

Oxygen (O)

IDEAL GAS

A_r = 15.9994 Oxygen (O)O₁(g)

IP(O, g) = 109837.02 ± 0.06 cm⁻¹
 S°(298.15 K) = 161.058 ± 0.020 J·K⁻¹·mol⁻¹

Δ_fH°(0 K) = 246.79 ± 0.10 kJ·mol⁻¹
 Δ_fH°(298.15 K) = 249.17 ± 0.10 kJ·mol⁻¹

Electronic Levels and Quantum Weights		
State	ε _i , cm ⁻¹	g _i
³ P ₂	0	5
³ P ₁	158.265	3
³ P ₀	226.977	1
¹ D ₂	15867.862	5
¹ S ₀	33792.583	1

Enthalpy of Formation

The enthalpy of formation is based on the dissociation energy of O₂(g), 41260 ± 15 cm⁻¹ (493.579 ± 0.18 kJ·mol⁻¹), as recommended by CODATA.¹ This value is derived from the spectroscopic study of Brix and Herzberg.² The products of dissociation are assumed to be oxygen atoms in their ground states. The justification for this is discussed by Gaydon³ and Krupenie.⁴

Heat Capacity and Entropy

The electronic levels for O(g) are given in the compilation by Moore.⁵ Our calculations indicate that, except for the five states lying below 34000 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 73768.20 cm⁻¹ above the ground state. Since the inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the lowest lying states (ε_i < 34000 cm⁻¹). The reported uncertainty in S°(298.15 K) is due to uncertainties in the relative atomic mass, the fundamental constants, and the position of the low lying electronic levels. The calculated value of S(298.15 K) is 0.0094 J·K⁻¹·mol⁻¹ greater than that recommended by CODATA¹ due to the use of a 1 bar standard state pressure (CODATA used 1 atm). The difference is due to our use of the current CODATA fundamental constants.⁶ Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures.⁷

References

- ¹J. D. Cox, Chairman, ICSU-CODATA Task Group on Key Values for Thermodynamics, J. Chem. Thermodyn. **10**, 903 (1978).
- ²P. Brix and G. Herzberg, Can. J. Phys. **32**, 110 (1954).
- ³A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed., Chapman and Hall Ltd., London, 330 pp. (1968).
- ⁴P. H. Krupenie, J. Phys. Chem. Ref. Data **1**, 423 (1972).
- ⁵C. E. Moore, NSRDS-NBS 3, Section 7 (1976).
- ⁶E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data **2**, 663 (1973).
- ⁷J. R. Downey, The Dow Chemical Company, Report AFOSR-TR-78-0960, Contract No. F44620-75-1-0048, (1978).

