	ϵ_i, cm⁻¹	g_i
$^2\Pi_g$	0	4

$\omega_e = [1900]\ cm^{-1}$ $\omega_e x_e = [12.0]\ cm^{-1}$ $\sigma = 2$
$B_e = [1.691]\ cm^{-1}$ $\alpha_e = [0.015]\ cm^{-1}$ $r_e = [1.193] \pm 0.003\ \text{Å}$

Enthalpy of Formation

The enthalpy of formation at 0 K for N₂⁻(g) is based on the electron affinity value derived from the Rydberg-Klein-type calculations of Gilmore.[1] Use of this adopted value, EA(N₂) = -1.6 ± 1.0 eV and auxiliary data[2] leads to $\Delta_f H° = 37 \pm 23\ kJ \cdot mol^{-1}$ and $D_0°(N_2^-) = 190 \pm 30\ kJ \cdot mol^{-1}$. Additional discussion on N₂⁻(g) may be found in the reviews by Lofthus and Krupenie[3] and Massey.[4]

The adopted EA is the only tabulated value for the ground state given in a recent compilation by Rosenstock et al.[5] This compilation contains results through the end of 1973 In support of the adopted value there are two additional studies to consider. First, Massey[4] discusses qualitatively the electronic and molecular structure as follows. The ground state of N₂ has a closed shell configuration. The corresponding configuration for N₂⁻ is obtained by adding an additional electron in an antibonding Πg 2p orbital. According to Mulliken's rule this reduces the binding energy by about 1.25 eV (~29 kJ·mol⁻¹). In contrast to O₂⁻(g), in the separated atom limit the ion N₂⁻ is not stable so that we expect the lowest level of N₂⁻ will be at least 1.25 eV above that for N₂ as well as occurring at a larger nuclear separation. Second, Birtwistle and Herzenberg[6] developed a theory of vibrational excitation through an intermediate state which predicts that the lowest energies of N₂⁻ and N₂ are separated by 1.925 eV (~44 kJ·mol⁻¹). Comparable results were obtained by Krauss and Mies[7] using a variational method.

$\Delta_f H°(0\ K)$ is converted to $\Delta_f H°(298.15\ 0K)$ by use of JANAF[2] enthalpies $H°(0\ K)-H°(298.15\ K)$ for N₂(g), N₂⁻(g), and e⁻ (ref). $\Delta_f H°(298.15\ K)$ should be changed by + 1.481 kJ·mol⁻¹ if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The vibrational constants are estimated based on trends implied in isoelectronic sequences involving (N₂⁻,NO, and O₂⁻) and N₂ and NO⁺), respectively. The value adopted for ω_e is ~35 cm⁻¹ and 65 cm⁻¹ lower than those calculated by Krauss and Mies[7] and Birtwistle and Herzenberg,[6] respectively.

We adopt the $r_e = 1.193 \pm 0.003$ Å value calculated by Birtwistle and Herzenberg[6] as it agrees with the value suggested from the above isoelectronic series. The calculations of Krauss and Mies[7] suggest $r_e = 1.22$ Å which, in our estimation, is too high. B_e is calculated from r_e while α_e is estimated from the aforementioned isoelectronic series. This α_e value is the same as one would calculate assuming a Morse potential for the electronic ground state.

No low lying excited states are assumed to exist.[3,4]

References

[1] F. R. Gilmore, J. Quant. Spectry. Radiative Transfer 5, 369 (1965).
[2] JANAF Thermochemical Tables: N₂(g), e⁻(ref), N(g), and N⁻(g).
[3] A. Lofthus and P. H. Krupenie, J. Phys. Chem. Ref. Data 6, 113 (1977).
[4] H. S. W. Massey, "Negative Ions," 3rd ed., Cambridge University Press, Cambridge, (1976).
[5] H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, J. Phys. Chem. Ref. Data 6, Supp. 1 (1977).
[6] D. F. Birtwistle and A. Herzenberg, J. Phys. B 4, 53 (1971).
[7] M. Krauss and F. H. Mies, Phys. Rev. A 1, 1592 (1970).

Standard State Pressure = $p° = 0.1$ MPa

T/K	C°p	S°	-(G°-H°(Tr))/T	H°-H°(Tr)	ΔfH°	ΔfG°	log Kf
	J·K⁻¹·mol⁻¹	J·K⁻¹·mol⁻¹	J·K⁻¹·mol⁻¹	kJ·mol⁻¹	kJ·mol⁻¹	kJ·mol⁻¹	
0	0.	0.	INFINITE	-8.674	154.808		
100	29.105	172.727	230.434	-5.771			
200	29.111	192.903	207.202	-2.860			
250	29.131	199.400	205.016	-1.404			
298.15	29.194	204.536	204.536	0.	148.615	151.015	-26.457
300	29.198	204.716	204.536	0.054	148.576	151.030	-26.297
350	29.339	209.227	204.892	1.517	147.543	151.521	-22.613
400	29.567	213.158	205.685	2.989	146.516	152.160	-19.870
450	29.874	216.658	206.713	4.475	145.497	152.926	-17.751
500	30.240	219.824	207.869	5.978	144.486	153.806	-16.068
600	31.062	225.409	210.339	9.042	142.489	155.858	-13.569
700	31.895	230.260	212.845	12.190	140.516	158.243	-11.808
800	32.661	234.570	215.297	15.419	138.556	160.909	-10.506
900	33.333	238.457	217.657	18.719	136.601	163.820	-9.508
1000	33.909	241.999	219.917	22.082	134.646	166.950	-8.721
1100	34.398	245.255	222.075	25.498	132.686	170.275	-8.086
1200	34.813	248.266	224.133	28.959	130.719	173.779	-7.564
1300	35.165	251.067	226.099	32.459	128.746	177.447	-7.130
1400	35.465	253.684	227.977	35.991	126.766	181.268	-6.763
1500	35.723	256.140	229.773	39.550	124.779	185.230	-6.450
1600	35.945	258.453	231.494	43.134	122.785	189.325	-6.181
1700	36.139	260.638	233.145	46.739	120.785	193.545	-5.947
1800	36.308	262.709	234.730	50.361	118.780	197.883	-5.742
1900	36.457	264.676	236.255	54.000	116.770	202.332	-5.562
2000	36.590	266.549	237.723	57.652	114.755	206.887	-5.403
2100	36.708	268.337	239.139	61.317	112.737	211.544	-5.262
2200	36.814	270.047	240.505	64.993	110.715	216.296	-5.136
2300	36.910	271.686	241.825	68.680	108.689	221.141	-5.022
2400	36.997	273.259	243.103	72.375	106.661	226.073	-4.920
2500	37.077	274.771	244.339	76.079	104.629	231.090	-4.828
2600	37.150	276.226	245.538	79.790	102.596	236.189	-4.745
2700	37.218	277.630	246.701	83.509	100.560	241.366	-4.670
2800	37.280	278.984	247.830	87.234	98.522	246.618	-4.601
2900	37.339	280.294	248.927	90.964	96.482	251.943	-4.538
3000	37.393	281.560	249.993	94.701	94.441	257.339	-4.481
3100	37.444	282.787	251.032	98.443	92.397	262.803	-4.428
3200	37.493	283.977	252.043	102.190	90.353	268.332	-4.380
3300	37.538	285.131	253.028	105.941	88.307	273.926	-4.336
3400	37.582	286.253	253.989	109.697	86.260	279.581	-4.295
3500	37.623	287.343	254.926	113.458	84.212	285.297	-4.258
3600	37.662	288.403	255.841	117.222	82.163	291.071	-4.223
3700	37.700	289.436	256.735	120.990	80.113	296.902	-4.192
3800	37.736	290.441	257.609	124.762	78.062	302.789	-4.162
3900	37.771	291.422	258.464	128.537	76.010	308.730	-4.135
4000	37.805	292.379	259.300	132.316	73.957	314.723	-4.110
4100	37.837	293.313	260.118	136.098	71.904	320.767	-4.087
4200	37.869	294.225	260.919	139.884	69.849	326.862	-4.065
4300	37.899	295.116	261.704	143.672	67.795	333.006	-4.045
4400	37.929	295.988	262.474	147.463	65.739	339.197	-4.027
4500	37.958	296.841	263.228	151.258	63.683	345.435	-4.010
4600	37.986	297.675	263.968	155.055	61.626	351.719	-3.994
4700	38.014	298.492	264.693	158.855	59.568	358.048	-3.979
4800	38.041	299.293	265.406	162.658	57.510	364.420	-3.966
4900	38.067	300.078	266.106	166.463	55.450	370.835	-3.953
5000	38.093	300.847	266.793	170.271	53.390	377.293	-3.942
5100	38.118	301.602	267.468	174.082	51.329	383.791	-3.931
5200	38.143	302.342	268.131	177.895	49.267	390.330	-3.921
5300	38.168	303.069	268.784	181.710	47.205	396.909	-3.912
5400	38.192	303.782	269.425	185.528	45.141	403.526	-3.903
5500	38.216	304.483	270.056	189.349	43.077	410.182	-3.896
5600	38.239	305.172	270.677	193.171	41.011	416.875	-3.888
5700	38.263	305.849	271.289	196.996	38.944	423.606	-3.882
5800	38.286	306.515	271.890	200.824	36.875	430.372	-3.876
5900	38.308	307.170	272.483	204.654	34.805	437.174	-3.870
6000	38.331	307.814	273.066	208.486	32.733	444.012	-3.865

Nitrogen, Ion (N₂⁻)

N₂⁻(g)

Nitrogen Oxide (N₂O)   IDEAL GAS $M_r = 44.0128$

$S°(298.15\ K) = 219.957\ \text{J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0\ K) = 85.48 \pm 0.4\ \text{kJ·mol}^{-1}$
$\Delta_f H°(298.15\ K) = 82.05 \pm 0.4\ \text{kJ·mol}^{-1}$

Vibrational Frequencies and Degeneracies
ν, cm⁻¹

1276.5(1)
589.2(2)
2223.7(1)

Ground State Quantum Weight: 1
Point Group: $C_{\infty v}$ $\sigma = 1$
Bond Distances: N-N = 1.1282 Å   N-O = 1.1842 Å
Bond Angle: N-N-O = 180°
Rotational Constant: $B_o = 0.421019$ cm⁻¹

Enthalpy of Formation

An analysis of the enthalpy of reaction data is summarized below. Carlton-Sutton et al [1] studied the direct decomposition at pressures of 40 to 50 atmospheres and made $P-V-T$ measurements in order to reduce the data. They obtained a similar but less certain enthalpy of formation by combustion of N₂O in CO. Flame calorimetric measurements of the combustion by Awbery and Griffiths[2] are in good agreement, but the bomb calorimetry of Fenning and Cotton[3] gives a enthalpy of formation about 0.2 kcal·mol⁻¹ larger. The selected enthalpy of formation is a weighted average of these values.

