$S°(298.15\ K) = 114.716 \pm 0.017\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 216.035 \pm 0.006\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 217\,999 \pm 0.006\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0.00	2

Enthalpy of Formation

The enthalpy of formation is calculated from the dissociation energy, $D_0°(H_2) = 36118.3 \pm 1\ cm^{-1}$ ($432.071 \pm 0.012\ kJ \cdot mol^{-1}$), from Herzberg[2] and auxiliary data from H_2.[3] The adopted value for the dissociation energy of hydrogen is the value recommended by CODATA.[1]

Earlier experimental values for $D_0°(H_2)$ were obtained by Herzberg and Monfils ($36113.0 \pm 0.3\ cm^{-1}$),[4] and Beutler ($36116 \pm 6\ cm^{-1}$).[5] Kolos and Wolniewicz[6] calculated the adiabatic dissociation energy of H_2, corrected for relativistic and radiative effects, to be $36117.4\ cm^{-1}$.

Heat Capacity and Entropy

The electronic levels for H(g) are given in the compilation by Moore.[7] Our calculations indicate that the inclusion of levels through $n = 12$ has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the first excited state lies at 82258 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 ground state. 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]

The thermal functions at 298 15 K differ from the CODATA recommendations for two reasons: a difference of $0.001\ J \cdot K^{-1} \cdot mol^{-1}$ in the entropy due to the use of more current fundamental constants and a difference of $0\ 1094\ J \cdot K^{-1} \cdot mol^{-1}$ in the entropy due to the use of a different standard state pressure.

References

[1] J. D. Cox, chairman, ICSU–CODATA Task Group on Key Values for Thermodynamics, J Chem. Thermodyn 10, 903 (1978).
[2] G. Herzberg, J. Mol. Spectrosc. 33, 147 (1970).
[3] JANAF Thermochemical Tables: H_2(g), 3–31–77.
[4] G. Herzberg and A. Monfils, J Mol. Spectrosc. 5, 482 (1960).
[5] H. Beutler, Z. Phys. Chem. B39, 315 (1935).
[6] W. Kolos and L. Wolniewicz, J. Chem. Phys. 49, 404 (1968).
[7] C. E. Moore, NSRDS–NBS 3, Section 6 (1972).
[8] J R. Downey, Jr., Dow Chemical Company, Thermal Research, to be published, (1977).
[9] E. R. Cohen and B. Taylor, J. Phys. Chem. Ref. Data 2, 663 (1973).

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	−6.197	216.035	216.035	INFINITE
100	20.786	92.009	133.197	−4.119	216.614	212 450	−110.972
200	20.786	106.417	116.618	−2.040	217.346	208 004	−54.325
250	20.786	111.055	115.059	−1.001	217.687	205.629	−42.964
298.15	20.786	114.716	114.716	0.	217.999	203.278	−35.613
300	20.786	114.845	114.717	0.038	218.011	203.186	−35.378
350	20.786	118.049	114.970	1.078	218.326	200.690	−29.951
400	20.786	120.825	115.532	2.117	218.637	198.150	−25.876
450	20.786	123.273	116.259	3.156	218.946	195.570	−22.701
500	20.786	125.463	117.072	4.196	219.254	192.957	−20.158
600	20.786	129.253	118.796	6.274	219.868	187.640	−16.335
700	20.786	132.457	120.524	8.353	220.478	182.220	−13.597
800	20.786	135.232	122.193	10.431	221.080	176.713	−11.538
900	20.786	137.681	123.781	12.510	221.671	171.132	−9.932
1000	20.786	139.871	125.282	14.589	222.248	165.485	−8.644
1100	20.786	141.852	126.700	16.667	222.807	159.782	−7.587
1200	20.786	143.660	128.039	18.746	223.346	154.028	−6.705
1300	20.786	145.324	129.305	20.824	223.865	148.230	−5.956
1400	20.786	146.865	130.505	22.903	224.361	142.394	−5.313
1500	20.786	148.299	131.644	24.982	224.836	136.522	−4.754
1600	20.786	149.640	132.728	27.060	225.289	130.620	−4.264
1700	20.786	150.900	133.760	29.139	225.721	124.689	−3.831
1800	20.786	152.088	134.745	31.217	226.132	118.734	−3.446
1900	20.786	153.212	135.688	33.296	226.525	112.757	−3.100
2000	20.786	154.278	136.591	35.375	226.898	106.760	−2.788
2100	20.786	155.293	137.458	37.453	227.254	100.744	−2.506
2200	20.786	156.260	138.291	39.532	227.593	94.712	−2.249
2300	20.786	157.184	139.092	41.610	227.916	88.664	−2.014
2400	20.786	158.068	139.864	43.689	228.224	82.603	−1.798
2500	20 786	158.917	140.610	45.768	228.518	76.530	−1.599
2600	20.786	159.732	141.330	47.846	228.798	70.444	−1.415
2700	20.786	160.516	142.026	49.925	229.064	64.349	−1.245
2800	20.786	161.272	142.700	52.004	229.318	58.243	−1.087
2900	20.786	162.002	143.353	54.082	229.560	52.129	−0.939
3000	20.786	162.706	143.986	56.161	229.790	46.007	−0.801
3100	20.786	163.388	144.601	58.239	230.008	39.877	−0.672
3200	20.786	164.048	145.199	60.318	230.216	33.741	−0.551
3300	20.786	164.688	145.780	62.397	230.413	27.598	−0.437
3400	20.786	165.308	146.345	64.475	230.599	21.449	−0.330
3500	20.786	165.911	146.895	66.554	230.776	15.295	−0.228
3600	20.786	166.496	147.432	68.632	230.942	9.136	−0.133
3700	20.786	167.066	147.955	70.711	231.098	2.973	−0.042
3800	20.786	167.620	148.465	72.790	231.244	−3.195	0.044
3900	20.786	168.160	148.963	74.868	231.381	−9.366	0.125
4000	20.786	168.686	149.450	76.947	231.509	−15.541	0.203
4100	20.786	169.200	149.925	79.025	231.627	−21 718	0.277
4200	20.786	169.700	150.390	81.104	231.736	−27.899	0.347
4300	20.786	170.190	150.845	83.183	231.836	−34.082	0.414
4400	20.786	170.667	151.290	85.261	231.927	−40.267	0.478
4500	20.786	171.135	151.726	87.340	232.009	−46.454	0.539
4600	20.786	171.591	152.153	89.418	232.082	−52.643	0.598
4700	20.786	172.038	152.571	91.497	232.147	−58.834	0.654
4800	20.786	172.476	152.981	93.576	232.204	−65.025	0.708
4900	20.786	172.905	153.383	95.654	232.253	−71.218	0.759
5000	20.786	173.325	153.778	97.733	232.294	−77.412	0.809
5100	20.786	173.736	154.165	99.811	232.327	−83.606	0.856
5200	20.786	174.140	154.546	101.890	232.353	−89.801	0.902
5300	20.786	174.536	154.919	103.969	232.373	−95.997	0.946
5400	20.786	174.924	155.286	106.047	232.386	−102.192	0.989
5500	20.786	175.306	155.646	108.126	232.392	−108.389	1.029
5600	20.786	175.680	156.001	110.204	232.393	−114.584	1.069
5700	20 786	176.048	156.349	112.283	232.389	−120.780	1.107
5800	20.786	176.410	156.692	114.362	232.379	−126.976	1.144
5900	20.786	176.765	157.029	116.440	232.365	−133.172	1.179
6000	20.786	177.114	157.361	118.519	232.348	−139.368	1.213