Enthalpy Reference Temperature = T _r = 298.15 K				Standard State Pressure = p° = 0.1 MPa			
T/K	C _p ^o	S°	-(G°-H°(T _r))/T	H°-H°(T _r)	Δ _f H°	Δ _f G°	log K _r
0	0.	0.	INFINITE	-6.725	246.790	246.790	INFINITE
100	23.703	135.947	181.131	-4.518	247.544	242.615	-126.729
200	22.734	152.153	163.085	-2.186	248.421	237.339	-61.986
250	22.246	157.170	161.421	-1.063	248.816	234.522	-49.001
298.15	21.911	161.058	161.058	0.	249.173	231.736	-40.599
300	21.901	161.194	161.059	0.041	249.187	231.628	-40.330
350	21.657	164.551	161.324	1.129	249.537	228.673	-34.128
400	21.482	167.430	161.912	2.207	249.868	225.670	-29.469
450	21.354	169.953	162.668	3.278	250.180	222.626	-25.842
500	21.257	172.197	163.511	4.343	250.474	219.549	-22.936
600	21.124	176.060	165.291	6.462	251.013	213.312	-18.570
700	21.040	179.310	167.067	8.570	251.494	206.990	-15.446
800	20.984	182.116	168.777	10.671	251.926	200.602	-13.098
900	20.944	184.585	170.399	12.767	252.320	194.163	-11.269
1000	20.915	186.790	171.930	14.860	252.682	187.681	-9.803
1100	20.893	188.782	173.373	16.950	253.018	181.165	-8.603
1200	20.877	190.599	174.734	19.039	253.332	174.619	-7.601
1300	20.864	192.270	176.019	21.126	253.627	168.047	-6.752
1400	20.853	193.816	177.236	23.212	253.906	161.453	-6.024
1500	20.845	195.254	178.390	25.296	254.171	154.840	-5.392
1600	20.838	196.599	179.486	27.381	254.421	148.210	-4.839
1700	20.833	197.862	180.530	29.464	254.659	141.564	-4.350
1800	20.830	199.053	181.527	31.547	254.884	134.905	-3.915
1900	20.827	200.179	182.479	33.630	255.097	128.234	-3.525
2000	20.826	201.247	183.391	35.713	255.299	121.552	-3.175
2100	20.827	202.263	184.266	37.796	255.488	114.860	-2.857
2200	20.830	203.232	185.106	39.878	255.667	108.159	-2.568
2300	20.835	204.158	185.914	41.962	255.835	101.450	-2.304
2400	20.841	205.045	186.693	44.045	255.992	94.734	-2.062
2500	20.851	205.896	187.444	46.130	256.139	88.012	-1.839
2600	20.862	206.714	188.170	48.216	256.277	81.284	-1.633
2700	20.877	207.502	188.871	50.303	256.405	74.551	-1.442
2800	20.894	208.261	189.550	52.391	256.525	67.814	-1.265
2900	20.914	208.995	190.208	54.481	256.637	61.072	-1.100
3000	20.937	209.704	190.846	56.574	256.741	54.327	-0.946
3100	20.963	210.391	191.466	58.669	256.838	47.578	-0.802
3200	20.991	211.057	192.068	60.767	256.929	40.826	-0.666
3300	21.022	211.704	192.653	62.867	257.014	34.071	-0.539
3400	21.056	212.332	193.223	64.971	257.094	27.315	-0.420
3500	21.092	212.943	193.777	67.079	257.169	20.555	-0.307
3600	21.130	213.537	194.318	69.190	257.241	13.794	-0.200
3700	21.170	214.117	194.845	71.305	257.309	7.030	-0.099
3800	21.213	214.682	195.360	73.424	257.373	0.265	-0.004
3900	21.257	215.234	195.862	75.547	257.436	-6.501	0.087
4000	21.302	215.772	196.353	77.675	257.496	-13.270	0.173
4100	21.349	216.299	196.834	79.808	257.554	-20.040	0.255
4200	21.397	216.814	197.303	81.945	257.611	-26.811	0.333
4300	21.445	217.318	197.763	84.087	257.666	-33.583	0.408
4400	21.495	217.812	198.213	86.234	257.720	-40.358	0.479
4500	21.545	218.295	198.654	88.386	257.773	-47.133	0.547
4600	21.596	218.769	199.086	90.543	257.825	-53.909	0.612
4700	21.647	219.234	199.510	92.705	257.876	-60.687	0.674
4800	21.697	219.690	199.925	94.872	257.926	-67.465	0.734
4900	21.748	220.138	200.333	97.045	257.974	-74.244	0.791
5000	21.799	220.578	200.734	99.222	258.021	-81.025	0.846
5100	21.849	221.010	201.127	101.405	258.066	-87.806	0.899
5200	21.899	221.435	201.514	103.592	258.110	-94.589	0.950
5300	21.949	221.853	201.893	105.784	258.150	-101.371	0.999
5400	21.997	222.264	202.267	107.982	258.189	-108.155	1.046
5500	22.045	222.668	202.634	110.184	258.224	-114.940	1.092
5600	22.093	223.065	202.995	112.391	258.255	-121.725	1.135
5700	22.139	223.457	203.351	114.602	258.282	-128.510	1.178
5800	22.184	223.842	203.701	116.818	258.304	-135.296	1.218
5900	22.229	224.222	204.046	119.039	258.321	-142.083	1.258
6000	22.273	224.596	204.385	121.264	258.332	-148.869	1.296

PREVIOUS: March 1977 (1 atm)

CURRENT: September 1982 (1 bar)

Oxygen (O)

O₁(g)

Methane (CH₄)

IDEAL GAS

 $M_r = 16.04276$ Methane (CH₄)C₁H₄(g)

$$S^\circ(298.15\text{ K}) = 186.251 \pm 0.04 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(0\text{ K}) = -66.911 \pm 0.34 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(298.15\text{ K}) = -74.873 \pm 0.34 \text{ kJ}\cdot\text{mol}^{-1}$$

Vibrational Frequencies and Degeneracies
 ν, cm^{-1}

2916.5 (1)
1534.0 (2)
3018.7 (3)
1306 (3)

Ground State Quantum Weight: [1]

$$\sigma = 12$$

Point Group: T_dBond Distance: C–H = $1.091 \pm 0.002 \text{ \AA}$ Bond Angle: H–C–H = 109.4712° Product of the Moments of Inertia: $I_A I_B I_C = 1.499 \times 10^{-118} \text{ g}^3\cdot\text{cm}^6$.