Source	Method	Reaction	$\Delta_f H°$(298.15 K), kcal·mol⁻¹	$\Delta_f H°$(298.15 K), kcal·mol⁻¹
1	Bomb calorimetry	N₂O(g) → N₂(g) + 0.5 O₂(g)	-19.52 ± 0.10	19.52
2	Bomb calorimetry	N₂O(g) + CO(g) → CO₂(g) + N₂(g)	-87.10 ± 0.30	19.46*
2	Flame calorimetry	N₂O(g) + CO(g) → CO₂(g) + N₂(g)	-87.09 ± 0.22	19.45*
3	Bomb calorimetry	N₂O(g) + CO(g) → CO₂(g) + N₂(g)	-87.37 ± 0.12	19.73*
3	Bomb calorimetry	N₂O(g) + H₂(g) → H₂O(l) + N₂(g)	-88.03 ± 0.12	19.71*

*Based on $\Delta_f H°$(298.15 K) = -68.32 (H₂O, l), -94.054 (CO₂, g), -26.417 (CO, g).

Heat Capacity and Entropy

The functions are based on the rotational constants of Pliva[4] and the frequencies determined by Tidwell et al.[5] The bond distances reported by Pliva were obtained from measurements of isotopic shifts in the infrared. They include higher-order corrections for vibration–rotation interaction and are in satisfactory agreement with the infrared and microwave studies of Douglas and Moller[6] and the electron diffraction data of Schomaker and Spurr.[7]

References

[1] T. Carlton-Sutton, H. R. Ambler, G. W. Williams, Proc. Phys. Soc. (London) 48, 189 (1936).
[2] J. H. Awbery, E. Griffiths, Proc. Roy. Soc. (London) A141, 17 (1933).
[3] R. W. Fenning, F. T. Cotton, Proc. Roy. Soc. (London) A141, 1 (1933).
[4] Pliva, J. Mol. Spectrosc. 12, 360 (1964).
[5] Tidwell, Plyler and Benedict, J. Opt. Soc. Am. 50, 1243 (1960).
[6] Douglas and Moller, J. Chem. Phys. 22, 275 (1954).
[7] Schomaker and Spurr, J. Amer. Chem. Soc. 64, 1184 (1942).

Nitrogen Oxide (N₂O)   N₂O₁(g)

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	-9.579	85.481	85.481	INFINITE
100	29.349	184.150	250.829	-6.668	84.038	90.269	-47.152
200	33.610	205.571	223.335	-3.553	82.787	97.018	-25.338
250	36.290	213.362	220.580	-1.805	82.351	100.629	-21.025
298.15	38.617	219.957	219.957	0.	82.048	104.179	-18.252
300	38.701	220.196	219.958	0.072	82.039	104.316	-18.163
350	40.817	226.324	220.437	2.061	81.832	108.046	-16.125
400	42.680	231.899	221.526	4.149	81.713	111.800	-14.600
450	44.338	237.023	222.967	6.325	81.665	115.565	-13.414
500	45.826	241.773	224.613	8.580	81.675	119.331	-12.466
600	48.389	250.363	228.204	13.295	81.827	126.851	-11.043
700	50.500	257.986	231.924	18.243	82.105	134.334	-10.024
800	52.241	264.846	235.618	23.383	82.467	141.772	-9.257
900	53.678	271.085	239.217	28.681	82.886	149.160	-8.657
1000	54.865	276.804	242.694	34.110	83.344	156.500	-8.175
1100	55.848	282.081	246.038	39.647	83.829	163.792	-7.778
1200	56.665	286.976	249.248	45.274	84.333	171.039	-7.445
1300	57.349	291.540	252.328	50.976	84.849	178.244	-7.162
1400	57.924	295.811	255.283	56.740	85.373	185.408	-6.918
1500	58.410	299.825	258.120	62.557	85.902	192.535	-6.705
1600	58.825	303.608	260.846	68.420	86.432	199.627	-6.517
1700	59.180	307.185	263.467	74.320	86.961	206.685	-6.351
1800	59.486	310.577	265.991	80.254	87.488	213.713	-6.202
1900	59.752	313.800	268.423	86.216	88.010	220.711	-6.068
2000	59.983	316.871	270.769	92.203	88.527	227.682	-5.946
2100	60.186	319.803	273.035	98.212	89.038	234.627	-5.836
2200	60.365	322.607	275.225	104.240	89.542	241.548	-5.735
2300	60.523	325.294	277.344	110.284	90.038	248.446	-5.642
2400	60.663	327.873	279.396	116.344	90.526	255.323	-5.557
2500	60.788	330.352	281.385	122.417	91.005	262.179	-5.478
2600	60.900	332.738	283.314	128.501	91.474	269.017	-5.405
2700	61.001	335.038	285.188	134.596	91.935	275.837	-5.336
2800	61.091	337.258	287.008	140.701	92.387	282.640	-5.273
2900	61.173	339.404	288.778	146.814	92.829	289.427	-5.213
3000	61.248	341.479	290.500	152.935	93.262	296.199	-5.157
3100	61.315	343.488	292.177	159.063	93.686	302.956	-5.105
3200	61.377	345.436	293.811	165.198	94.101	309.700	-5.055
3300	61.434	347.325	295.405	171.339	94.508	316.431	-5.009
3400	61.486	349.160	296.959	177.485	94.905	323.150	-4.965
3500	61.533	350.943	298.476	183.636	95.295	329.857	-4.923
3600	61.577	352.677	299.957	189.791	95.676	336.554	-4.883
3700	61.618	354.365	301.405	195.951	96.049	343.240	-4.846
3800	61.655	356.009	302.821	202.115	96.414	349.916	-4.810
3900	61.690	357.611	304.205	208.282	96.772	356.583	-4.776
4000	61.722	359.173	305.560	214.453	97.121	363.240	-4.743
4100	61.752	360.697	306.886	220.626	97.464	369.888	-4.712
4200	61.780	362.186	308.185	226.803	97.799	376.529	-4.683
4300	61.806	363.640	309.458	232.982	98.127	383.162	-4.654
4400	61.830	365.061	310.705	239.164	98.447	389.786	-4.627
4500	61.853	366.451	311.929	245.348	98.760	396.404	-4.601
4600	61.874	367.810	313.129	251.534	99.066	403.015	-4.576
4700	61.894	369.141	314.307	257.723	99.364	409.619	-4.552
4800	61.913	370.445	315.463	263.913	99.654	416.217	-4.529
4900	61.931	371.721	316.598	270.106	99.937	422.810	-4.507
5000	61.947	372.973	317.713	276.299	100.211	429.396	-4.486
5100	61.963	374.200	318.808	282.495	100.476	435.977	-4.465
5200	61.978	375.403	319.885	288.692	100.732	442.553	-4.445
5300	61.992	376.584	320.944	294.891	100.980	449.124	-4.426
5400	62.005	377.743	321.985	301.090	101.218	455.690	-4.408
5500	62.018	378.880	323.009	307.292	101.445	462.252	-4.390
5600	62.030	379.998	324.017	313.494	101.662	468.811	-4.373
5700	62.041	381.096	325.009	319.697	101.868	475.365	-4.356
5800	62.052	382.175	325.985	325.902	102.061	481.916	-4.340
5900	62.062	383.236	326.946	332.108	102.242	488.463	-4.325
6000	62.072	384.279	327.893	338.314	102.409	495.009	-4.309

PREVIOUS: December 1964 (1 atm)   CURRENT December 1964 (1 bar)

Nitrogen Oxide (N₂O)   N₂O₁(g)

Nitrogen Oxide, Ion (N₂O⁺)   IDEAL GAS $M_r = 44.012251$ Nitrogen Oxide, Ion (N₂O⁺)   N₂O⁺(g)

$S°(298.15 \text{ K}) = 233.856 \pm 0.04 \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = 1329.592 \pm 0.63 \text{ kJ·mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = 1333.399 \pm 0.63 \text{ kJ·mol}^{-1}$

Electronic Levels and Quantum Weights

State	ϵ, cm⁻¹	g_i
X²π₃/₂	0	2
X²π₁/₂	132.4	2
A²Σ⁺	28229	2

Vibrational Frequencies and Degeneracies

ν, cm⁻¹

1736.6(1)
461.2(2)
1126.4(1)

Point Group: C∞ᵥ   σ = 1
Bond Distances: N-N = 1.155 Å   N-O = 1.185 Å
Bond Angle: N-N-O = 180°
Rotational Constant: $B_0 = 0.411407$ cm⁻¹

Enthalpy of Formation

The ionization potential of 104000 cm⁻¹ (297.35 kcal mol⁻¹) has been obtained by Tanaka et al.[1] from a Rydberg series terminating on X²π₃/₂. Other Rydberg series terminating on X²π₁/₂ and A²Σ⁺ were also obtained and confirm the adopted value. This value in conjunction with the enthalpy of formation of N₂O(g)[2] was used to calculate the adopted enthalpy of formation.

Heat Capacity and Entropy

The electronic, vibrational and rotational constants are those reported by Herzberg[3] from the work of Callomon and Creutzberg.[4]

References

[1] Y. Tanaka, A. S. Jura and F. L. LeBlanc, J. Chem. Phys. 28, 350 (1958).
[2] JANAF Thermochemical Tables: N₂O(g), 12-31-64.
[3] G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Von Nostrand Co., Inc., New York, (1966).
[4] J. H. Callomon and F. C. Creutzberg, Proc. Int. Conf. Spectrosc., 1st Bombay 1, 171 (1967).