PREVIOUS. March 1977 (1 atm) CURRENT March 1982 (1 bar)

Hydrogen, Ion (H^+) — IDEAL GAS — M_r = 1.00739 — Hydrogen, Ion (H^+) — H_1^+(g)

$S°(298.15\ K) = 108\ 946 \pm 0.02\ J\ K^{-1}\ mol^{-1}$

$\Delta_f H°(0\ K) = 1528\ 085 \pm 0.04\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [1536.246]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(H^+, g, 0\ K)$ is calculated from $\Delta_f H°(H, g, 0\ K)$[1] using the spectroscopic value of IP(H) = 109678.764 ± 0.005 cm^{-1} (1312.0498 ± 0.0001 $kJ \cdot mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ \cdot mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ \cdot mol^{-1}$, which is derived from the 1973 CODATA fundamental constants[3]. Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(H^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(H, g, 0\ K)$ by using IP(H) with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for H(g), H^+(g), and e^-(ref). $\Delta_f H°(H \rightarrow H^+ + e^-, 298.15\ K)$ 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 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The thermodynamic functions of the proton gas are calculated using the recent CODATA fundamental constants[2] and assuming that the proton is an ideal monatomic gas. Since there is no electron associated with this species, there is only a translational contribution to the thermochemical function.

References

[1]JANAF Thermochemical Tables: H(g), 3-31-82 ; e^-(ref), 3-31-82.
[2]C. E. Moore, U. S. Nat. Bur. Stand., NSRDS-NBS-3, Section 6, (1972).
[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).

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
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−6.197	1528.085		
100	20.786	86.239	127.427	−4.119			
200	20.786	100.647	110.848	−2.040			
250	20.786	105.285	109.289	−1.001			
298.15	20.786	108.946	108.946	0.	1536.246	1516.990	−265 770
300	20 786	109 075	108.947	0.038	1536.297	1516.871	−264.111
350	20.786	112.279	109.200	1 078	1537.651	1513.526	−225.881
400	20.786	115.055	109.762	2.117	1539.001	1509.987	−197.184
450	20.786	117.503	110.489	3.156	1540.349	1506.280	−174.844
500	20.786	119.693	111.302	4.196	1541.697	1502.422	−156.957
600	20.786	123.483	113.026	6.274	1544.389	1494.314	−130.092
700	20.786	126.687	114.754	8.353	1547.078	1485.755	−110.868
800	20.786	129.463	116.423	10 431	1549.758	1476.812	−96.426
900	20.786	131.911	118.011	12.510	1552.428	1467.533	−85.173
1000	20.786	134.101	119.512	14.589	1555.084	1457 958	−76.156
1100	20.786	136.082	120.930	16 667	1557 721	1448.117	−68.765
1200	20.786	137.891	122.269	18.746	1560.339	1438.038	−62.596
1300	20 786	139.554	123.536	20.824	1562.936	1427.740	−57.367
1400	20.786	141.095	124.735	22.903	1565.511	1417.244	−52.878
1500	20.786	142.529	125.874	24.982	1568.065	1406.564	−48.981
1600	20.786	143.870	126.958	27.060	1570.596	1395.715	−45.565
1700	20.786	145.130	127.990	29.139	1573.107	1384.708	−42.547
1800	20.786	146.319	128.976	31.217	1575.597	1373.554	−39.859
1900	20.786	147.442	129.918	33.296	1578.068	1362.261	−37.451
2000	20.786	148.509	130.821	35.375	1580.520	1350.840	−35.280
2100	20.786	149.523	131.688	37.453	1582.954	1339.296	−33.313
2200	20.786	150.490	132.521	39.532	1585.372	1327.636	−31.522
2300	20.786	151.414	133.322	41.610	1587.774	1315.867	−29.884
2400	20.786	152.298	134.095	43.689	1590.161	1303.994	−28.381
2500	20.786	153.147	134.840	45.768	1592.533	1292.021	−26.995
2600	20.786	153.962	135.560	47.846	1594.891	1279.954	−25.715
2700	20.786	154.747	136.256	49.925	1597.236	1267.797	−24.527
2800	20.786	155.503	136.930	52.004	1599.569	1255.553	−23.423
2900	20.786	156.232	137.583	54.082	1601.889	1243.225	−22.393
3000	20.786	156.937	138.216	56.161	1604.198	1230.818	−21.430
3100	20.786	157.618	138.831	58.239	1606.495	1218.334	−20.529
3200	20.786	158.278	139.429	60.318	1608.781	1205.777	−19.682
3300	20.786	158.918	140.010	62.397	1611.057	1193.148	−18.886
3400	20.786	159.538	140.575	64.475	1613.322	1180.450	−18.135
3500	20.786	160.141	141.125	66.554	1615.576	1167.685	−17.427
3600	20.786	160.726	141.662	68.632	1617.821	1154.857	−16.757
3700	20.786	161.296	142.185	70.711	1620.056	1141.966	−16.122
3800	20.786	161.850	142.695	72.790	1622.281	1129.014	−15.519
3900	20.786	162.390	143.193	74.868	1624.497	1116.005	−14.947
4000	20.786	162.916	143.680	76.947	1626.703	1102.938	−14.403
4100	20.786	163.430	144.155	79.025	1628.899	1089.817	−13.884
4200	20.786	163.931	144.620	81.104	1631.087	1076.642	−13.390
4300	20.786	164.420	145.075	83.183	1633.265	1063.416	−12.918
4400	20 786	164.897	145.520	85.261	1635.435	1050.138	−12.467
4500	20.786	165.365	145.956	87.340	1637.596	1036.812	−12.035
4600	20.786	165.821	146.383	89.418	1639.748	1023.437	−11.621
4700	20.786	166.268	146.801	91 497	1641.891	1010.016	−11.225
4800	20 786	166.706	147.211	93.576	1644.027	996.549	−10.845
4900	20.786	167.135	147.613	95.654	1646.154	983.038	−10.479
5000	20.786	167.555	148.008	97.733	1648.274	969.484	−10.128
5100	20.786	167.966	148.395	99.811	1650.386	955.887	−9 790
5200	20.786	168.370	148.776	101.890	1652 491	942.249	−9.465
5300	20.786	168.766	149.149	103.969	1654.588	928.570	−9.152
5400	20.786	169.154	149.516	106.047	1656.680	914.852	−8.849
5500	20.786	169.536	149.877	108.126	1658.765	901 095	−8.558
5600	20.786	169.910	150.231	110.204	1660.845	887 301	−8.276
5700	20.786	170.278	150.579	112.283	1662.919	873.469	−8.004
5800	20 786	170 640	150.922	114.362	1664.988	859.601	−7.742
5900	20.786	170 995	151.259	116 440	1667.053	845 697	−7.487
6000	20.786	171 344	151.591	118.519	1669 113	831 758	−7.241

PREVIOUS March 1977 (1 atm) — CURRENT March 1982 (1 bar)

EA(H, g) = 0.754209 ± 0.000003 eV
$S°$(298.15 K) = 108.960 ± 0.017 J K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 143.27 ± 0.02 kJ·mol^{-1}
$\Delta_f H°$(298 15 K) = [139.032] kJ·mol^{-1}

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

$\Delta_f H°(H^-, g, 0 K)$ is calculated from $\Delta_f H°$(H, g, 0 K)[1] using the adopted electron affinity of EA(H) = 0.754209 ± 0.000003 eV (72.7695 ± 0.0003 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[2] is based on extensive Hylleras–type variational calculations on two election systems.[3,4,5] Additional information on H^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[2,6] Rosenstock *et al.*[7] and Massey[8] Experimentally, Dehmer and Chupka[9] have reported EA(H) ≥0.7540 ± 0.0003 eV.