Enthalpy of Formation

Rossini¹ measured the enthalpy of combustion of methane gas. His value at 298.15 K was corrected to the presently accepted molecular weight of water. The enthalpy of formation was calculated using -68.3174 and $-94.0540 \text{ kcal}\cdot\text{mol}^{-1}$ for the enthalpy of formation of H₂O(l) and CO₂(g), respectively.

Heat Capacity and Entropy

Stevenson and Ibers,² calculated the bond distance from an analysis of available spectroscopic data. Vibrational frequencies listed by Jones and McDowell³ are consistent with their results of a force constant calculation. The principal moments of inertia are: $I_A = I_B = I_C = 0.5313 \times 10^{-39} \text{ g}\cdot\text{cm}^2$.

References

¹F. D. Rossini, J. Res. Nat. Bur. Stand. 6, 37 (1931).²D. P. Stevenson and J. A. Ibers, J. Chem. Phys. 33, 100 (1960).³L. H. Jones and R. S. McDowell, J. Mol. Spectrosc. 3, 632 (1959).

Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$				Standard State Pressure = $p^\circ = 0.1\text{ MPa}$			
T/K	C_p°	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		$\text{kJ}\cdot\text{mol}^{-1}$		ΔG°	$\log K_r$
		S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$		
0	0.	0.	INFINITE	-10.024	-66.911	-66.911	INFINITE
100	33.258	149.500	216.485	-6.698	-69.644	-64.353	33.615
200	33.473	172.577	189.418	-3.368	-72.027	-58.161	15.190
250	34.216	180.113	186.829	-1.679	-73.426	-54.536	11.395
298.15	35.639	186.251	186.251	0.	-74.873	-50.768	8.894
300	35.708	186.472	186.252	0.066	-74.929	-50.618	8.813
350	37.874	192.131	186.694	1.903	-76.461	-46.445	6.932
400	40.500	197.356	187.704	3.861	-77.969	-42.054	5.492
450	43.374	202.291	189.053	5.957	-79.422	-37.476	4.350
500	46.342	207.014	190.614	8.200	-80.802	-32.741	3.420
600	52.227	215.987	194.103	13.130	-83.308	-22.887	1.993
700	57.794	224.461	197.840	18.635	-85.452	-12.643	0.943
800	62.932	232.518	201.675	24.675	-87.238	-2.115	0.138
900	67.601	240.205	205.532	31.205	-88.692	8.616	-0.500
1000	71.795	247.549	209.370	38.179	-89.849	19.492	-1.018
1100	75.529	254.570	213.162	45.549	-90.750	30.472	-1.447
1200	78.833	261.287	216.895	53.270	-91.437	41.524	-1.807
1300	81.744	267.714	220.558	61.302	-91.945	52.626	-2.115
1400	84.305	273.868	224.148	69.608	-92.308	63.761	-2.379
1500	86.556	279.763	227.660	78.153	-92.553	74.918	-2.609
1600	88.537	285.413	231.095	86.910	-92.703	86.088	-2.810
1700	90.283	290.834	234.450	95.853	-92.780	97.265	-2.989
1800	91.824	296.039	237.728	104.960	-92.797	108.445	-3.147
1900	93.188	301.041	240.930	114.212	-92.770	119.624	-3.289
2000	94.399	305.853	244.057	123.592	-92.709	130.802	-3.416
2100	95.477	310.485	247.110	133.087	-92.624	141.975	-3.531
2200	96.439	314.949	250.093	142.684	-92.521	153.144	-3.636
2300	97.301	319.255	253.007	152.371	-92.409	164.308	-3.732
2400	98.075	323.413	255.854	162.141	-92.291	175.467	-3.819
2500	98.772	327.431	258.638	171.984	-92.174	186.622	-3.899
2600	99.401	331.317	261.359	181.893	-92.060	197.771	-3.973
2700	99.971	335.080	264.020	191.862	-91.954	208.916	-4.042
2800	100.489	338.725	266.623	201.885	-91.857	220.058	-4.105
2900	100.960	342.260	269.171	211.958	-91.773	231.196	-4.164
3000	101.389	345.690	271.664	222.076	-91.705	242.332	-4.219
3100	101.782	349.021	274.106	232.235	-91.653	253.465	-4.271
3200	102.143	352.258	276.498	242.431	-91.621	264.598	-4.319
3300	102.474	355.406	278.842	252.662	-91.609	275.730	-4.364
3400	102.778	358.470	281.139	262.925	-91.619	286.861	-4.407
3500	103.060	361.453	283.391	273.217	-91.654	297.993	-4.447
3600	103.319	364.360	285.600	283.536	-91.713	309.127	-4.485
3700	103.560	367.194	287.767	293.881	-91.798	320.262	-4.521
3800	103.783	369.959	289.894	304.248	-91.911	331.401	-4.555
3900	103.990	372.658	291.982	314.637	-92.051	342.542	-4.588
4000	104.183	375.293	294.032	325.045	-92.222	353.687	-4.619
4100	104.363	377.868	296.045	335.473	-92.422	364.838	-4.648
4200	104.531	380.385	298.023	345.918	-92.652	375.993	-4.676
4300	104.688	382.846	299.967	356.379	-92.914	387.155	-4.703
4400	104.834	385.255	301.879	366.855	-93.208	398.322	-4.729
4500	104.972	387.612	303.758	377.345	-93.533	409.497	-4.753
4600	105.101	389.921	305.606	387.849	-93.891	420.679	-4.777
4700	105.223	392.182	307.424	398.365	-94.281	431.869	-4.800
4800	105.337	394.399	309.213	408.893	-94.702	443.069	-4.822
4900	105.445	396.572	310.973	419.432	-95.156	454.277	-4.843
5000	105.546	398.703	312.707	429.982	-95.641	465.493	-4.863
5100	105.642	400.794	314.414	440.541	-96.157	476.722	-4.883
5200	105.733	402.847	316.095	451.110	-96.703	487.961	-4.902
5300	105.818	404.861	317.750	461.688	-97.278	499.210	-4.920
5400	105.899	406.840	319.382	472.274	-97.882	510.470	-4.938
5500	105.976	408.784	320.990	482.867	-98.513	521.741	-4.955
5600	106.049	410.694	322.575	493.469	-99.170	533.025	-4.972
5700	106.118	412.572	324.137	504.077	-99.852	544.320	-4.988
5800	106.184	414.418	325.678	514.692	-100.557	555.628	-5.004
5900	106.247	416.234	327.197	525.314	-101.284	566.946	-5.019
6000	106.306	418.020	328.696	535.942	-102.032	578.279	-5.034