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = p° = 0.1 MPa

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	-10.622	1329.592		
100	33.467	193.445	268.380	-7.494			
200	37.926	217.872	237.588	-3.943			
250	40.258	226.590	234.540	-1.988			
298.15	42.262	233.856	233.856	0.	1333.399	1345.131	-235.661
300	42.335	234.117	233.856	0.078	1333.435	1345.203	-234.221
350	44.212	240.787	234.379	2.243	1334.443	1347.086	-201.042
400	45.924	246.804	235.562	4.497	1335.529	1348.819	-176.138
450	47.485	252.304	237.121	6.833	1336.680	1350.412	-156.752
500	48.903	257.382	238.896	9.243	1337.885	1351.874	-141.229
600	51.329	266.520	242.756	14.259	1340.416	1354.436	-117.914
700	53.267	274.584	246.738	19.492	1343.058	1356.565	-101.228
800	54.801	281.801	250.678	24.899	1345.765	1358.310	-88.689
900	56.016	288.329	254.504	30.442	1348.508	1359.714	-78.916
1000	56.983	294.283	258.189	36.094	1351.267	1360.811	-71.081
1100	57.759	299.751	261.722	41.832	1354.032	1361.632	-64.659
1200	58.387	304.805	265.104	47.641	1355.796	1362.201	-59.295
1300	58.900	309.499	268.341	53.506	1359.554	1362.539	-54.747
1400	59.324	313.880	271.439	59.418	1362.305	1362.666	-50.842
1500	59.677	317.985	274.407	65.368	1365.045	1362.596	-47.450
1600	59.973	321.847	277.252	71.351	1367.774	1362.343	-44.476
1700	60.225	325.490	279.984	77.361	1370.491	1361.921	-41.847
1800	60.439	328.939	282.608	83.395	1373.196	1361.338	-39.505
1900	60.623	332.212	285.134	89.448	1375.889	1360.606	-37.406
2000	60.783	335.325	287.566	95.519	1378.568	1359.732	-35.513
2100	60.922	338.294	289.912	101.604	1381.234	1358.725	-33.796
2200	61.043	341.131	292.176	107.702	1383.887	1357.591	-32.233
2300	61.150	343.847	294.364	113.812	1386.527	1356.336	-30.803
2400	61.245	346.452	296.480	119.932	1389.154	1354.967	-29.490
2500	61.329	348.954	298.529	126.061	1391.767	1353.489	-28.280
2600	61.404	351.361	300.515	132.197	1394.368	1351.907	-27.160
2700	61.471	353.679	302.442	138.341	1396.956	1350.224	-26.122
2800	61.532	355.916	304.312	144.491	1399.532	1348.447	-25.156
2900	61.587	358.076	306.129	150.647	1402.095	1346.576	-24.254
3000	61.636	360.165	307.895	156.809	1404.647	1344.619	-23.412
3100	61.681	362.187	309.614	162.975	1407.187	1342.576	-22.622
3200	61.723	364.146	311.288	169.145	1409.717	1340.451	-21.881
3300	61.761	366.046	312.919	175.319	1412.235	1338.247	-21.183
3400	61.796	367.890	314.508	181.497	1414.743	1335.968	-20.525
3500	61.828	369.682	316.059	187.678	1417.242	1333.614	-19.903
3600	61.859	371.424	317.573	193.862	1419.730	1331.190	-19.315
3700	61.887	373.119	319.052	200.050	1422.209	1328.696	-18.758
3800	61.914	374.770	320.496	206.240	1424.680	1326.136	-18.229
3900	61.939	376.378	321.908	212.433	1427.141	1323.511	-17.726
4000	61.964	377.947	323.290	218.628	1429.594	1320.822	-17.248
4100	61.987	379.477	324.642	224.825	1432.039	1318.073	-16.792
4200	62.009	380.971	325.965	231.025	1434.476	1315.263	-16.358
4300	62.031	382.431	327.261	237.227	1436.905	1312.397	-15.942
4400	62.053	383.857	328.532	243.431	1439.326	1309.473	-15.545
4500	62.073	385.252	329.777	249.638	1441.740	1306.494	-15.165
4600	62.094	386.616	330.997	255.846	1444.147	1303.462	-14.801
4700	62.115	387.952	332.195	262.056	1445.545	1300.378	-14.452
4800	62.135	389.260	333.370	268.269	1448.936	1297.243	-14.117
4900	62.155	390.541	334.524	274.483	1451.319	1294.058	-13.795
5000	62.176	391.797	335.657	280.700	1453.695	1290.824	-13.485
5100	62.197	393.028	336.770	286.919	1456.062	1287.544	-13.187
5200	62.217	394.236	337.863	293.139	1458.420	1284.216	-12.900
5300	62.238	395.422	338.938	299.362	1460.771	1280.844	-12.623
5400	62.260	396.585	339.995	305.587	1463.112	1277.427	-12.357
5500	62.281	397.728	341.034	311.814	1465.444	1273.966	-12.099
5600	62.303	398.850	342.057	318.043	1467.767	1270.464	-11.850
5700	62.326	399.953	343.063	324.275	1470.079	1266.920	-11.610
5800	62.348	401.037	344.053	330.508	1472.380	1263.336	-11.378
5900	62.371	402.103	345.028	336.744	1474.670	1259.712	-11.153
6000	62.395	403.152	345.988	342.983	1476.947	1256.050	-10.935

PREVIOUS: December 1970 (1 atm)   CURRENT: December 1970 (1 bar)

Nitrogen Oxide, Ion (N₂O⁺)

Nitrogen Oxide (N₂O₃)   IDEAL GAS $M_r = 76.0116$ N₂O₃(g)

$S°(298.15 K) = 308.54 ± 2.1 J·K^{-1}·mol^{-1}$

$\Delta_f H°(0 K) = $ Unknown
$\Delta_f H°(298.15 K) = 82.843 ± 0.8 kJ·mol^{-1}$

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
		J·K⁻¹·mol⁻¹		kJ·mol⁻¹			
0	4.157	0	INFINITE	-14.920	89.618	89.618	INFINITE
100	43.290	249.899	360.299	-11.040	86.239	103.226	-53.920
200	56.497	284.180	314.268	-6.018	83.984	121.191	-31.652
250	61.524	297.344	309.597	-3.063	83.297	130.577	-27.283
298.15	65.615	308.539	308.539	0.	82.843	139.727	-24.480
300	65.761	308.946	308.541	0.122	82.829	140.080	-24.390
350	69.450	319.366	309.355	3.504	82.540	149.647	-22.334
400	72.738	328.858	311.208	7.060	82.394	159.246	-20.795
450	75.698	337.599	313.661	10.772	82.365	168.855	-19.600
500	78.370	345.715	316.466	14.625	82.431	178.462	-18.644
600	82.931	360.422	322.592	22.698	82.781	197.640	-17.206
700	86.579	373.491	328.947	31.181	83.339	216.741	-16.171
800	89.478	385.248	335.262	39.989	84.033	235.752	-15.393
900	91.780	395.925	341.418	49.056	84.815	254.671	-14.781
1000	93.617	405.694	347.364	58.330	85.656	273.499	-14.286
1100	95.095	414.688	353.081	67.768	86.533	292.242	-13.877
1200	96.294	423.016	358.567	77.339	87.432	310.903	-13.533
1300	97.276	430.764	363.826	87.019	88.344	329.489	-13.239
1400	98.087	438.003	368.868	96.789	89.259	348.004	-12.984
1500	98.764	444.794	373.706	106.632	90.173	366.453	-12.761
1600	99.333	451.187	378.351	116.538	91.079	384.843	-12.564
1700	99.816	457.224	382.815	126.496	91.974	403.175	-12.388
1800	100.228	462.941	387.109	136.499	92.854	421.455	-12.230
1900	100.583	468.370	391.244	146.540	93.716	439.688	-12.088
2000	100.890	473.537	395.230	156.614	94.557	457.875	-11.958
2100	101.157	478.466	399.078	166.716	95.377	476.021	-11.840
2200	101.391	483.178	402.794	176.844	96.172	494.129	-11.732
2300	101.598	487.689	406.388	186.994	96.943	512.200	-11.632
2400	101.780	492.017	409.866	197.163	97.687	530.238	-11.540
2500	101.942	496.175	413.236	207.349	98.405	548.246	-11.455
2600	102.087	500.177	416.503	217.551	99.095	566.226	-11.376
2700	102.216	504.032	419.674	227.766	99.759	584.180	-11.302
2800	102.333	507.751	422.754	237.993	100.396	602.110	-11.233
2900	102.438	511.344	425.747	248.232	101.006	620.017	-11.168
3000	102.533	514.819	428.658	258.481	101.589	637.904	-11.107
3100	102.619	518.182	431.492	268.738	102.147	655.773	-11.050
3200	102.698	521.441	434.253	279.004	102.680	673.622	-10.996
3300	102.770	524.603	436.943	289.278	103.188	691.456	-10.945
3400	102.836	527.672	439.566	299.558	103.672	709.275	-10.897
3500	102.896	530.653	442.126	309.845	104.133	727.080	-10.851
3600	102.952	533.553	444.626	320.137	104.572	744.872	-10.808
3700	103.003	536.374	447.068	330.435	104.989	762.652	-10.767
3800	103.050	539.122	449.454	340.738	105.385	780.423	-10.728
3900	103.094	541.799	451.788	351.045	105.760	798.182	-10.690
4000	103.135	544.410	454.071	361.356	106.115	815.931	-10.655
4100	103.173	546.957	456.305	371.672	106.451	833.673	-10.621
4200	103.208	549.444	458.494	381.991	106.767	851.406	-10.589
4300	103.240	551.873	460.637	392.313	107.064	869.133	-10.558
4400	103.271	554.246	462.738	402.639	107.342	886.851	-10.528
4500	103.300	556.568	464.797	412.967	107.602	904.564	-10.500
4600	103.326	558.838	466.817	423.299	107.842	922.271	-10.473
4700	103.352	561.061	468.798	433.633	108.063	939.974	-10.447
4800	103.375	563.237	470.743	443.969	108.265	957.672	-10.422
4900	103.397	565.369	472.653	454.308	108.446	975.367	-10.398
5000	103.418	567.458	474.528	464.648	108.606	993.057	-10.374
5100	103.438	569.506	476.370	474.991	108.744	1010.746	-10.352
5200	103.456	571.515	478.181	485.336	108.860	1028.429	-10.331
5300	103.474	573.485	479.960	495.682	108.952	1046.114	-10.310
5400	103.491	575.420	481.710	506.031	109.020	1063.794	-10.290
5500	103.506	577.319	483.432	516.380	109.062	1081.474	-10.271
5600	103.521	579.184	485.125	526.732	109.077	1099.156	-10.253
5700	103.535	581.016	486.791	537.085	109.063	1116.835	-10.235
5800	103.549	582.817	488.431	547.439	109.018	1134.517	-10.217
5900	103.561	584.587	490.046	557.794	108.942	1152.196	-10.201
6000	103.574	586.328	491.636	568.151	108.831	1169.881	-10.185

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p° = 0.1$ MPa

PREVIOUS: December 1964 (1 atm)   CURRENT: December 1964 (1 bar)

Vibrational Frequencies and Degeneracies

ν, cm⁻¹	ν, cm⁻¹	ν, cm⁻¹
1863(1)	783(1)	313(1)
1589(1)	627(1)	253(1)
1297(1)	407(1)	[Rotation]

Ground State Quantum Weight: 1
Point Group: C_s σ = 1
Bond Distances: N–N = 2.08 Å N–O (nitroso) = 1.12 Å N–O(nitro) = 1.18 Å
Bond Angles: O–N–N (nitroso) = 110° O–N–O = 134°
Product of Moments of Inertia: $I_A I_B I_C = 4.6201 × 10^{-114}$ g³·cm⁶

Enthalpy of Formation

Equilibria for the reaction N₂O₄(g) → NO(g) + NO₂(g) have been studied by Beattie and Bell,[1] Verhoek and Daniels,[2] and Abel and Proist.[3] The results of Beattie and Bell are the most extensive, but they depend on the early analysis of Giauque and Kemp[4] for the simultaneous equilibrium N₂O₄(g) → 2 NO₂(g). The JANAF analysis of the tetroxide dissociation has been used to recalculate the data of Beattie and Bell. Non-ideality of N₂O₄ and NO₂ was allowed for by use of the equations of state of Giauque and Kemp, while non-ideality of NO and N₂O₃ was removed by extrapolation of the equilibrium constants to zero pressure in a manner similar to that of Beattie and Bell. The data of Verhoek and Daniels and of Abel and Proist have not been recalculated. 2nd and 3rd law analyses of the results are summarized below. The enthalpy of formation was obtained from $\Delta_f H°(298.15 K) = 9.70$ kcal·mol⁻¹.