$\Delta_f H°(H^-, g, 298.15 K)$ is obtained from $\Delta_f H°$(H, g, 0 K) by using EA(H) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for H^-(g), H(g), and e^-(ref). $\Delta_r H°(H^- \rightarrow H + e^-, 298.15 K)$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al.[7] $\Delta_f H°$(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 ground state electronic configuration for H^-(g) is given by Hotop and Lineberger[2,6] and Rosenstock *et al.*[7] A comparison of the isoelectronic sequence – H^-(g), He(g), Li^+(g) – would suggest that stable electronic states may exist at 0 8 EA(H) or roughly 6400 cm^{-1}. This would greatly affect the entropy. However, Pekeris[4] states that he was unable to find any bound states. In addition, Seman and Branscomb[10] state that theoretical and semiempirical evidence suggests that atomic negative ions have very few if any excited states below the continuum. We assume no stable excited states exist.

Reference

[1]JANAF Thermochemical Tables H(g) and e^-(ref), 3–31–82.
[2]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, **14**, 731 (1985).
[3]C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).
[4]C. L. Pekeris, Phys. Rev. **126**, 1470 (1962).
[5]K. Aaskamar, Nucl. Instr. Meth. **90**, 263 (1970).
[6]H. Hotop and W C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975).
[7]H. M. Rosenstock, K. Draxel *et al.*, J. Phys. Chem. Ref. Data **6**, Supp. 1 (1977).
[8]H. S. W. Massey, "Negative Ions," 3rd ed., Cambridge University Press, Cambridge, (1976).
[9]P. M. Dehmer and W. A. Chupka, Bull. Am. Phys Soc **20**, 729 (1975).
[10]M. L. Seman and L. M. Branscomb, Phys. Rev. **125**, 1602 (1962).

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	−6.197	143.266		
100	20.786	86.253	127.440	−4.119			
200	20.786	100.661	110.861	−2.040			
250	20.786	105.299	109.302	−1.001			
298.15	20.786	108.960	108.960	0.	139.032	132.282	−23.175
300	20.786	109.089	108.960	0.038	139.006	132.240	−23.025
350	20 786	112.293	109.213	1.078	138.281	131 170	−19.576
400	20.786	115.068	109.776	2.117	137.553	130.203	−17.003
450	20.786	117.517	110.502	3.156	136.823	129.328	−15.012
500	20.786	119.707	111.315	4.196	136 091	128.535	−13.428
600	20.786	123.496	113.039	6.274	134.627	127.161	−11.070
700	20.786	126.701	114.768	8.353	133.158	126.033	−9.405
800	20 786	129.476	116.437	10.431	131.682	125.116	−8.169
900	20 786	131.924	118.024	12.510	130.194	124.384	−7.219
1000	20 786	134.114	119.526	14.589	128.692	123.819	−6.468
1100	20.786	136.096	120.943	16.667	127.173	123.405	−5.860
1200	20.786	137.904	122.283	18.746	125.634	123.130	−5.360
1300	20.786	139.568	123.549	20.824	124.073	122.985	−4.942
1400	20.786	141.108	124.749	22.903	122.491	122.960	−4.588
1500	20.786	142.542	125.888	24.982	120.887	123.050	−4.285
1600	20.786	143.884	126.971	27.060	119.262	123.247	−4.024
1700	20.786	145.144	128.004	29.139	117.615	123.546	−3.796
1800	20 786	146.332	128.989	31.217	115.948	123.943	−3.597
1900	20.786	147.456	129.932	33.296	114.262	124.433	−3.421
2000	20 786	148.522	130.835	35.375	112.557	125.012	−3.265
2100	20.786	149.536	131.701	37.453	110.834	125.677	−3.126
2200	20.786	150.503	132.534	39.532	109.094	126.425	−3.002
2300	20.786	151.427	133.336	41.610	107.339	127.252	−2.890
2400	20.786	152.312	134.108	43.689	105.568	128.156	−2.789
2500	20.786	153.160	134.853	45 768	103.783	129.133	−2.698
2600	20.786	153.976	135.573	47.846	101.984	130.183	−2.615
2700	20.786	154 760	136.269	49.925	100.172	131.302	−2.540
2800	20.786	155.516	136.943	52.004	98.348	132.488	−2.472
2900	20.786	156.245	137.596	54.082	96.511	133.740	−2.409
3000	20 786	156.950	138.230	56.161	94.662	135.055	−2.352
3100	20.786	157.632	138.845	58.239	92.802	136.432	−2.299
3200	20.786	158.292	139.442	60.318	90.931	137.869	−2.250
3300	20.786	158.931	140.023	62.397	89.049	139.365	−2.206
3400	20.786	159.552	140.589	64.475	87.157	140.918	−2.165
3500	20.786	160.154	141.139	66.554	85.255	142.527	−2.127
3600	20.786	160 740	141.675	68.632	83.342	144.190	−2.092
3700	20.786	161.309	142.198	70.711	81.420	145.907	−2.060
3800	20.786	161.864	142.709	72.790	79.488	147.676	−2.030
3900	20.786	162.404	143.207	74.868	77.546	149.496	−2.002
4000	20.786	162.930	143.693	76.947	75.595	151.365	−1.977
4100	20.786	163.443	144.169	79.025	73.635	153.284	−1.953
4200	20.786	163.944	144.634	81.104	71.665	155.250	−1.931
4300	20.786	164.433	145.088	83.183	69.686	157.264	−1.910
4400	20.786	164.911	145.534	85.261	67.699	159.323	−1.891
4500	20.786	165.378	145.969	87.340	65.702	161.428	−1.874
4600	20 786	165.835	146.396	89.418	63.697	163.577	−1.857
4700	20 786	166.282	146.815	91.497	61.684	165.770	−1.842
4800	20.786	166.720	147.225	93.576	59.662	168.007	−1.828
4900	20.786	167.148	147.627	95.654	57.632	170.285	−1.815
5000	20 786	167.568	148.022	97.733	55.594	172.604	−1.803
5100	20.786	167.980	148.409	99.811	53.549	174.965	−1.792
5200	20 786	168.383	148.789	101.890	51.497	177.366	−1.782
5300	20 786	168.779	149.163	103.969	49.437	179.806	−1.772
5400	20.786	169.168	149.530	106.047	47.372	182.285	−1.763
5500	20.786	169.549	149.890	108.126	45.300	184.802	−1.755
5600	20.786	169.924	150.245	110.204	43.222	187.358	−1.748
5700	20.786	170.292	150.593	112.283	41.139	189.950	−1.741
5800	20 786	170.653	150.936	114.362	39.051	192.579	−1.734
5900	20.786	171.009	151.273	116.440	36.958	195.244	−1.729
6000	20 786	171.358	151.605	118.519	34.862	197.944	−1.723