PREVIOUS: March 1961 (1 atm)

CURRENT: March 1961 (1 bar)

Methane (CH₄)C₁H₄(g)

Methyl (CH₃)

IDEAL GAS

M_r = 15.03482 Methyl (CH₃)C₁H₃(g)

$$S^\circ(298.15\text{ K}) = 194.171 \pm 1.3\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(0\text{ K}) = 149.031 \pm 0.8\text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(298.15\text{ K}) = 145.687 \pm 0.8\text{ kJ}\cdot\text{mol}^{-1}$$

Electronic Levels and Quantum Weights	
$\epsilon_i, \text{cm}^{-1}$	g_i
0	2
46205	2
Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	
[3002] (1)	
580 (1)	
[3184] (2)	
1383 (2)	

Point Group: D_{3h} $\sigma = 6$

Bond Distance: C–H = 1.079 Å

Bond Angle: H–C–H = 120°

Product of the Moments of Inertia: $I_A I_B I_C = 4.99 \times 10^{-119}\text{ g}^3\cdot\text{cm}^6$

Enthalpy of Formation

Chupka¹ measured the photoionization spectrum of methane and from the onset of CH₃⁺ production has reported $\Delta_a H^\circ(\text{CH}_3\text{--H}) = 103.244 \pm 0.12\text{ kcal}\cdot\text{mol}^{-1}$. The value was corrected for the thermal rotation energy of the fragment ions and is the value adopted here.

Dibeler *et al.*² had earlier reported $\Delta_a H^\circ(\text{CH}_3\text{--H}) = 101.7 \pm 0.5\text{ kcal}\cdot\text{mol}^{-1}$ but they did not apply the rotational energy correction, which bring them closer to Chupka.

The photoionization values are in good agreement with earlier electron impact determinations as summarized by Stevenson³ who gives $\Delta_a H^\circ(\text{CH}_3\text{--H}) = 101.9 \pm 1\text{ kcal}\cdot\text{mol}^{-1}$. Kinetic determinations have been recently reviewed by Kerr⁴ and yield $\Delta_a H^\circ(\text{CH}_3\text{--H}) = 102.5 \pm 1\text{ kcal}\cdot\text{mol}^{-1}$ again in excellent agreement.

Heat Capacity and Entropy

The structure, bond length, angles and electronic levels are those reported by Herzberg.⁵ A set of vibrational frequencies have been reported by Andrews and Pimentel⁶ in an argon matrix, of which only two were observed. Milligan and Jacox⁷ observed $\nu_2 = 611\text{ cm}^{-1}$ in an argon matrix and disagreed with Andrews and Pimentel who reported 730 cm^{-1} . Later, Tan and Pimentel⁸ agreed that the earlier values were for a methyl radical interacting with an alkali halide molecule. This would affect the ν_2 mode strongest, thus, we adopt the remaining in plane frequencies which appear to be of the correct magnitudes. The ν_2 mode is taken from the analysis of Herzberg⁵ since this represents the gas phase molecule and is in reasonable agreement with the matrix value of Milligan and Jacox.⁷ The uncertainty in the entropy reflects the uncertainties in the vibrational frequencies.