Source	Temp. Range	T/K	ΔS°, cal·K⁻¹·mol⁻¹ 2nd law	3rd law	Δ_fH°(298.15 K), kcal·mol⁻¹ 2nd law	3rd law
1a	278–318	298	33.25	—	9.527	—
1b	278–318	298	33.04 ± 0.35	33.77	9.476 ± 0.096	9.695
1c	278–318	298	33.56 ± 0.31	33.77	9.642 ± 0.093	9.706
2	298–318	308	38.8 ± 0.52	33.78	11.1 ± 0.155	9.59
3	291–308	294	32.9 ± 1.9	33.77	9.60 ± 0.6	9.86

a) given by authors b) from author's K_p values c) from recalculated K_p values

Heat Capacity and Entropy

The functions are similar to those calculated by Hisatsune[5] based on the analysis of Devlin and Hisatsune[6] of the Raman and infrared spectra in terms of Urey–Bradley force constants. Devlin and Hisatsune used observed isotopic shifts in the spectra along with force constants transferred from nitrogen oxides and oxyhalides in order to select the N–N bond distance and the O–N–N bond angle.

The unobserved mode was assumed to be free internal rotation around the N–N bond, leading to $S°(298.15 K) = 73.91$ cal·K⁻¹·mol⁻¹ which is in good agreement with $74.13 ± 0.52$ cal·K⁻¹·mol⁻¹ obtained from the recalculated 2nd law of Beattie and Bell. The principal moments of inertia are $I_A = 22.694 × 10^{-39}$, $I_B = 29.577 × 10^{-39}$, and $I_C = 6.883 × 10^{-39}$ g·cm², while the reduced moment for internal rotation was calculated as $I_r = 0.990 × 10^{-39}$ g·cm².

References

[1]Beattie and Bell, J. Chem. Soc. 1957, 1681 (1957).
[2]Verhoek and Daniels, J. Amer. Chem. Soc. 53, 1250 (1931).
[3]Abel and Proist, Z. Elektrochem. 35, 712 (1929).
[4]Giauque and Kemp, J. Chem. Phys. 6, 40 (1938).
[5]I. C. Hisatsune, J. Phys. Chem. 65, 2249 (1961).
[6]Devlin and Hisatsune, Spectrochim. Acta 17, 218 (1961).

Nitrogen Oxide (N₂O₃)   N₂O₃(g)

Nitrogen Oxide (N₂O₄)   CRYSTAL $M_r = 92.0110$ Nitrogen Oxide (N₂O₄)   N₂O₄(cr)

$S°(298.15 \text{ K}) = 150.290 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$T_{fus} = 261.95 \pm 0.05 \text{ K}$

$\Delta_f H°(0 \text{ K}) = -30.399 \pm 1.7 \text{ kJ}\cdot\text{mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = -35.046 \pm 1.7 \text{ kJ}\cdot\text{mol}^{-1}$
$\Delta_{fus} H° = 14.652 \pm 0.013 \text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation
The enthalpy of formation was calculated from that of the liquid using the measured enthalpy of melting and the enthalpy of the crystal and liquid.

Heat Capacity and Entropy
Giauque and Kemp[1] measured the low temperature heat capacity from 15–295 K. The entropy was obtained by integration of these data using $S°(15 \text{ K}) = 0.34 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Fusion Data
The temperature and enthalpy of fusion were also measured by Giauque and Kemp.[1]

Reference
[1] W. F. Giauque and J. D. Kemp, J. Chem. Phys. 6, 40 (1938).

T/K			Enthalpy Reference Temperature = T_r = 298.15 K J·K⁻¹·mol⁻¹		Standard State Pressure = $p°$ = 0.1 MPa kJ·mol⁻¹		
	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	-21.390	-30.399	-30.399	INFINITE
100	60.702	56.130	237.659	-18.153	-35.874	9.156	-4.783
200	91.701	108.002	160.472	-10.494	-36.947	54.843	-14.324
261.950	110.918	135.224	151.325	-4.218	---- CRYSTAL <--> LIQUID ----		
298.15	122.103	150.290	150.290	0.	-35.046	99.603	-17.450
300	122.675	151.047	150.292	0.226	-34.982	100.438	-17.488
400	153.636	190.991	155.526	14.186	-29.882	144.891	-18.921
500	167.360	227.068	166.310	30.379	-22.746	187.782	-19.617

Nitrogen Oxide (N₂O₄)   N₂O₄(cr)

Nitrogen Oxide (N₂O₄)   LIQUID $M_r = 92.0110$

$S°(298.15 \text{ K}) = 209.198 \text{ J·K}^{-1}\text{·mol}^{-1}$
$T_{fus} = 261.95 \pm 0.05 \text{ K}$

$\Delta_f H°(298.15 \text{ K}) = -19.564 \pm 1.7 \text{ kJ·mol}^{-1}$
$\Delta_{fus} H° = 14.652 \pm 0.013 \text{ kJ·mol}^{-1}$

Enthalpy of Formation

The enthalpy of formation was calculated from that of the gas using the calorimetrically measured enthalpy of vaporization to the equilibrium mixture, in conjunction with the fraction of NO_2 dimerized $\alpha = 0.161$.

Heat Capacity and Entropy

Giauque and Kemp[1] measured the low temperature heat capacity from 15–295 K. Above 295 K the heat capacity was smoothly extrapolated. $S°(l, 298.15 \text{ K})$ is calculated from $C_p°$.

Fusion and Vaporization Data

Giauque and Kemp[1] measured the temperature and enthalpy of fusion and also the boiling point and the calorimetric value of the enthalpy of vaporization to the equilibrium mixture. The enthalpy of vaporization (f = 1 atm) to a hypothetical pure N_2O_4 gas at 294.25 K was calculated to be 6.91 kcal·mol⁻¹.

References

[1] W. F. Giauque and J. D. Kemp, J. Chem Phys. 6, 40 (1938).

Nitrogen Oxide (N₂O₄)   N₂O₄(l)

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
		J·K⁻¹·mol⁻¹			kJ·mol⁻¹		
0	0	0					
100	112.884	72.843	325.324	-25.248	-27.487	15.871	-8.290
200	127.528	155.582	221.720	-13.227	-24.199	58.075	-15.168
261.950	136.843	191.160	210.426	-5.047	--- CRYSTAL <--> LIQUID ---		
298.15	142.509	209.198	209.198	0.	-19.564	97.521	-17.085
300	142.842	210.081	209.201	0.264	-19.463	98.247	-17.106
400	160.833	253.638	215.019	15.448	-13.139	136.576	-17.835
500	178.824	291.459	226.598	32.431	-5.213	173.120	-18.086

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

Nitrogen Oxide (N₂O₄)

CRYSTAL-LIQUID

0 to 261.95 K crystal
above 261.95 K liquid

Refer to the individual tables for details.

M_r = 92.0110 Nitrogen Oxide (N₂O₄) $N_2O_4(cr,l)$

T/K	C_p°	S°	$-(G^\circ-H^\circ(T_r))/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
		J·K⁻¹·mol⁻¹			kJ·mol⁻¹		
0	0.	0.	INFINITE	-36.872	-30.399	-30.399	INFINITE
100	60.702	56.130	392.476	-33.635	-35.874	9.156	-4.783
200	91.701	108.002	237.881	-25.976	-36.947	54.843	-14.324
261.950	110.918	135.224	210.426	-19.699	——— CRYSTAL <—> LIQUID ———		
261.950	136.843	191.160	210.426	-5.047	TRANSITION		
298.15	142.509	209.198	209.198	0.	-19.564	97.521	-17.085
300	142.842	210.081	209.201	0.264	-19.463	98.247	-17.106
400	160.833	253.638	215.019	15.448	-13.139	136.576	-17.835
500	178.824	291.459	226.598	32.431	-5.213	173.120	-18.086

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = p° = 0.1 MPa

PREVIOUS: CURRENT: December 1964

Nitrogen Oxide (N₂O₄) $N_2O_4(cr,l)$

Nitrogen Oxide (N₂O₄) IDEAL GAS $M_r = 92.0110$ N₂O₄(g)

$S°(298.15\ K) = 304.376\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 18.72 \pm 1.7\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 9.08 \pm 1.7\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm⁻¹	ν, cm⁻¹	ν, cm⁻¹
1373 (1)	1710(1)	1748(1)
823 (1)	480(1)	385(1)
260 (1)	430(1)	1261(1)
[50](1)	675(1)	750(1)

$\sigma = 4$

Ground State Quantum Weight: 1
Point Group: D_{2h}
Bond Distances: N–N = 1.750 Å N–O = 1.180 Å
Bond Angle: O–N–O = 133.7°
Product of the Moments of Inertia: $I_A I_B I_C = 9.935917 \times 10^{-114}\ g^3\cdot cm^6$

Enthalpy of Formation

Giauque and Kemp[1] calculated idealized equilibrium constants for the reaction N₂O₄(g) = 2 NO₂(g) from the work of Bodenstein and Boes,[2] Verhoek and Daniels[3] and Wourtzel.[4] The 2nd and 3rd law analysis of these equilibrium constants has been repeated using more recent functions. The results are shown below.