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

Mercury Hydride (HgH) — IDEAL GAS — M_r = 201.59794 — Mercury Hydride (HgH) — $H_1Hg_1(g)$

$S°(298.15\ K) = [219.705]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 243.35 \pm 16.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 238.49 \pm 16.7\ kJ·mol^{-1}$

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

$\omega_e = 1387\ cm^{-1}$ $\omega_e x_e = 83.01\ cm^{-1}$ $\sigma = 1$
$B_e = 5.549\ cm^{-1}$ $\alpha_e = 0.312\ cm^{-1}$ $r_e = 1.74\ Å$

Enthalpy of Formation

The enthalpy of formation is calculated from $D_0^0 = 8.671\ kcal·mol^{-1}$ = taken from Herzberg.[1]

Heat Capacity and Entropy

Molecular constants are taken from Herzberg.[1]

Reference

[1]G. Herzberg, "Spectra of Diatomic Molecules," 2nd Edition, D. Van Nostrand Company, Inc., New York (1950).

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

	J·K⁻¹mol⁻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	−8.711	243.353	243.353	INFINITE
100	29.132	187.686	245.898	−5.821	243.038	233.028	−121.721
200	29.265	207.901	222.422	−2.904	242.023	223.389	−58.343
250	29.563	214.459	220.197	−1.434	239.098	218.955	−45.748
298.15	30.043	219.705	219.705	0.	238.488	215.132	−37.690
300	30.064	219.891	219.706	0.056	238.465	214.987	−37.433
350	30.708	224.572	220.074	1.574	237.870	211.121	−31.508
400	31.417	228.719	220.900	3.127	237.318	207.338	−27.076
450	32.133	232.461	221.980	4.716	236.810	203.622	−23.636
500	32.822	235.882	223.202	6.340	236.342	199.960	−20.890
600	34.057	241.979	225.835	9.686	235.510	192.763	−16.782
700	35.084	247.308	228.530	13.145	176.026	192.269	−14.347
800	35.931	252.050	231.179	16.697	176.023	194.591	−12.705
900	36.636	256.324	233.739	20.326	176.086	196.908	−11.428
1000	37.233	260.216	236.195	24.020	176.200	199.216	−10.406
1100	37.747	263.789	238.544	27.770	176.352	201.511	−9.569
1200	38.199	267.093	240.787	31.568	176.531	203.790	−8.871
1300	38.603	270.167	242.930	35.408	176.733	206.054	−8.279
1400	38.970	273.042	244.979	39.287	176.951	208.301	−7.772
1500	39.308	275.742	246.941	43.201	177.183	210.533	−7.331
1600	39.623	278.289	248.822	47.148	177.425	212.748	−6.946
1700	39.919	280.700	250.626	51.125	177.677	214.948	−6.605
1800	40.201	282.990	252.361	55.131	177.938	217.133	−6.301
1900	40.471	285.171	254.031	59.165	178.206	219.303	−6.029
2000	40.731	287.253	255.641	63.225	178.483	221.459	−5.784
2100	40.983	289.247	257.194	67.311	178.767	223.601	−5.562
2200	41.227	291.159	258.695	71.422	179.060	225.729	−5.359
2300	41.466	292.997	260.146	75.556	179.361	227.844	−5.174
2400	41.700	294.767	261.552	79.715	179.670	229.945	−5.005
2500	41.930	296.473	262.915	83.896	179.988	232.033	−4.848
2600	42.157	298.122	264.238	88.101	180.315	234.109	−4.703
2700	42.380	299.718	265.522	92.327	180.651	236.171	−4.569
2800	42.601	301.263	266.771	96.576	180.996	238.221	−4.444
2900	42.819	302.762	267.987	100.847	181.352	240.259	−4.328
3000	43.035	304.217	269.170	105.140	181.717	242.284	−4.219
3100	43.249	305.631	270.324	109.454	182.093	244.297	−4.116
3200	43.462	307.008	271.449	113.790	182.479	246.297	−4.020
3300	43.674	308.349	272.547	118.147	182.875	248.285	−3.930
3400	43.884	309.656	273.619	122.525	183.283	250.261	−3.845
3500	44.093	310.931	274.667	126.924	183.700	252.225	−3.764
3600	44.301	312.176	275.691	131.343	184.129	254.177	−3.688
3700	44.508	313.392	276.694	135.784	184.568	256.117	−3.616
3800	44.715	314.582	277.675	140.245	185.018	258.044	−3.547
3900	44.921	315.746	278.637	144.727	185.479	259.960	−3.482
4000	45.126	316.886	279.579	149.229	185.951	261.864	−3.420
4100	45.330	318.003	280.502	153.752	186.434	263.756	−3.360
4200	45.534	319.098	281.408	158.295	186.928	265.636	−3.304
4300	45.738	320.171	282.297	162.859	187.433	267.504	−3.250
4400	45.941	321.225	283.170	167.443	187.949	269.360	−3.198
4500	46.143	322.260	284.027	172.047	188.476	271.204	−3.148
4600	46.346	323.276	284.870	176.671	189.013	273.037	−3.100
4700	46.548	324.275	285.697	181.316	189.562	274.858	−3.055
4800	46.749	325.257	286.511	185.981	190.121	276.667	−3.011
4900	46.950	326.223	287.312	190.666	190.692	278.464	−2.968
5000	47.152	327.174	288.100	195.371	191.274	280.249	−2.928
5100	47.352	328.110	288.875	200.096	191.866	282.022	−2.888
5200	47.553	329.031	289.638	204.841	192.470	283.785	−2.851
5300	47.753	329.939	290.390	209.607	193.085	285.535	−2.814
5400	47.954	330.833	291.131	214.392	193.711	287.273	−2.779
5500	48.154	331.715	291.861	219.197	194.348	289.000	−2.745
5600	48.353	332.584	292.580	224.023	194.996	290.715	−2.712
5700	48.553	333.442	293.290	228.868	195.656	292.419	−2.680
5800	48.753	334.288	293.989	233.733	196.326	294.110	−2.649
5900	48.952	335.123	294.679	238.618	197.008	295.790	−2.619
6000	49.151	335.948	295.360	243.524	197.701	297.459	−2.590

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

Mercury Hydride (HgH) $H_1Hg_1(g)$

$S°(298.15\ K) = 206.589\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 28.535 \pm 0.21\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 26.359 \pm 0.21\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0	1

$\omega_e = 2309.06\ cm^{-1}$ $\omega_e x_e = 39.73\ cm^{-1}$ $\sigma = 2$
$B_e = 6.512\ cm^{-1}$ $\alpha_e = 0.1715\ cm^{-1}$

Enthalpy of Formation

Using the calculated thermal functions and functions for H_2(g) and I_2(g) given in the JANAF tables, equilibrium data from the literature are used to calculate $\Delta_f H°$(298 15 K) for the reaction $H_2(g) + I_2(g) \rightarrow 2\ HI(g)$.