The principal moments of inertia are: $I_A = I_B = 0.2923 \times 10^{-39}$, and $I_C = 0.5846 \times 10^{-39}\text{ g}\cdot\text{cm}^2$.

References

- W. A. Chupka, J. Chem. Phys. **48**, 2337 (1968).
- V. H. Dibeler, M. Krauss, R. M. Reese and F. N. Harlee, J. Chem. Phys. **42**, 3791 (1965).
- D. P. Stevenson, Discuss. Faraday Soc. **10**, 35 (1951).
- J. A. Kerr, Chem. Revs. **66**, 465 (1966).
- G. Herzberg, Electronic Spectra of Polyatomic Molecules, D. Van Nostrand Co., Inc., New York, (1966).
- L. Andrews and G. C. Pimentel, J. Chem. Phys. **47**, 3637, (1967).
- D. E. Milligan and M. E. Jacox, J. Chem. Phys. **47**, 5146 (1967).
- L. Y. Tan and G. C. Pimentel, J. Chem. Phys. **48**, 5202 (1968).

Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$				Standard State Pressure = $p^\circ = 0.1\text{ MPa}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log K_f$
0	0.	0.	INFINITE	-10.407	149.031	149.031	INFINITE
100	33.395	155.665	226.465	-7.080	147.800	147.438	-77.014
200	35.638	179.380	197.609	-3.646	146.868	147.432	-38.505
250	37.162	187.495	194.799	-1.826	146.297	147.637	-30.847
298.15	38.693	194.170	194.170	0.	145.687	147.950	-25.920
300	38.753	194.410	194.171	0.072	145.663	147.964	-25.763
350	40.392	200.506	194.649	2.050	144.997	148.400	-22.147
400	42.041	206.008	195.730	4.111	144.320	148.932	-19.449
450	43.668	211.054	197.156	6.254	143.644	149.549	-17.359
500	45.252	215.737	198.783	8.477	142.976	150.241	-15.696
600	48.288	224.258	202.333	13.155	141.682	151.817	-13.217
700	51.174	231.921	206.021	18.130	140.477	153.602	-11.462
800	53.926	238.935	209.703	23.386	139.383	155.554	-10.157
900	56.527	245.438	213.316	28.910	138.411	157.635	-9.149
1000	58.954	251.521	216.836	34.686	137.557	159.817	-8.348
1100	61.187	257.247	220.252	40.694	136.814	162.080	-7.697
1200	63.217	262.659	223.562	46.916	136.167	164.406	-7.156
1300	65.048	267.793	226.769	53.331	135.602	166.783	-6.701
1400	66.690	272.675	229.875	59.919	135.105	169.201	-6.313
1500	68.156	277.327	232.885	66.663	134.662	171.652	-5.977
1600	69.463	281.768	235.802	73.545	134.262	174.131	-5.685
1700	70.628	286.015	238.632	80.551	133.896	176.634	-5.427
1800	71.667	290.082	241.378	87.667	133.554	179.158	-5.199
1900	72.594	293.982	244.045	94.881	133.230	181.701	-4.995
2000	73.422	297.727	246.636	102.182	132.917	184.260	-4.812
2100	74.165	301.327	249.155	109.562	132.610	186.835	-4.647
2200	74.831	304.793	251.606	117.013	132.305	189.424	-4.497
2300	75.430	308.133	253.991	124.526	131.999	192.027	-4.361
2400	75.971	311.355	256.315	132.097	131.688	194.644	-4.236
2500	76.459	314.466	258.579	139.719	131.369	197.273	-4.122
2600	76.902	317.474	260.787	147.387	131.041	199.916	-4.016
2700	77.304	320.384	262.940	155.098	130.701	202.571	-3.919
2800	77.670	323.202	265.042	162.847	130.348	205.239	-3.829
2900	78.003	325.933	267.095	170.630	129.980	207.921	-3.745
3000	78.309	328.583	269.101	178.446	129.595	210.615	-3.667
3100	78.588	331.155	271.061	186.291	129.193	213.322	-3.594
3200	78.845	333.655	272.979	194.163	128.772	216.042	-3.527
3300	79.082	336.084	274.854	202.060	128.331	218.777	-3.463
3400	79.300	338.449	276.690	209.979	127.869	221.524	-3.403
3500	79.501	340.750	278.488	217.919	127.385	224.286	-3.347
3600	79.687	342.992	280.248	225.879	126.879	227.061	-3.295
3700	79.860	345.178	281.974	233.856	126.349	229.852	-3.245
3800	80.020	347.310	283.665	241.850	125.796	232.656	-3.198
3900	80.169	349.391	285.324	249.860	125.217	235.476	-3.154
4000	80.308	351.422	286.951	257.884	124.613	238.311	-3.112
4100	80.438	353.407	288.548	265.921	123.984	241.161	-3.072
4200	80.559	355.346	290.115	273.971	123.328	244.027	-3.035
4300	80.672	357.243	291.654	282.033	122.645	246.909	-2.999
4400	80.778	359.099	293.166	290.105	121.936	249.807	-2.966
4500	80.878	360.916	294.652	298.188	121.199	252.721	-2.934
4600	80.972	362.694	296.112	306.281	120.436	255.652	-2.903
4700	81.060	364.437	297.547	314.382	119.645	258.600	-2.874
4800	81.143	366.144	298.958	322.492	118.827	261.565	-2.846
4900	81.221	367.818	300.347	330.611	117.982	264.547	-2.820
5000	81.295	369.460	301.712	338.737	117.111	267.548	-2.795
5100	81.365	371.070	303.057	346.870	116.214	270.565	-2.771
5200	81.432	372.651	304.380	355.009	115.292	273.601	-2.748
5300	81.495	374.203	305.683	363.156	114.345	276.654	-2.727
5400	81.554	375.726	306.966	371.308	113.373	279.726	-2.706
5500	81.611	377.223	308.230	379.467	112.379	282.815	-2.686
5600	81.666	378.694	309.475	387.630	111.362	285.923	-2.667
5700	81.718	380.140	310.702	395.800	110.324	289.050	-2.649
5800	81.767	381.562	311.911	403.974	109.266	292.195	-2.631
5900	81.815	382.960	313.104	412.153	108.188	295.357	-2.615
6000	81.860	384.336	314.280	420.337	107.094	298.539	-2.599