	$\Delta_f H°(298.15\ K)$, kcal·mol⁻¹	
Source	2nd law	3rd law
2	13.634 ± 0.015*	13.644
3	14.429 ± 0.126	13.672
4	13.599 ± 0.019**	13.657

*Ten points rejected because of statistically significant scatter.
**One point rejected.

The 2nd law value of Verhoek and Daniels[3] was not considered significant due to the extremely small temperature range and the use of only three temperatures. The adopted value was 13.65 ± 0.03 kcal·mol⁻¹ which leads to 2.17 kcal·mol⁻¹ for the enthalpy of formation of N₂O₄(g).

Heat Capacity and Entropy

The structural parameters were taken from the electron diffraction measurements of Smith and Hedberg.[5] The vibrational frequencies are those chosen by Hitsatsune et al.[6] The torsional frequency of 50 cm⁻¹ was estimated in order to bring the entropy of the gas into agreement with that determined by Giauque and Kemp[1] from low temperature heat capacities and heats of fusion and vaporization. The principal moments of inertia are: $I_A = 12.5103 \times 10^{-39}$, $I_B = 22.6126 \times 10^{-39}$, and $I_C = 35.1229 \times 10^{-39}\ g\cdot cm^2$.

References

¹W. F. Guauque and J. D. Kemp, J. Chem. Phys. 6, 40 (1938).
²Bodenstein and Boes, Zeits. fur physik. Chem. 100, 75 (1922).
³Verhoek and Daniels, J. Amer. Chem. Soc. 53, 1250 (1931).
⁴Wourtzel, Compt. Rend. 169, 1397 (1919).
⁵D. W. Smith and K. Hedberg, J. Chem. Phys. 25, 1282 (1956).
⁶I. C. Hitsatsune, J. P. Devlin and V. Wada, J. Chem. Phys. 33, 714 (1960).

Nitrogen Oxide (N₂O₄)

Enthalpy Reference Temperature = T_r = 298.15 K				J·K⁻¹·mol⁻¹	Standard State Pressure = $p°$ = 0.1 MPa	kJ·mol⁻¹		
T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	-16.398	18.718	18.718	INFINITE
100	46.262	239.166	363.098	-12.393	14.011	40.737	-21.279
200	63.206	276.398	311.015	-6.923	10.749	68.860	-17.984
250	70.823	291.339	305.613	-3.568	9.732	83.513	-17.449
298.15	77.256	304.376	304.376	0.	9.079	97.787	-17.132
300	77.487	304.854	304.377	0.143	9.060	98.338	-17.122
350	83.340	317.248	305.343	4.167	8.673	113.251	-16.902
400	88.521	328.722	307.557	8.466	8.523	128.204	-16.742
450	93.121	339.419	310.509	13.009	8.557	143.163	-16.618
500	97.204	349.446	313.907	17.769	8.769	158.109	-16.518
600	104.012	367.795	321.388	27.844	9.542	187.911	-16.359
700	109.314	384.244	329.213	38.522	10.667	217.555	-16.234
800	113.439	399.122	337.037	49.668	12.030	247.019	-16.129
900	116.665	412.677	344.700	61.180	13.554	276.303	-16.035
1000	119.208	425.106	352.127	72.978	15.189	305.410	-15.953
1100	121.235	436.566	359.290	85.004	16.899	334.350	-15.877
1200	122.867	447.187	366.177	97.212	18.661	363.132	-15.807
1300	124.196	457.076	372.794	109.567	20.456	391.765	-15.741
1400	125.290	466.331	379.148	122.044	22.272	420.259	-15.680
1500	126.198	474.997	385.251	134.619	24.097	448.623	-15.622
1600	126.959	483.167	391.118	147.278	25.922	476.865	-15.568
1700	127.603	490.884	396.762	160.007	27.742	504.994	-15.517
1800	128.152	498.193	402.196	172.796	29.550	533.014	-15.468
1900	128.623	505.135	407.432	185.635	31.340	560.936	-15.421
2000	129.030	511.743	412.484	198.518	33.110	588.764	-15.377
2100	129.385	518.047	417.362	211.439	34.855	616.503	-15.335
2200	129.694	524.074	422.077	224.394	36.573	644.162	-15.294
2300	129.967	529.845	426.638	237.377	38.262	671.741	-15.256
2400	130.208	535.381	431.054	250.386	39.920	699.247	-15.219
2500	130.421	540.701	435.334	263.418	41.545	726.685	-15.183
2600	130.612	545.820	439.486	276.469	43.138	754.059	-15.149
2700	130.783	550.753	443.516	289.539	44.698	781.373	-15.117
2800	130.936	555.512	447.431	302.625	46.224	808.630	-15.085
2900	131.074	560.109	451.238	315.726	47.718	835.831	-15.055
3000	131.200	564.555	454.942	328.840	49.178	862.983	-15.026
3100	131.313	568.859	458.547	341.966	50.606	890.087	-14.998
3200	131.417	573.029	462.060	355.102	52.002	917.144	-14.971
3300	131.511	577.075	465.484	368.249	53.368	944.157	-14.945
3400	131.597	581.002	468.824	381.404	54.703	971.132	-14.920
3500	131.677	584.818	472.084	394.568	56.010	998.066	-14.895
3600	131.750	588.528	475.268	407.739	57.288	1024.964	-14.872
3700	131.817	592.139	478.378	420.918	58.538	1051.826	-14.849
3800	131.879	595.655	481.418	434.102	59.762	1078.657	-14.827
3900	131.936	599.082	484.391	447.293	60.960	1105.455	-14.806
4000	131.990	602.423	487.300	460.490	62.132	1132.220	-14.785
4100	132.039	605.683	490.148	473.691	63.279	1158.958	-14.765
4200	132.085	608.865	492.937	486.897	64.402	1185.669	-14.746
4300	132.128	611.973	495.669	500.108	65.501	1212.353	-14.727
4400	132.168	615.011	498.347	513.323	66.575	1239.011	-14.709
4500	132.206	617.982	500.973	526.542	67.626	1265.644	-14.691
4600	132.241	620.888	503.548	539.764	68.653	1292.255	-14.674
4700	132.274	623.733	506.075	552.990	69.654	1318.845	-14.657
4800	132.305	626.518	508.555	566.219	70.630	1345.413	-14.641
4900	132.334	629.246	510.991	579.451	71.581	1371.962	-14.625
5000	132.361	631.920	513.383	592.685	72.504	1398.491	-14.610
5100	132.387	634.541	515.733	605.923	73.400	1425.003	-14.595
5200	132.411	637.112	518.042	619.163	74.267	1451.494	-14.580
5300	132.434	639.635	520.313	632.405	75.104	1477.973	-14.566
5400	132.456	642.110	522.545	645.649	75.908	1504.434	-14.553
5500	132.476	644.541	524.742	658.896	76.680	1530.880	-14.539
5600	132.496	646.928	526.902	672.145	77.417	1557.315	-14.526
5700	132.514	649.273	529.029	685.395	78.116	1583.734	-14.513
5800	132.532	651.578	531.122	698.648	78.776	1610.145	-14.501
5900	132.549	653.844	533.183	711.902	79.394	1636.539	-14.489
6000	132.564	656.072	535.212	725.157	79.968	1662.928	-14.477

Nitrogen Oxide (N₂O₄) N₂O₄(g)

Nitrogen Oxide (N₂O₅)   IDEAL GAS $M_r = 108.0104$ N₂O₅(g)

$S^\circ(298.15\ \text{K}) = 346.548 \pm 4.2\ \text{J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H^\circ(0\ \text{K}) = \text{Unknown}$

$\Delta_f H^\circ(298.15\ \text{K}) = 11.297 \pm 1.3\ \text{kJ·mol}^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm⁻¹	ν, cm⁻¹	ν, cm⁻¹	ν, cm⁻¹	ν, cm⁻¹
1728(1)	614 (1)	[614](1)	[Rotation]	860(1)
1338(1)	353 (1)	[Rotation]	1728(1)	743(1)
743(1)	[85](1)	577 (1)	1247(1)	353(1)

$\sigma = 2$

Ground State Quantum Weight: 1

Point Group: C₂ᵥ

Bond Distances: O–N = 1.21 Å   N–O' = 1.46 Å

Bond Angles: O–N–O = 134°   N–O'–N = 95°

O–N–O planes perpendicular to N–O–N plane

Product of the Moments of Inertia: $I_A I_B I_C = 2.066 \times 10^{-113}\ \text{g}^3\text{·cm}^6$

Enthalpy of Formation

The enthalpy of formation was obtained by recalculation of the calorimetric data of Ray and Ogg for the reaction of N₂O₅(g) with NO. The stoichiometry of the reaction products, originally based on the results for N₂O₄ → 2 NO₂ from Giauque and Kemp[1] was based on the JANAF analysis of this simultaneous equilibrium. A correction of 0.29 kcal·mol⁻¹ was made in the enthalpy of reaction because of the additional formation of N₂O₃ from NO and NO₂.

Confirmation of the enthalpy of formation was obtained by combination of the enthalpies of hydrolysis and sublimation of N₂O₅(cr). The results are summarized below. 2nd law values are given for the enthalpies of sublimation, but 3rd law analyses suggest that the value from Russ and Pokorny[4] is more reliable. Most of the uncertainty in this path, however, arises from the enthalpy of hydrolysis.

Source	Method	Reaction	$\Delta_f H^\circ$(298.15 K) kcal·mol⁻¹	$\Delta_f H^\circ$(298.15 K) kcal·mol⁻¹
2	Calorimetric	N₂O₅(g) + NO(g) → 0.724 NO₂(g) + 1.138 N₂O₄(g)	-16.05 ± 0.20	2.67
3	Calorimetric	N₂O₅(cr) + H₂O(l) → 2 HNO₃(aq)	-20.2 ± 0.5	--
4	Vapor Pressure	N₂O₅(cr) → N₂O₅(g)	13.37 ± 0.06	2.79*
5	Vapor Pressure	N₂O₅(cr) → N₂O₅(g)	13.25 ± 0.12	2.67*

*Using reaction 2 and $\Delta_f H^\circ$(298.15 K) = -68.32(H₂O, l), -49.55(HNO₃, aq).

Heat Capacity and Entropy

Ray and Ogg[6] reported S°(298.15 K) = 85 ± 0.5 cal·K⁻¹·mol⁻¹ from combination of kinetic and thermochemical values. This entropy was recalculated as follows. The rate data of Ray and Ogg[6] and of Daniels and Johnston[7] give for the reaction N₂O₅(g) → NO₂(g) + NO₃(g) + O₂(g) at 25°C the equilibrium constant $K = 5.15 \times 10^{-7}$ moles² liter⁻² = 3.08×10^{-4} atm². The resulting value of $\Delta_f H^\circ$(298.15 K) = 4.79 kcal·mol⁻¹ leads to S°(298.15 K) = 82.8 cal·K⁻¹·mol⁻¹ for N₂O₅(g) when combined with the JANAF entropies and heats of formation of the components of the reaction.