Source	$\Delta H°$(298.15 K), $kcal \cdot mol^{-1}$
Taylor and Crist[4] (667 to 764 K)	−2.375 ± .005
Bodenstin[5] (556 to 781 K)	−2.053 ± .133
Bright and Hagerty[6] (696 and 779 K)	−2.219 ± .070
Rittenberg and Urey[7] (671 and 741 K)	−2.156 ± .072

The data of Taylor and Crist are the most concordant and are given the most weight. Converting to the solid state of iodine, which has been adopted as a JANAF reference state gives the standard enthalpy of formation of hydrogen iodide.

Heat Capacity and Entropy

Molecular constants are from Cowan and Gordy[1] and Boyd and Thompson.[2] The calculated functions are in reasonable agreement with the compilation of Kelley.[3]

References

[1]M. Cowan and W. Gordy, Phys. Rev. 104, 551 (1956).
[2]D. R. J. Boyd and H. W. Thompson, Spectrochim. Acta 5, 308 (1952).
[3]K. K. Kelley, U. S. Bur. Mines Bull. 584, (1960).
[4]A. H. Taylor and R. H. Crist, J Amer. Chem. Soc. 65, 1377 (1941).
[5]M. Bodenstein, Z. physikal. Chem. 29, 295 (1899).
[6]N. F. H. Bright and R. P. Hagerty, Trans. Faraday Soc. 43, 697 (1947).
[7]D. Rittenberg and H. C. Urey, J. Amer. Chem. Soc. 56, 1885 (1934).

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
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	−8.656	28.535	28.535	INFINITE
100	29 114	174.773	232.489	−5.772	28.396	19.004	−9.927
200	29.124	194.956	209.255	−2.860	27.494	9.940	−2.596
250	29.134	201.456	207.069	−1.403	26.939	5.615	−1.173
298.15	29.156	206.589	206.589	0.	26.359	1.560	−0.273
300	29.158	206.770	206.590	0.054	26.336	1 406	−0.245
350	29.216	211.268	206.945	1.513	25.665	−2.698	0.403
400	29.328	215.176	207.735	2.976	16.987	−6.428	0.839
450	29.502	218.640	208.758	4.447	15.710	−9.279	1.077
500	29.736	221.760	209.905	5.928	−5.622	−10.088	1.054
600	30.348	227.233	212.349	8.931	−5.961	−10.948	0.953
700	31 064	231.964	214.820	12.001	−6.243	−11.756	0.877
800	31.798	236.160	217.230	15.144	−6.466	−12.528	0.818
900	32.496	239.946	219.547	18.359	−6.633	−13.275	0.770
1000	33.135	243.404	221.763	21.641	−6.754	−14.006	0.732
1100	33.706	246.589	223.877	24.984	−6.838	−14.727	0.699
1200	34.211	249.544	225.894	28.380	−6 897	−15.441	0.672
1300	34.655	252.300	227.821	31.824	−6.942	−16.151	0.649
1400	35.046	254.883	229.662	35.309	−6.982	−16.858	0.629
1500	35.391	257.313	231.425	38.832	−7.027	−17.562	0.612
1600	35.696	259.607	233.116	42.386	−7.087	−18.263	0.596
1700	35.967	261 780	234.739	45.970	−7.168	−18.959	0.583
1800	36.209	263.842	236.299	49.579	−7.277	−19 649	0.570
1900	36.427	265.806	237.800	53.211	−7 416	−20.333	0.559
2000	36.623	267.680	239.248	56.863	−7.589	−21.009	0.549
2100	36 802	269.471	240.645	60.535	−7.794	−21.675	0.539
2200	36 966	271 187	241.994	64.223	−8.030	−22.330	0.530
2300	37 116	272.833	243.300	67.927	−8.294	−22.975	0.522
2400	37.255	274.416	244.563	71.646	−8.581	−23.607	0.514
2500	37.384	275.939	245.788	75.378	−8.886	−24.227	0.506
2600	37.504	277.408	246.976	79.123	−9.204	−24.834	0.499
2700	37 617	278.825	248.130	82.879	−9.528	−25.429	0.492
2800	37.723	280.195	249.251	86.646	−9.854	−26.012	0.485
2900	37.823	281.521	250.341	90.423	−10.176	−26.583	0.479
3000	37.918	282.805	251.401	94.210	−10.489	−27.144	0.473
3100	38.009	284.050	252.435	98.006	−10.789	−27.694	0.467
3200	38.095	285.258	253.442	101.812	−11.073	−28.235	0.461
3300	38.178	286.431	254.424	105.625	−11.338	−28.767	0.455
3400	38.258	287.572	255.382	109.447	−11.580	−29.291	0.450
3500	38.335	288.682	256.317	113.277	−11.799	−29.809	0.445
3600	38.409	289.763	257.232	117.114	−11.993	−30.321	0.440
3700	38.481	290.817	258.125	120.959	−12.161	−30.828	0.435
3800	38.550	291.844	258.999	124.810	−12.303	−31.330	0.431
3900	38.618	292.846	259.854	128.669	−12.417	−31.829	0.426
4000	38.684	293.825	260.691	132.534	−12.504	−32.326	0.422
4100	38.749	294 781	261.511	136.405	−12.565	−32.821	0.418
4200	38.812	295.715	262.314	140.283	−12.599	−33.314	0.414
4300	38.874	296.629	263.102	144.168	−12.607	−33.807	0.411
4400	38.934	297.523	263.874	148.058	−12.590	−34.300	0.407
4500	38.994	298.399	264.631	151.955	−12.549	−34.794	0.404
4600	39.052	299.257	265.375	155.857	−12.484	−35.289	0.401
4700	39.110	300.097	266.105	159.765	−12.395	−35.786	0.398
4800	39.166	300.921	266.822	163.679	−12.284	−36.284	0.395
4900	39.222	301.729	267.526	167.598	−12.151	−36.786	0.392
5000	39.277	302.522	268.218	171.523	−11.998	−37.290	0.390
5100	39.332	303.301	268.898	175.454	−11.823	−37.798	0.387
5200	39.385	304.065	269.567	179.389	−11.630	−38.309	0.385
5300	39.439	304.816	270.225	183.331	−11.416	−38.824	0.383
5400	39.491	305.553	270.872	187.277	−11 185	−39.343	0.381
5500	39.544	306.278	271.510	191.229	−10.935	−39.867	0.379
5600	39.595	306.991	272.137	195.186	−10.667	−40.395	0.377
5700	39.647	307 693	272.754	199.148	−10.382	−40.929	0.375
5800	39 698	308.383	273.363	203.115	−10.080	−41.467	0.373
5900	39 748	309 062	273.962	207.087	−9.760	−42.011	0.372
6000	39 798	309.730	274.553	211.065	−9.425	−42.561	0.371