PREVIOUS: June 1969 (1 atm)

CURRENT: June 1969 (1 bar)

Methyl (CH₃)C₁H₃(g)

Hydroxyl (OH)

IDEAL GAS

 $M_r = 17.00734$ Hydroxyl (OH) $H_2O_1(g)$

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MALCOLM W. CHASE

$$S^\circ(298.15\text{ K}) = 183.708 \pm 0.04 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(0\text{ K}) = 38.390 \pm 1.21 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(298.15\text{ K}) = 38.987 \pm 1.21 \text{ kJ}\cdot\text{mol}^{-1}$$

Electronic States and Molecular Constants ($\sigma = 1$)						
State	$\epsilon_i, \text{ cm}^{-1}$	g_i	$\omega_e, \text{ cm}^{-1}$	$\omega_e x_e, \text{ cm}^{-1}$	$B_e, \text{ cm}^{-1}$	$r_e, \text{ \AA}$
$X^2\Pi_i$	0	2	3735.21	82.81	18.871	0.714
	139.7	2				
$A^2\Sigma^+$	32403	2	3184.28	97.84	17.355	0.807
$B^2\Sigma^+$	68372	2	940	105	5.54	0.65
$C^2\Sigma^+$	89420	2	2339	32	4.20	0.16
						2.16

Enthalpy of Formation

$\Delta_f H^\circ(\text{OH}, g, 0\text{ K})$ is calculated from the relation $\Delta_f H^\circ(\text{OH}, g, 0\text{ K}) = 1/2 D_0^\circ(\text{O}_2) + 1/2 D_0^\circ(\text{H}_2) = D_0^\circ(\text{OH})$, are as follows: $D_0^\circ(\text{O}_2) = 117.967 \pm 0.042 \text{ kcal}\cdot\text{mol}^{-1}$ and $D_0^\circ(\text{H}_2) = 103.267 \pm 0.003 \text{ kcal}\cdot\text{mol}^{-1}$ were taken from the CODATA¹ selection. Barrow² in a refinement of the work of Barrow and Downie³ obtains a value of D_0° for $\text{OH}(X^2\Pi_{3/2}) \rightarrow \text{O}(^3P_2) + \text{H}(^2S_{1/2})$ of 35427 cm^{-1} from an extrapolation of $\Delta_{\text{vap}}G$ versus v ; it was increased to $35450 \pm 100 \text{ cm}^{-1}$ to account for the fact that $\Delta_{\text{vap}}G$ yields slightly low values at high v . Felenbok⁴ obtains a value of D_e for $\text{OH}(B^2\Sigma^+)$ of 1315 cm^{-1} and $G(\text{O})$ for this state of 441 cm^{-1} . Using $T_e(B^2\Sigma^+)$ given by Rosen⁵ and the zero point energy of HO (including the Dunham correction, see Herzberg⁶ of 847.0 cm^{-1} , this yields $D_0^\circ(\text{OH}) = 35451 \text{ cm}^{-1}$ with an estimated uncertainty of 100 cm^{-1} . A value of $D_0^\circ(\text{OH}) = 35450 \pm 100 \text{ cm}^{-1} = 101.356 \pm 0.29 \text{ kcal}\cdot\text{mol}^{-1}$ was adopted. Combining the above values, one obtains $\Delta_f H^\circ(\text{OH}, g, 0\text{ K}) = 9.261 \pm 0.29 \text{ kcal}\cdot\text{mol}^{-1}$ which is in good agreement with the last JANAF⁷ selection.