The molecular structure is the nonplanar configuration from the electron diffraction study of Akishin et al.[8] A planar model (also point group C₂ᵥ) was assumed by Hisatsune et al.[9] in their approximate molecular coordinate analysis of the infrared and Raman spectra. The frequency assignments of these authors are listed above in the order for the planar model, although the vibrations for the nonplanar form will separate differently into the species 5A₁, 3A₂, 3B₁, and 4B₂. Hisatsune et al.[9] estimated the N–O'–N deformation frequency (8 cm⁻¹) from combination bands in the solid and gas phase spectra. The JANAF thermodynamic functions were obtained using these frequencies and assuming the two NO₂ groups to be hindered internal rotators. Barriers to internal rotation of 4.4 kcal·mol⁻¹ (corresponding to torsional vibrations of about 55 cm⁻¹) were selected in order to give the observed entropy at room temperature. The principal moments of inertia for the nonplanar model were taken as $I_A = 30.60 \times 10^{-39}$, $I_B = 40.15 \times 10^{-39}$, and $I_C = 16.82 \times 10^{-39}$ g·cm², while $I_r = 4.693 \times 10^{-39}$ g·cm² was used for the reduced moment of inertia of the O₂ tops.

References

[1] Giauque and Kemp, J. Chem. Phys. 6, 40 (1938).
[2] J. D. Ray and R. A. Ogg, J. Phys. Chem. 61, 1087 (1957).
[3] R. A. Ogg, J. Chem. Phys. 15, 337 (1947).
[4] Russ and Pokorny, Monatsh. 34, 1027 (1913).
[5] F. Daniels and A. C. Bright, J. Amer. Chem. Soc. 42, 1131 (1920).
[6] J. D. Ray and R. A. Ogg, J. Chem. Phys. 26, 984 (1957).
[7] F. Daniels and Johnston, J. Amer. Chem. Soc. 43, 53 (1921).
[8] Akishin, Vilkov and Rosolovskii, Zhur. Strukt. Khim. 1, 1 (1960).
[9] Hisatsune, Devlin and Wada, Spectrochim. Acta 18, 1641 (1962).

Nitrogen Oxide (N₂O₅)

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-(G^\circ-H^\circ(T_r))/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log K_f$
	J·K⁻¹·mol⁻¹	J·K⁻¹·mol⁻¹	J·K⁻¹·mol⁻¹	kJ·mol⁻¹	kJ·mol⁻¹	kJ·mol⁻¹	
0							
100							
200	78.203	311.842	354.795	-8.591	12.733	83.104	-21.704
298.15	96.303	346.548	346.548	0.	11.297	118.013	-20.675
300	96.604	347.145	346.550	0.178	11.283	118.675	-20.663
400	110.851	376.991	350.523	10.587	11.349	154.497	-20.175
500	121.190	402.904	358.466	22.219	12.395	190.178	-19.868
600	128.382	425.677	367.809	34.720	14.013	225.590	-19.639
700	133.432	445.869	377.546	47.826	15.940	260.703	-19.454
800	137.001	463.930	387.235	61.356	18.018	295.528	-19.296
900	139.599	480.224	396.677	75.192	20.164	330.089	-19.158
1000	141.444	495.031	405.784	89.248	22.324	364.409	-19.035
1100	142.829	508.579	414.522	103.463	24.470	398.514	-18.924
1200	143.971	521.058	422.886	117.805	26.591	432.424	-18.823
1300	144.816	532.616	430.888	132.246	28.680	466.158	-18.730
1400	145.528	543.375	438.543	146.764	30.731	499.734	-18.645
1500	146.078	553.434	445.871	161.345	32.741	533.163	-18.566
1600	146.553	562.877	452.892	175.977	34.706	566.460	-18.493
1700	146.879	571.772	459.626	190.649	36.623	599.636	-18.425
1800	147.179	580.176	466.091	205.352	38.487	632.699	-18.360
1900	147.454	588.141	472.307	220.084	40.300	665.662	-18.300
2000	147.704	595.711	478.290	234.842	42.064	698.530	-18.244
2100	147.846	602.921	484.054	249.620	43.773	731.311	-18.190
2200	147.981	609.802	489.615	264.411	45.424	764.013	-18.140
2300	148.109	616.383	494.985	279.216	47.018	796.640	-18.092
2400	148.230	622.689	500.175	294.033	48.558	829.198	-18.047
2500	148.344	628.742	505.198	308.861	50.043	861.694	-18.004
2600	148.450	634.562	510.062	323.701	51.475	894.131	-17.963
2700	148.549	640.167	514.777	338.551	52.857	926.516	-17.925
2800	148.641	645.571	519.353	353.411	54.188	958.850	-17.888
2900	148.726	650.788	523.796	368.279	55.470	991.134	-17.852
3000	148.804	655.832	528.113	383.156	56.704	1023.378	-17.819
3100	148.851	660.712	532.312	398.038	57.892	1055.582	-17.786
3200	148.896	665.438	536.399	412.926	59.032	1087.746	-17.756
3300	148.939	670.021	540.379	427.818	60.127	1119.875	-17.726
3400	148.980	674.468	544.258	442.714	61.180	1151.974	-17.698
3500	149.019	678.787	548.040	457.614	62.190	1184.041	-17.671
3600	149.057	682.985	551.730	472.517	63.161	1216.080	-17.645
3700	149.092	687.070	555.333	487.425	64.094	1248.092	-17.620
3800	149.126	691.046	558.853	502.336	64.989	1280.082	-17.596
3900	149.156	694.920	562.292	517.250	65.849	1312.047	-17.573
4000	149.185	698.697	565.655	532.167	66.674	1343.989	-17.551
4100	149.206	702.381	568.945	547.086	67.465	1375.912	-17.529
4200	149.227	705.977	572.165	562.008	68.223	1407.816	-17.509
4300	149.247	709.488	575.318	576.932	68.948	1439.704	-17.489
4400	149.267	712.920	578.407	591.858	69.640	1471.572	-17.470
4500	149.285	716.274	581.433	606.785	70.301	1503.426	-17.451
4600	149.303	719.556	584.400	621.715	70.929	1535.266	-17.433
4700	149.319	722.767	587.310	636.646	71.525	1567.093	-17.416
4800	149.335	725.911	590.165	651.578	72.088	1598.908	-17.400
4900	149.350	728.990	592.967	666.513	72.616	1630.713	-17.384
5000	149.365	732.007	595.718	681.448	73.111	1662.506	-17.368
5100	149.378	734.965	598.419	696.386	73.569	1694.290	-17.353
5200	149.391	737.866	601.073	711.324	73.990	1726.062	-17.339
5300	149.402	740.712	603.681	726.264	74.373	1757.831	-17.324
5400	149.413	743.505	606.244	741.204	74.714	1789.590	-17.311
5500	149.423	746.246	608.765	756.146	75.014	1821.343	-17.298
5600	149.432	748.939	611.244	771.089	75.269	1853.094	-17.285
5700	149.441	751.584	613.683	786.033	75.477	1884.838	-17.273
5800	149.448	754.183	616.083	800.977	75.635	1916.581	-17.261
5900	149.455	756.738	618.446	815.922	75.741	1948.317	-17.249
6000	149.461	759.250	620.772	830.868	75.791	1980.057	-17.238

Nitrogen Oxide (N₂O₅)   N₂O₅(g)

Azide (N₃)   IDEAL GAS M_r = 42.0201   Azide (N₃)   N₃(g)

$\Delta_f H°(0\ K) = 416.97 \pm 20.9\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 414.22 \pm 20.9\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = [226.469 \pm 2.1]\ J\cdot K^{-1}\cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm⁻¹	g_i
$X^2\Pi_{3/2}$	0	2
$X^2\Pi_{1/2}$	71.3	2
$A^2\Sigma_u^+$	36811	2

Vibrational Frequencies and Degeneracies

ν_i, cm⁻¹

[1800](1)
[500](2)
[1200](1)

Point Group: $D_{\infty h}$ $\sigma = 2$
Bond Distance: N–N = 1.1815 Å
Bond Angle: N–N–N = 180°
Rotational Constant: B_0 = 0.431085 cm⁻¹

Enthalpy of Formation

Okabe and Mele[1] have measured the photodissociation onset of the process

$$CN\cdot N_3(g) \rightarrow CN(g) + N_3(g) \qquad \Delta H°(0\ K) = 96 \pm 2.5\ kcal\cdot mol^{-1}$$

Using a value of $\Delta_f H°(CN\cdot N_3,\ g,\ 298.15\ K) = 107 \pm 3\ kcal\cdot mol^{-1}$ and $\Delta_f H°(CN,\ g,\ 298.15\ K) = 104 \pm 2.5\ kcal\cdot mol^{-1}$[2], we derive $\Delta_f H°(N_3, g, 298.15\ K) = 99 \pm 5\ kcal\cdot mol^{-1}$. The enthalpy of formation of CN·N₃ is obtained from $\Delta_f H°(CN\cdot N_3, cr, 298.15\ K) = 92.6 \pm 3\ kcal\cdot mol^{-1}$ and an estimated $\Delta_{sub} H°(298.15\ K) = 14.4 \pm 3\ kcal\cdot mol^{-1}$. The enthalpy of sublimation is similar to that for ICN(cr).[3] A rough confirmation of $\Delta_{sub} H°$ can be made by assuming a boiling point of 227°C (500 K), from the facts that CN·N₃ sublimes in vacuo at 40°C and can be heated as a liquid to 170°C. Thus, using the Trouton rule, $\Delta_{vap} H° = 11\ kcal\cdot mol^{-1}$, in addition the enthalpy of melting would be expected to be about 3.6 kcal·mol⁻¹ for this 5 atom molecule, thus $\Delta_{sub} H° = 14.6\ kcal\cdot mol^{-1}$.

Heat Capacity and Entropy

The electronic levels and rotational constants have been reported by Douglas and Jones[4] and Thrush.[5] The vibrational frequencies were estimated from the isoelectronic species NCO, NNO⁺, and the related molecules NCN and NNO.[2]

References

[1]H. Okabe and A. Mele, J. Chem. Phys. 51, 2100 (1959).
[2]JANAF Thermochemical Tables: CN(g), 6-30-69; ICN(g), 6-30-69; NCO(g), 12-31-70; NNO⁺(g), 12-31-70; NCN(g), 12-31-70; N₂O(g), 12-31-64.
[3]U. S. Nat. Bur. Stand. Tech. Note 270-3, (1968).
[4]A. E. Douglas and W. J. Jones, Can. J. Phys. 43, 2216 (1965).
[5]B. A. Thrush, Proc. Roy. Soc. (London) 235A, 143 (1956).