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

Triiodosilane ($SiHI_3$) **IDEAL GAS** M_r = 409.80694 **Triiodosilane ($SiHI_3$)** **$H_1I_3Si_1$(g)**

$S°(298\ 15\ K) = [375\ 009 \pm 2.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-66.36 \pm 20.9]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298\ 15\ K) = [-74.48 \pm 20.9]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2190(1)	717(2)
286(1)	399(2)
122(1)	80(2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances. SiH = [1.50] Å Si–I = [2.435] Å
Bond Angles: H–Si–I = [106.81]° I–Si–I = [112]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.04795 \times 10^{-110}]\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(298\ 15\ K)$ is estimated by linear interpolation between the values[1] of SiI_4(g) and SiH_4(g). There are no experimental $\Delta_f H°$ data for SiH_3I, SiH_2I_2, and $SiHI_3$. Data for the iodomethanes[2] have a surprising progression, (SiH_3I, g),[1] they are of doubtful use in predicting $\Delta_f H°$ of the iodosilanes. We conclude, as did Hunt and Sirtl,[3] that the available data justify only linear interpolation.

Heat Capacity and Entropy

The molecular structure is estimated by comparison with SiH_3I, SiI_4 and the various bromo–, chloro–, and fluorosilanes.[1] The principal moments of inertia are. $I_A = I_B = 174.6 \times 10^{-39}$ and $I_C = 343.48 \times 10^{-39}\ g \cdot cm^2$.

Vibrational frequencies are from liquid–phase Raman spectra of Hengge and Hoefler.[4] Infrared data, also presumably for the liquid phase, were reported[4] for ν_1 and ν_4.

We neglect excited states and assume the electronic ground state to be a singlet. We expect that contributions from excited states should be unimportant, as discussed on the tables for SiH_3Br and SiH_2Cl_2.[1]

References

[1]JANAF Thermochemical Tables: H_3ISI(g), HI_3Si(g), BrH_3Si(g), Br_2H_2Si(g), Br_3HSi(g), ClH_3Si(g), Cl_2H_2Si(g),Cl_3HSi(g) 12–31–76; FH_3Si(g), F_2H_2Si(g), F_3HSi(g), I_4Si(g), H_4Si(g)6–30–76.
[2]S. A Kudchadker and A. P. Kudchadker, J. Phys. Chem. Ref. Data 4, 457 (1975).
[3]L. P. Hunt and E. Sirtl, J. Electrochem. Soc 120, 806 (1973).
[4]E. Hengge and F. Hoefler, Z. Naturforsch. A26, 768 (1971).

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
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−19.135	−66.361	−66.361	INFINITE
100	58.844	297.407	442.714	−14.531	−68.098	−83.270	43.496
200	74.448	343.359	382.414	−7.811	−71.302	−97.213	25.389
250	79.878	360.582	376.369	−3.947	−72.928	−103.503	21.626
298.15	83.884	375.009	375.009	0.	−74.475	−109.250	19.140
300	84 018	375.528	375.011	0.155	−74.535	−109.466	19.060
350	87.179	388.728	376.046	4.439	−76.229	−115.157	17.186
400	89.637	400.536	378.382	8.862	−101.860	−119.782	15.642
450	91.605	411.211	381.446	13.394	−105.232	−121.819	14.140
500	93.228	420.949	384.917	18.016	−168.739	−117.785	12.305
600	95.791	438.185	392.396	27.474	−168.754	−107.590	9.367
700	97.757	453.105	400.026	37.155	−168.641	−97.404	7.268
800	99.322	466.264	407.500	47.012	−168.438	−87.240	5.696
900	100.590	478.039	414.695	57.009	−168.175	−77.105	4.475
1000	101.625	488.692	421.570	67.122	−167.878	−67.002	3.500
1100	102.479	498.419	428.121	77.328	−167.570	−56.930	2.703
1200	103.186	507.367	434.357	87.613	−167.272	−46.885	2.041
1300	103.776	515.651	440.296	97.962	−167.008	−36.863	1.481
1400	104.272	523.360	445.957	108.365	−166.800	−26.860	1.002
1500	104.691	530.569	451.360	118.814	−166.670	−16.870	0.587
1600	105.048	537.337	456.524	129.301	−166.640	−6.885	0.225
1700	105.354	543.715	461.467	139.821	−216.905	3.549	−0.109
1800	105.617	549.744	466.205	150.370	−216.894	16.516	−0.479
1900	105.846	555.461	470.754	160.944	−216.982	29.485	−0.811
2000	106.045	560.896	475.126	171.538	−217.172	42.462	−1.109
2100	106.219	566.074	479.335	182.152	−217.463	55.450	−1.379
2200	106.373	571.019	483.391	192.782	−217.849	68.454	−1.625
2300	106.509	575.750	487.304	203.426	−218.317	81.478	−1.850
2400	106.629	580.286	491.085	214.083	−218.856	94.524	−2.057
2500	106.737	584.641	494.740	224.751	−219.448	107.594	−2.248
2600	106.833	588.829	498.279	235.430	−220.077	120.688	−2.425
2700	106.920	592.863	501.708	246.118	−220.726	133.807	−2.589
2800	106.998	596.752	505.033	256.814	−221.379	146.949	−2.741
2900	107.068	600.508	508.261	267.517	−222.018	160.115	−2.884
3000	107 132	604.139	511.397	278.227	−222.631	173.303	−3.017
3100	107.191	607.653	514.446	288.943	−223.205	186.510	−3.143
3200	107.244	611.057	517.412	299.665	−223.729	199.735	−3.260
3300	107.292	614.358	520.300	310.392	−224.193	212.976	−3.371
3400	107.337	617.562	523.114	321.123	−224.590	226.230	−3.476
3500	107.378	620.674	525.857	331.859	−224.916	239.494	−3.574
3600	107.416	623.699	528.533	342.599	−609.316	263.227	−3.819
3700	107.450	626.643	531.145	353.342	−609.071	287.462	−4.058
3800	107.483	629.509	533.696	364.089	−608.746	311.688	−4.284
3900	107.513	632.301	536.188	374.839	−608.340	335.905	−4.499
4000	107.540	635.023	538.625	385.591	−607.852	360.110	−4.703
4100	107.566	637.679	541.009	396.347	−607.283	384.302	−4.896
4200	107.590	640.271	543.342	407.104	−606.634	408.480	−5.080
4300	107.612	642.803	545.626	417.865	−605.905	432.640	−5.256
4400	107.633	645.278	547.862	428.627	−605.099	456.783	−5.423
4500	107.653	647.697	550.054	439.391	−604.218	480.907	−5.582
4600	107.671	650.063	552.203	450.157	−603.263	505.011	−5.735
4700	107.688	652.379	554.309	460.925	−602.237	529.093	−5.880
4800	107.705	654.646	556.376	471.695	−601.142	553.153	−6.020
4900	107.720	656.867	558.405	482.466	−599.981	577.188	−6.153
5000	107.734	659.043	560.396	493.239	−598.756	601.200	−6.281
5100	107 748	661.177	562.351	504.013	−597.470	625.186	−6.403
5200	107.760	663.269	564.272	514 788	−596.124	649.147	−6.521
5300	107.772	665.322	566.159	525.565	−594.722	673.081	−6.634
5400	107 784	667.337	568.014	536.343	−593.266	696.988	−6.742
5500	107.795	669.315	569.838	547.122	−591.756	720.868	−6.846
5600	107.805	671.257	571.632	557.902	−590 197	744.720	−6.946
5700	107.815	673.165	573.396	568.683	−588.590	768.544	−7.043
5800	107.824	675.040	575.133	579.465	−586.937	792.339	−7.136
5900	107.833	676 884	576.842	590.248	−585.240	816.105	−7.225
6000	107.841	678 696	578.524	601.031	−583.500	839.842	−7.311