A review of earlier work is given in references.⁷⁻⁹

Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels were taken from Rosen.⁵ Comparison of the results of these calculations with those of the more exact treatment given by Haar *et al.*¹⁰ suggests that errors in the tables due to approximations in our calculations may be neglected above 400 K . Below this, they may be appreciable. It is recommended that $H^\circ(0\text{ K}) - H^\circ(298.15\text{ K})$, $S^\circ(298.15\text{ K})$ and $C_p^\circ(298.15\text{ K})$ be taken as $-2.107 \text{ kcal}\cdot\text{mol}^{-1}$, $43.890 \text{ kJ}\cdot\text{mol}^{-1}$, and $7.144 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. These errors result from dealing with the ground state ($X^2\Pi_i$) as two separate electronic states separated by 139.7 cm^{-1} .

The thermodynamic functions are calculated using first-order anharmonic corrections to Q_i^v and Q_i^r in the partition function $Q = Q_i^v Q_i^r Q_i^t \exp(-\epsilon_i/kT)$. The National Bureau of Standards prepared this table¹¹ by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H^\circ$ selected by NBS,¹¹ we recalculate the table in terms of 1973 fundamental constants,¹² 1975 atomic weights¹³ and current JANAF reference states for the elements.

References

- ¹CODATA Task Group on Key Values for Thermodynamics, Final Set of Key Values for Thermodynamics—Part I, November, 1971 (Bulletin No. 5).
- ²R. F. Barrow, Arkiv Fysik **11**, 281 (1956).
- ³R. F. Barrow and A. R. Downie, Proc. Phys. Soc. (London) **A69**, 178 (1956).
- ⁴P. Felenbok, Ann. d'Astr. **26**, 393 (1963).
- ⁵B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, Oxford, (1970).
- ⁶G. Herzberg and A. Monfils, J. Mol. Spectrosc. **5**, 482 (1960).
- ⁷JANAF Thermochemical Tables, 2nd ed., NSRDS—NBS 37, (1971).
- ⁸P. Gray, Trans. Faraday Soc. **55**, 408 (1959).
- ⁹R. Edse, "Third Combustion Symposium," Williams and Wilkins Co., Baltimore, p. 611, (1949).
- ¹⁰L. Haar, A. S. Friedman, and C. W. Beckett, U.S. Nat. Bur. Stand. Monograph 20, (1961).
- ¹¹S. Abramowitz *et al.*, U. S. Nat. Bur. Stand. Report 10904, 239, (1972).
- ¹²CODATA Task Group on Fundamental Constants, CODATA Bulletin **11**, (December 1973).
- ¹³IUPAC Commission on Atomic Weights, Pure Appl. Chem. **47**, 75 (1976); **37**, 589 (1974).

Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$							Standard State Pressure = $p^\circ = 0.1\text{ MPa}$		
T/K	C_p°	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		$\text{kJ}\cdot\text{mol}^{-1}$			$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log K_r$
		S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$				
0	0.	0.	INFINITE	-9.172	38.390	38.390	INFINITE		
100	32.627	149.590	210.980	-6.139	38.471	37.214	-19.438		
200	30.777	171.592	186.471	-2.976	38.832	35.803	-9.351		
250	30.283	178.402	184.204	-1.450	38.930	35.033	-7.320		
298.15	29.986	183.708	183.708	0.	38.987	34.277	-6.005		
300	29.977	183.894	183.709	0.055	38.988	34.248	-5.963		
350	29.780	188.499	184.073	1.549	39.019	33.455	-4.993		
400	29.650	192.466	184.880	3.035	39.029	32.660	-4.265		
450	29.567	195.954	185.921	4.515	39.020	31.864	-3.699		
500	29.521	199.066	187.082	5.992	38.995	31.070	-3.246		
600	29.527	204.447	189.542	8.943	38.902	29.493	-2.568		
700	29.663	209.007	192.005	11.902	38.764	27.935	-2.085		
800	29.917	212.983	194.384	14.880	38.598	26.399	-1.724		
900	30.264	216.526	196.651	17.888	38.416	24.884	-1.444		
1000	30.676	219.736	198.801	20.935	38.230	23.391	-1.222		
1100	31.124	222.680	200.840	24.024	38.046	21.916	-1.041		
1200	31.586	225.408	202.775	27.160	37.867	20.458	-0.891		
1300	32.046	227.955	204.615	30.342	37.697	19.014	-0.764		
1400	32.492	230.346	206.368	33.569	37.535	17.583	-0.656		
1500	32.917	232.602	208.043	36.839	37.381	16.163	-0.563		
1600	33.319	234.740	209.645	40.151	37.234	14.753	-0.482		
1700	33.694	236.771	211.182	43.502	37.093	13.352	-0.410		
1800	34.044	238.707	212.657	46.889	36.955	11.960	-0.347		
1900	34.369	240.557	214.078	50.310	36.819	10.575	-0.291		
2000	34.670	242.327	215.446	53.762	36.685	9.197	-0.240		
2100	34.950	244.026	216.767	57.243	36.551	7.826	-0.195		
2200	35.209	245.658	218.043	60.752	36.416	6.462	-0.153		
2300	35.449	247.228	219.278	64.285	36.278	5.103	-0.116		
2400	35.673	248.741	220.474	67.841	36.137	3.750	-0.082		
2500	35.881	250.202	221.635	71.419	35.992	2.404	-0.050		
2600	36.075	251.613	222.761	75.017	35.843	1.063	-0.021		
2700	36.256	252.978	223.855	78.633	35.689	-0.271	0.005		
2800	36.426	254.300	224.918	82.267	35.530	-1.600	0.030		
2900	36.586	255.581	225.954	85.918	35.365	-2.924	0.053		
3000	36.736	256.824	226.962	89.584	35.194	-4.241	0.074		
3100	36.878	258.031	227.945	93.265	35.017	-5.552	0.094		
3200	37.013	259.203	228.904	96.960	34.834	-6.858	0.112		
3300	37.140	260.344	229.839	100.667	34.644	-8.158	0.129		
3400	37.261	261.455	230.753	104.387	34.448	-9.452	0.145		
3500	37.376	262.537	231.645	108.119	34.246	-10.741	0.160		
3600	37.486	263.591	232.518	111.863	34.037	-12.023	0.174		
3700	37.592	264.620	233.372	115.617	33.821	-13.300	0.188		
3800	37.693	265.624	234.208	119.381	33.599	-14.570	0.200		
3900	37.791	266.604	235.026	123.155	33.371	-15.834	0.212		
4000	37.885	267.562	235.827	126.939	33.136	-17.093	0.223		
4100	37.976	268.499	236.613	130.732	32.894	-18.346	0.234		
4200	38.064	269.415	237.383	134.534	32.646	-19.593	0.244		
4300	38.150	270.311	238.138	138.345	32.391	-20.833	0.253		
4400	38.233	271.189	238.879	142.164	32.130	-22.068	0.262		
4500	38.315	272.050	239.607	145.991	31.862	-23.297	0.270		
4600	38.394	272.893	240.322	149.827	31.587	-24.520	0.278		
4700	38.472	273.719	241.023	153.670	31.305	-25.737	0.286		
4800	38.549	274.530	241.713	157.521	31.017	-26.947	0.293		
4900	38.625	275.326	242.391	161.380	30.722	-28.152	0.300		
5000	38.699	276.107	243.057	165.246	30.420	-29.350	0.307		
5100	38.773	276.874	243.713	169.120	30.111	-30.542	0.313		
5200	38.846	277.627	244.358	173.001	29.796	-31.729	0.319		
5300	38.919	278.368	244.993	176.889	29.473	-32.909	0.324		
5400	38.991	279.096	245.617	180.784	29.144	-34.083	0.330		
5500	39.062	279.812	246.233	184.687	28.807	-35.251	0.335		
5600	39.134	280.517	246.839	188.597	28.464	-36.412	0.340		
5700	39.206	281.210	247.436	192.514	28.113	-37.568	0.344		
5800	39.278	281.892	248.024	196.438	27.756	-38.716	0.349		
5900	39.350	282.564	248.604	200.369	27.391	-39.860	0.353		
6000	39.423	283.226	249.175	204.308	27.019	-40.997	0.357		

PREVIOUS: June 1977 (1 atm)

CURRENT: June 1977 (1 bar)

Hydroxyl (OH)

 $H_2O_1(g)$