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K⁻¹·mol⁻¹	$S°$ J·K⁻¹·mol⁻¹	$-(G°-H°(T_r))/T$ J·K⁻¹·mol⁻¹	$H°-H°(T_r)$ kJ·mol⁻¹	$\Delta_f H°$ kJ·mol⁻¹	$\Delta_f G°$ kJ·mol⁻¹	log K_f
0	0.	0.	INFINITE	-10.253	416.969	416.969	INFINITE
100	31.448	188.244	259.348	-7.110	415.757	420.905	-219.858
200	35.960	211.175	230.051	-3.775	414.727	426.487	-111.387
250	38.562	219.485	227.128	-1.911	414.408	429.467	-89.732
298.15	40.762	226.469	226.469	0.	414.216	432.387	-75.752
300	40.842	226.721	226.470	0.075	414.211	432.499	-75.305
350	42.864	233.172	226.974	2.169	414.119	435.556	-65.003
400	44.686	239.016	228.120	4.359	414.118	438.620	-57.278
450	46.339	244.377	229.633	6.635	414.196	441.679	-51.269
500	47.838	249.338	231.358	8.990	414.340	444.725	-46.460
600	50.407	258.295	235.117	13.907	414.782	450.764	-39.242
700	52.470	266.226	239.006	19.054	415.365	456.716	-34.081
800	54.113	273.344	242.861	24.387	416.033	462.578	-30.203
900	55.421	279.796	246.612	29.866	416.748	468.354	-27.183
1000	56.467	285.691	250.229	35.462	417.484	474.048	-24.762
1100	57.308	291.114	253.703	41.152	418.228	479.669	-22.778
1200	57.992	296.131	257.032	46.919	418.971	485.222	-21.121
1300	58.552	300.796	260.221	52.747	419.709	490.712	-19.717
1400	59.015	305.152	263.277	58.626	420.437	496.147	-18.511
1500	59.402	309.238	266.206	64.547	421.156	501.530	-17.465
1600	59.727	313.082	269.017	70.504	421.865	506.865	-16.547
1700	60.003	316.711	271.717	76.491	422.563	512.156	-15.737
1800	60.239	320.148	274.313	82.503	423.252	517.406	-15.015
1900	60.442	323.410	276.812	88.538	423.932	522.618	-14.368
2000	60.617	326.515	279.220	94.591	424.602	527.795	-13.783
2100	60.770	329.477	281.543	100.660	425.264	532.938	-13.256
2200	60.904	332.302	283.787	106.744	425.918	538.050	-12.775
2300	61.022	335.017	285.956	112.841	426.565	543.132	-12.335
2400	61.127	337.616	288.054	118.948	427.204	548.187	-11.931
2500	61.219	340.113	290.087	125.066	427.837	553.215	-11.559
2600	61.376	342.516	292.058	131.192	428.464	558.464	-11.215
2700	61.376	344.831	293.970	137.326	429.084	563.196	-10.896
2800	61.443	347.064	295.826	143.467	429.699	568.152	-10.599
2900	61.503	349.221	297.630	149.614	430.308	573.086	-10.322
3000	61.558	351.307	299.385	155.767	430.912	577.999	-10.064
3100	61.607	353.327	301.093	161.926	431.510	582.892	-9.822
3200	61.652	355.283	302.756	168.089	432.104	587.766	-9.594
3300	61.693	357.181	304.376	174.256	432.693	592.621	-9.380
3400	61.731	359.024	305.957	180.427	433.278	597.459	-9.179
3500	61.766	360.813	307.499	186.602	433.858	602.279	-8.989
3600	61.798	362.554	309.004	192.780	434.434	607.083	-8.809
3700	61.827	364.248	310.474	198.962	435.006	611.871	-8.638
3800	61.855	365.897	311.911	205.146	435.574	616.643	-8.476
3900	61.880	367.504	313.316	211.332	436.138	621.401	-8.323
4000	61.904	369.071	314.690	217.522	436.697	626.144	-8.177
4100	61.926	370.600	316.035	223.713	437.253	630.874	-8.037
4200	61.946	372.092	317.352	229.907	437.806	635.589	-7.905
4300	61.966	373.550	318.642	236.102	438.354	640.292	-7.778
4400	61.984	374.975	319.907	242.300	438.899	644.982	-7.657
4500	62.001	376.368	321.146	248.499	439.440	649.660	-7.541
4600	62.018	377.731	322.361	254.700	439.978	654.325	-7.430
4700	62.033	379.065	323.553	260.903	440.512	658.979	-7.324
4800	62.048	380.371	324.724	267.107	441.042	663.622	-7.222
4900	62.063	381.650	325.872	273.312	441.568	668.253	-7.124
5000	62.077	382.904	327.001	279.519	442.091	672.874	-7.029
5100	62.090	384.134	328.109	285.728	442.610	677.485	-6.939
5200	62.103	385.340	329.198	291.937	443.125	682.085	-6.852
5300	62.116	386.523	330.268	298.148	443.637	686.676	-6.768
5400	62.128	387.684	331.321	304.360	444.144	691.256	-6.687
5500	62.141	388.824	332.356	310.574	444.649	695.828	-6.608
5600	62.153	389.944	333.374	316.788	445.149	700.390	-6.533
5700	62.165	391.044	334.377	323.004	445.644	704.944	-6.460
5800	62.177	392.125	335.363	329.222	446.135	709.489	-6.390
5900	62.189	393.188	336.334	335.440	446.622	714.025	-6.321
6000	62.202	394.234	337.290	341.659	447.103	718.553	-6.256

PREVIOUS: December 1970 (1 atm)   CURRENT: December 1970 (1 bar)

Azide (N₃)   N₃(g)

Silicon Nitride, Alpha (α-Si₃N₄) CRYSTAL(α) $M_r = 140.2833$ Silicon Nitride, Alpha (Si₃N₄) N₄Si₃(cr)

$S°(298.15 \text{ K}) = [112.967 \pm 16.7] \text{ J·K}^{-1}\cdot\text{mol}^{-1}$

$\Delta_f H°(298.15 \text{ K}) = -744.752 \pm 29.3 \text{ kJ·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = \text{Unknown}$

T/K	C°ₚ	S°	-[G°-H°(T_r)]/T	H°-H°(T_r)	ΔfH°	ΔfG°	log Kf
		J·K⁻¹·mol⁻¹			kJ·mol⁻¹		
0							
100							
200							
298.15	99.533	112.967	112.967	0.	-744.752	-647.343	113.412
300	99.788	113.583	112.969	0.184	-744.787	-646.739	112.607
400	110.667	143.790	117.014	10.711	-746.459	-613.792	80.153
500	120.708	169.582	125.007	22.288	-747.595	-580.482	60.643
600	129.704	192.417	134.374	34.826	-748.151	-546.998	47.620
700	138.072	213.048	144.162	48.220	-748.186	-513.462	38.315
800	145.812	232.003	153.973	62.424	-747.729	-479.956	31.338
900	152.298	249.566	163.631	77.342	-746.830	-445.533	25.916
1000	158.155	265.920	173.051	92.869	-745.635	-413.227	21.585
1100	163.678	281.258	182.198	108.966	-744.100	-380.058	18.047
1200	168.490	295.712	191.061	125.581	-742.280	-347.041	15.106
1300	172.551	309.362	199.641	142.637	-740.233	-314.187	12.624
1400	175.920	322.276	207.944	160.065	-738.019	-281.496	10.503
1500	178.657	334.510	215.977	177.799	-735.694	-248.968	8.670
1600	180.548	346.102	223.751	195.762	-733.327	-216.597	7.071
1700	182.171	357.098	231.274	213.900	-881.495	-183.033	5.624
1800	183.452	367.548	238.557	232.183	-878.469	-142.034	4.122
1900	184.539	377.496	245.610	250.584	-875.367	-101.205	2.782
2000	185.435	386.986	252.444	269.084	-872.202	-60.541	1.581
2100	185.780	396.041	259.068	287.645	-869.010	-20.037	0.498
2200	186.111	404.692	265.492	306.240	-865.814	20.316	-0.482
2300	186.429	412.977	271.725	324.867	-862.612	60.523	-1.375
2400	186.734	420.913	277.777	343.525	-859.403	100.590	-2.189
2500	187.025	428.541	283.656	362.213	-856.187	140.524	-2.936
2600	187.303	435.882	289.371	380.930	-852.962	180.329	-3.623
2700	187.567	442.956	294.929	399.673	-849.729	220.009	-4.256
2800	187.818	449.782	300.338	418.443	-846.487	259.570	-4.842
2900	188.056	456.377	305.606	437.236	-843.236	299.015	-5.386
3000	188.280	462.756	310.738	456.053	-839.977	338.347	-5.891

Enthalpy Reference Temperature - T_r = 298.15 K   Standard State Pressure - p° = 0.1 MPa

Enthalpy of Formation

The equilibria (A) Si₃N₄(cr) = 3 Si(l) + 2 N₂(g) and (B) Si₃N₄(cr) = 3 Si(cr) + 2 N₂(g) have been investigated by three groups. Pehlke and Elliott[1] made four series of measurements which mainly concerned reaction (A). Hincke and Brantley[2] made a single series of measurements which covered reactions (A) and (B). Matignon[3] also gave a single equilibrium point for reaction (C) 3 SiO₂(cr) + 6 C + 2 N₂ = Si₃N₄(cr) + 6 CO(g). Below are shown 2nd and 3rd law analyses of the data. It should be noted that these analyses are based on the estimated enthalpy capacities above 900 K and on an estimated entropy. The uncertainty due to these estimates is estimated as ±7 kcal·mol⁻¹ in ΔfH°(298.15 K).