PREVIOUS. December 1976 (1 atm) CURRENT December 1976 (1 bar)

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K)$ = [50.208] $J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298\ 15\ K) = -57.820 \pm 0.046\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The value of $\Delta_f H°(298.15\ K)$ is taken from Gunn and Green.[1] The corresponding value reported by Messer *et al.*[2] was -15.16 ± 0.6 $kcal \cdot mol^{-1}$. In this latter paper, the results of the previous investigations were also reviewed.

Heat Capacity and Entropy

$C_p°$ and $S°(298.15\ K)$ are estimated by comparison with those for NaH(cr) and LiH(cr).

Decomposition Data

T_{dcm} = 690 K was assumed to be the temperature at which the value of $\Delta_f G°$ changes from negative to positive.

References

[1]S.R. Gunn and L.G Green, J. Amer. Chem. Soc. 80, 4782 (1958).
[2]C.E. Messer, L.G. Fasolino and C.E. Thalmayer, J. Amer. Chem. Soc. 77, 4524 (1955).

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	37.907	50.208	50.208	0.	−57.820	−53.010	9.287
300	38.074	50.443	50.209	0.070	−57.776	−52.980	9.225
400	44.141	62.267	51.780	4.195	−55.104	−51.768	6.760
500	48.534	72.608	54.933	8.837	−51.924	−51.293	5.359
600	51.923	81.766	58.657	13.865	−48.360	−51.496	4.483
700	54.606	89.977	62.555	19.196	−44.498	−52.320	3.904
800	56.819	97.418	66.455	24.771	−40 400	−53.715	3.507
900	58.440	104.207	70.278	30.536	−36.122	−55.635	3.229
1000	59.831	110 438	73.987	36.451	−31.708	−58.038	3.032
1100	60.966	116.195	77.565	42.493	−27.187	−60.889	2.891
1200	61.923	121.542	81.010	48.639	−22.580	−64.156	2.793
1300	62.701	126.531	84.322	54.871	−17.907	−67.810	2.725
1400	63.301	131.200	87.505	61.173	−13.188	−71.825	2.680
1500	63.722	135.583	90.566	67.526	−8.439	−76.179	2.653

PREVIOUS: CURRENT: March 1963

Potassium Hydride (KH) — IDEAL GAS — M_r = 40.10624 — Potassium Hydride (KH) — $H_1K_1(g)$

$S°(298.15\ K) = 198.024\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 125.53 \pm 14.6\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 123.01 \pm 14.6\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 985.0\ cm^{-1}$ $\omega_e x_e = 14.65\ cm^{-1}$ $\sigma = 1$
$B_e = cm^{-1}$ $\alpha_e = 0.0673\ cm^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from $D_0° = 1.86 \pm 0.15$ eV as reported by Gaydon.[1]

Heat Capacity and Entropy

All molecular and spectroscopic constants are obtained from Herzberg.[2]

References

[1]A.G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd., (1953).
[2]G Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., (1950).

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⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−8.795	125.530	125.530	INFINITE
100	29.136	165.689	224.657	−5.897	125.197	117.224	−61.232
200	29.583	185.963	200.811	−2.970	124.183	109.630	−28.632
250	30.243	192.630	198.530	−1 475	123.605	106.058	−22.160
298.15	31.036	198.024	198.024	0.	123.010	102.731	−17.998
300	31.068	198.216	198.025	0.057	122.986	102.606	−17.865
350	31.917	203.069	198.406	1.632	119.945	99.357	−14.828
400	32.711	207.384	199.263	3.248	119.245	96.465	−12.597
450	33.419	211.279	200.386	4.902	118.605	93.656	−10.871
500	34.034	214.832	201.655	6.589	118.017	90.916	−9.498
600	35.019	221.129	204.389	10.044	116.968	85.597	−7.452
700	35.752	226.585	207.179	13.584	116.043	80 443	−6.003
800	36.309	231.397	209.912	17.188	115.194	75.416	−4.924
900	36.746	235.700	212.542	20.842	114.378	70.493	−4.091
1000	37.098	239.590	215.055	24.535	113.556	65.661	−3.430
1100	37.391	243.140	217.450	28.259	33.742	65.523	−3.111
1200	37.640	246.404	219.728	32.011	33.876	68.406	−2.978
1300	37.858	249.426	221.898	35.786	34.012	71.278	−2.864
1400	38.052	252.239	223.966	39.582	34.147	74.140	−2.766
1500	38.228	254.870	225 939	43.396	34.277	76.992	−2.681
1600	38.389	257.342	227.826	47.227	34.402	79.835	−2.606
1700	38.540	259.674	229.631	51.074	34.520	82.671	−2.540
1800	38.681	261.881	231.362	54.935	34.629	85.500	−2.481
1900	38.816	263.976	233.024	58.810	34.728	88.324	−2.428
2000	38 944	265.971	234.622	62.698	34.817	91.142	−2.380
2100	39 068	267.874	236.160	66.598	34.893	93.956	−2.337
2200	39 188	269.694	237.643	70.511	34.956	96.767	−2.298
2300	39.305	271.438	239.075	74.436	35.004	99.576	−2.261
2400	39 419	273.114	240.459	78.372	35.034	102.383	−2.228
2500	39.530	274.725	241.797	82.319	35.045	105.189	−2.198
2600	39.640	276.278	243.094	86.278	35.034	107.994	−2.170
2700	39.747	277.776	244.351	90.247	34.999	110.801	−2.144
2800	39.854	279.223	245.571	94.227	34.937	113.610	−2.119
2900	39.959	280.623	246.755	98.218	34.845	116.421	−2.097
3000	40.062	281.980	247.907	102.219	34.721	119.236	−2.076
3100	40.165	283.295	249.027	106.230	34.561	122.056	−2.057
3200	40.267	284.572	250.118	110.252	34.361	124.881	−2.038
3300	40.369	285.813	251.181	114.284	34.127	127.713	−2.022
3400	40.469	287.019	252.218	118.326	33.841	130.553	−2.006
3500	40.569	288.194	253.229	122.378	33.508	133.402	−1.991
3600	40.669	289.338	254.216	126.440	33.119	136.261	−1.977
3700	40.767	290.454	255.180	130.511	32.672	139.132	−1.964
3800	40.866	291.542	256.123	134.593	32.163	142.016	−1.952
3900	40.964	292.605	257.045	138.685	31.586	144.915	−1.941
4000	41.062	293.643	257.947	142.786	30.944	147.828	−1.930
4100	41.159	294.659	258.830	146.897	30.226	150.759	−1.921
4200	41.256	295.652	259.695	151.018	29.423	153.708	−1.912
4300	41.353	296.623	260.542	155.148	28.535	156.677	−1.903
4400	41.450	297.575	261.373	159.288	27.834	159.641	−1.895
4500	41.546	298.508	262.188	163.438	26.830	162.648	−1.888
4600	41.643	299.422	262.988	167.598	25.740	165.678	−1.881
4700	41.739	300.319	263.772	171.767	24.581	168.731	−1.875
4800	41.835	301.198	264.543	175.945	23.441	171.797	−1.870
4900	41.930	302.062	265.300	180.134	22.107	174.901	−1.864
5000	42.026	302.910	266.044	184.331	20.683	178.034	−1.860
5100	42.121	303.743	266.775	188.539	19.166	181.196	−1.856
5200	42.217	304.562	267.494	192.756	17.557	184.389	−1.852
5300	42.312	305.367	268.201	196.982	15.855	187.613	−1.849
5400	42.407	306.159	268.896	201.218	14.061	190.870	−1.846
5500	42.502	306.938	269.581	205.464	12.177	194.162	−1.844
5600	42.597	307.705	270.255	209.718	10.202	197.488	−1.842
5700	42.692	308.459	270.918	213.983	8.484	200.803	−1.840
5800	42.787	309.203	271.572	218.257	6.379	204.196	−1.839
5900	42.881	309.935	272.216	222.540	4.195	207.625	−1.838
6000	42.976	310.656	272.851	226.833	1.933	211.092	−1.838