Source	Data Points	T/K	Reaction	ΔfH°(298.15 K), kcal·mol⁻¹ 2nd law	3rd law	Drift cal·K⁻¹·mol⁻¹	ΔfH°(298.15K) kcal·mol⁻¹
Pehlke - 1	9	1699-1934	A	190.1 ± 7.6	211.79	11.8 ± 4.3	-177.04
Pehlke - 2	9	1691-1939	A	210.7 ± 8.6	213.29	1.8 ± 4.9	-178.53
Pehlke - 3	10	1692-1966	A	212.3 ± 3.3	212.61	0.1 ± 1.9	-177.85
Pehlke - 4	6	1690-1872	A	207.0 ± 7.5	212.47	2.6 ± 4.3	-177.71
Pehlke	30**	1690-1966	A	212.8 ± 3.2	212.67	-0.2 ± 1.8	-177.91
Hinke	4	1709-1802	A	196.0 ± 18.5	213.43	10.3 ± 10.4	-178.67
Pehlke	4	1659-1666	B		177.41		-177.41
Hinke	3	1606-1675	B		177.82	22.8 ± 11.8	-177.82
Matignon	1	1700	C		318.9		-175.1

**Four points rejected due to failure of a statistical test; this set is a combination of the first four sets.

The adopted ΔfH°(α-Si₃N₄, 298.15 K) = -178 ± 7 kcal·mol⁻¹.

McClaine and Coppel[4] have investigated the decomposition reaction (B). The conclude that at 1618 K the equilibrium pressure is roughly 0.15 mm. This corresponds to ΔfH°(298.15 K) = 182.3 kcal·mol⁻¹, and was not given any weight in the adopted value.

Heat Capacity and Entropy

The enthalpy of α-Si₃N₄ has been measured at three temperatures, in the range 373-858 K, by Sato.[5] The heat capacity is calculated from the data assuming that a limit of 45 cal·K⁻¹·mol⁻¹ is attained by 3000 K. The entropy is obtained from the equilibrium data of Pehlke and Elliott.[1]

Decomposition Data

The temperature of decomposition, T_dm = 2151 K, is calculated as the point at which the decomposition pressure of nitrogen reaches a fugacity of 1 atm.

References

[1] R. D. Pehlke and J. F. Elliott, Trans. Met. Soc. AIME 215, 781 (1959).
[2] W. B. Hincke and L. R. Brantley, J. Amer. Chem. Soc. 52, 48 (1930).
[3] C. Matignon, Bull. Soc. Chim. France 13, 791 (1913).
[4] L. A. McClaine and C. P. Coppel, A. D. Little, Inc., "Equilibrium Studies of Refractory Nitrides," Tech. Rept. AFML-TR-65-99, Part 11, (December 1966).
[5] S. Sato, Bull. Chem. Soc. Japan 13, 41 (1938).

Phosphorus Nitride (P₃N₅)   CRYSTAL $M_r = 162.95478$

$S°(298.15\ \text{K}) = [184.096 \pm 25.1]\ \text{J·K}^{-1}\ \text{mol}^{-1}$

$\Delta_f H°(0\ \text{K}) = \text{Unknown}$

$\Delta_f H°(298.15\ \text{K}) = -320.155 \pm 20.9\ \text{kJ·mol}^{-1}$

Enthalpy of Formation

The enthalpy of formation is based on the work of Stock and Wrede[1] who burned P_3N_5 in oxygen. They report a $\Delta_f H°(298.15\ \text{K}) = -949.4$ kcal·mol⁻¹ for the reaction $2\ P_3N_5(cr) + 7.5\ O_2(g) \rightarrow 1.5\ P_4O_{10}(\text{amorph}) + 5\ N_2(g)$. In[2] a value of -947.7 kcal·mol⁻¹ is used for the above reaction and we adopt this value. Using the JANAF value of $P_4O_{10}(cr)$ and correcting this to $P_4O_{10}(\text{amorph})$ by adding 13.8 kcal·mol⁻¹, from[2] we obtain $\Delta_f H°(298.15\ \text{K})\ P_4O_{10}(\text{amorph}) = -716.5$ kcal·mol⁻¹. Thus, we derive $\Delta_f H°(P_3N_5,\ cr,\ 298.15\ \text{K}) = -63.525$ kcal·mol⁻¹; however, because of the uncertainties in the enthalpy of reaction and correction for amorphous P_4O_{10}, we round the value to -64 ± 5 kcal·mol⁻¹.

Heat Capacity and Entropy

Sato[3] gave an equation for the heat capacity in the range 273–578 K. Judging from his results for $Be_3N_2(cr)$ in the same paper, we believe his values will be slightly high at the upper end of the range. Thus, taking 8.2 cal·K⁻¹ g atom as the limiting value, a curve was drawn through Sato's values at the low end and approaching the limit asymptotically. The entropy was estimated from that of $Si_3N_4(cr)$ by assuming that the ratio $C_p°(298.15\ \text{K})/S°(298.15\ \text{K})$ on a gram atom basis would be the same for $P_3N_5(cr)$.

Decomposition Data

$T_{\text{dec}}^m = 730$ K is calculated as the point at which the total pressure reaches a fugacity of 1 atm. This corresponds to $\log K_p° = 0.76$ for the reaction $P_3N_5(cr) \rightarrow 0.75\ P_4(g) + 2.5\ N_2(g)$. The temperature of decomposition has been reported by Postnikov and Kuzmin[4] as 1073 K. This has been confirmed by Moreau and Rocquet[5] and Huffman et. al.[6] However, it was also noted that $P_3N_5(cr)$ is not reformed on cooling the decomposition products; thus the decomposition is non equilibrium. It is known that the decomposition of AlN, BN and Be_3N_2 is kinetically limited and the equilibrium pressure is not attained until the average energy is greater than the activation energy. It appears that this is also the case for P_3N_5 and a high activation energy is expected.

References

[1] A. Stock and F. Wrede, Chem. Ber. 40, 2923 (1907).
[2] U. S. Nat. Bur. Stand. Tech. Note 270–1, (1965).
[3] S. Sato, Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 34, 584 (1938).
[4] V. F. Postnikov and L. L. Kuzmin, J. Appl. Chem. (USSR) 8, 429 (1935).
[5] H. Moreau and P. Rocquet, Compt. Rend. 198, 1691 (1934); Bull. Soc. Chim. France 3, 1801 (1936).
[6] E. O. Huffman, G. Tarbutton, G. V. Elmore, A. J. Smith and M. G. Rountree, J. Amer. Chem. Soc. 79, 1765 (1957).

Phosphorus Nitride (P₃N₅)   N₅P₃(cr)

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-(G°-H°(T_r))/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
	(J·K⁻¹·mol⁻¹)			(kJ·mol⁻¹)			
0							
100							
200							
298.15	148.950	184.096	184.096	0.	-320.155	-195.482	34.248
300	149.787	185.020	184.099	0.276	-320.146	-194.708	33.902
400	192.464	234.376	190.538	17.535	-319.936	-152.610	19.929
500	217.568	280.175	203.962	38.107	-314.612	-111.344	11.632
600	234.304	321.385	220.160	60.735	-307.339	-71.348	6.211
700	246.856	358.500	237.317	84.828	-298.751	-32.680	2.439
800	255.224	392.032	254.596	109.949	-289.301	4.694	-0.306
900	261.500	422.480	271.584	135.807	-279.283	40.846	-2.371
1000	265.266	450.236	288.083	162.153	-268.934	75.864	-3.963
1100	267.888	475.646	303.995	188.816	-258.412	109.835	-5.216
1200	269.868	499.045	319.287	215.709	-438.505	146.079	-6.359
1300	271.207	520.703	333.958	242.768	-425.504	194.267	-7.806
1400	271.904	540.831	348.025	269.929	-412.515	241.454	-9.009
1500	271.960	559.596	361.511	297.128	-399.588	287.715	-10.019

Continuation of discussions of selected N species

Nitrogen

Continued from page 1606

[5]E. E. Ferguson, D. B. Dunkin and F. C. Fehsenfeld, J. Chem. Phys. 57, (August 15, 1972).
[6]J. D. Payzant, R. Yamdagni and P. Kebarle, Can. J. Chem. 49, 3308 (1971).
[7]D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, Chem. Phys. Letters, in press.
[8]D. E. Milligan and H. E. Jacox, J. Chem. Phys. 55, 3404 (1971).
[9]R. M. Hochstrasser and A. P. Marchetti, J. Chem. Phys. 50, 1727 (1969).
[10]J. W. Sidman, J. Amer. Chem. Soc. 79, 2669 (1957).
[11]D. Williams, J. Amer. Chem. Soc. 61, 2987 (1939).
[12]G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand, Company, Inc., Princeton, New Jersey (1966).

Decomposition Data

[1]The melting point of VN has been reported to be approximately 2323 K by Rostoker and Yamamoto.[15] However, Farber and Srivastava[3] in their mass spectrometric studies observed solid nitride at temperatures as high as 2412 K. Liquid vanadium metal, presumably formed from decomposition of the nitride, was deposited in the sample. We assume that VN decomposes to its elements prior to melting. $T_{dem} = 2619$ K is the temperature at which the fugacity is 1 atm for the decomposition reaction $VN(cr) \rightarrow V(l) + 0.5 N_2(g)$ approaches zero. $\Delta_{dem}H°$ is the negative of the heat of formation of VN(cr) at T_{dem}.

Continued from page 1615

References
[1]A. D. Mah, U. S. Bur. Mines RI 6177, (1963).
[2]JANAF Thermochemical Tables: $V_2O_3(cr)$ and $V(g)$, 6-30-73, $V_2O_4(cr)$, 12-31-73.
[3]R. E. Slade and G. I. Higson, J. Chem. Soc. 115, 215 (1919).
[4]V. V. Voleinik and B. A. Shaddenov, Fiz. Khim. Elektrokhim. Rasplov. Salei Shlakov, No. 1, 157 (1969).
[5]M. Farber and R. D. Srivastava, J. Chem. Soc. Faraday Trans. 1, 69, 390 (1973).
[6]G. Brauer and W. D. Schnell, J. Less-Common Metals 6, 326 (1964).
[7]V. A. Kozheurov, V. M. Zhikharev, V. I. Shishkov, and G. V. Gritsishina, Izv. Vyssh. Ucheb Zaved., Chem. Met. No 8, 10 (1972).
[8]C. H. Shomate and K. K. Kelley, J. Amer. Chem. Soc. 71, 314 (1949).
[9]E. G. King, J. Amer. Chem. Soc. 71, 316 (1949).
[10]S. Satoh, Sci. Papers Inst. Phys. Chem. Research (Tokoyo) 34, 241 (1938).
[11]H. Hahn, Z Anorg. Chem. 258, 58 (1949).
[12]E. T. Turkdogan and E. M. Fenn, J. Iron Steel Inst. 181, 343 (1955).
[13]D Potter and R. Geils, Scripta Met. 6, 395 (1972).
[14]E. K. Storms, Los Alamos Scientific Laboratory, LA-2942, (August 1964).
[15]W. Rostoker and A. Yamamoto, Trans. ASM 46, 1136 (1954).