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

$S°(298.15\ K) = 78.907 \pm 0.84\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 516\ K$
$T_{fus} = 679\ K$

$\Delta_f H°(0\ K) = -421.22 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_f H(298.15\ K) = -424.72 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 6.443 \pm 0.63\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 8.619 \pm 0.63\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of KOH(cr) is obtained from its enthalpy of solution in water, the enthalpy of hydrolysis of metallic potassium, and appropriate auxiliary data.

Reshetnikov[1] determined calorimetrically the enthalpy of solution of KOH(cr) in 650 H_2O as $-13.665 \pm 0.009\ kcal \cdot mol^{-1}$. Combining this result with enthalpy of dilution data for KOH reported by Parker[2] we derive $\Delta_{sln} H°(KOH, cr) = -13.77 \pm 0.01\ kcal \cdot mol^{-1}$.

The enthalpy of hydrolysis of metallic potassium has been determined by various investigators.[3-5] The data are summarized below for the reaction $K(cr) + (n + 1)H_2O(l) \rightarrow KOH \cdot nH_2O + 0.5\ H_2(g)$.

Source	n moles of H_2O	$\Delta_r H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(KOH, aq, \infty, 298.15\ K)$* kcal·mol^{-1}	$\Delta_f H°(KOH, cr, 298.15\ K)$ kcal·mol^{-1}
Gunn and Green[3a,3b]	∞	−46.958 ± 0.22	−115.273 ± 0.22	−101.50 ± 0.02
Messer *et al.*[4]	∞	−47.02 ± 0.15	−115.34 ± 0.15	−101.57 ± 0.16
Ketchen and Wallace[5]	∞	−46.89 ± 0.24	−115.21 ± 0.24	−101.44 ± 0.25

*Based on $\Delta_f H$ (H_2O, l, 298.15 K) = −68.315 kcal·mol^{-1}.[6]

The values of $\Delta_f H°(KOH, cr, 298.15\ K)$ given in the last column are calculated from $\Delta_f H°(KOH, aq, \infty, 298.15\ K)$ and the enthalpy of solution of KOH(cr) at infinite dilution given above. The adopted value for $\Delta_f H°(KOH, cr, 298.15\ K)$ is from the work of Gunn and Green.[3a,3b]

Earlier investigations pertaining to the determination of $\Delta_f H°(KOH, cr, 298.15\ K)$ have been reviewed by Bichowsky and Rossini[7] and Messer *et al.*[4] and are only of historical interest.

Heat Capacity and Entropy

The low temperature heat capacities for KOH(cr) in the temperature range 20–298 K are from the recent work of Stull *et al.*.[8] These data contain a broad lambda type transition with a heat capacity peak at 227.5 K. Powers and Blalock[9] measured high temperature enthalpy data for KOH(cr) in both the α and β phases in a Bunsen ice calorimeter. Their enthalpy data are scattered and not precise enough to accurately define the heat capacities for the α phase. Therefore, the selected heat capacities between 298 and 516 K are estimated by graphical extrapolation of the low temperature heat capacity data. Heat capacities for the β phase are from Powers and Blalock.[9]

$S°(298.15\ K)$ is calculated from the smoothed $C_p°$ data and is based on an extrapolation of $S°(20\ K) = 0.199\ cal \cdot K^{-1} \cdot mol^{-1}$.

Transition and Fusion Data

Several values for the enthalpy of the α–β transition and the enthalpy of melting of KOH have been reported in the literature.

Source	Method	T_{trs}/K	$\Delta_{trs} H°$ kcal·mol^{-1}	T_{fus}/K	$\Delta_{fus} H°$ kcal·mol^{-1}
Powers and Blalock[9]	Calorimetric	522	1.346	673	2.244
Seward and Martin[10]	Freezing Point			683	1.830
Kelly[11]	Freezing Point			633	1.980
Reshetnikov and Baranskaya[12]	Thermographic	515	1.540 ± 0.5	679	1.980 ± 0.15
Maurice[13]	Freezing Point	517		678	2.13 ± 0.07

The selected values are from the work of Reshetnikov and Baranskaya[12] and Maurice.[13]

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ for the monomer and dimer are calculated from the selected enthalpies of vaporization and the enthalpy of melting at 298.15 K. See the ideal gas table for details.

References

[1]N. A. Reshetnikov, Zhur. Neorg. Khim. 6, 682 (1961).
[2]V. B. Parker, NSRDS–NBS 2, 1965.
[3]a) S. R. Gunn and L. G. Green, J. Amer. Chem. Soc. 80, 4782 (1958). b) S. R. Gunn, J. Phys. Chem. 71, 1386 (1967).
[4]C. E. Messer, L. C. Fasolino and C. O. Thalmayer, J. Amer. Chem. Soc. 77, 4524 (1955).

Continued on page 1358

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	−12.163	−421.223	−421.223	INFINITE
100	34.100	23.857	130.178	−10.632	−424.377	−409.500	213.901
200	53.932	53.620	84.784	−6.233	−425.375	−394.110	102.931
298.15	64.894	78.907	78.907	0.	−424.718	−378.899	66.382
300	65.011	79.309	78.909	0.120	−424.706	−378.615	65.923
400	71.672	98.894	81.534	6.944	−426.299	−362.909	47.391
500	79.580	115.714	86.721	14.496	−424.845	−347.213	36.273
516.000	80.961	118.242	87.660	15.780	ALPHA <--> BETA		
516.000	78.659	130.729	87.660	22.224	TRANSITION		
600	78.659	142.593	94.541	28.831	−416.594	−332.908	28.982
679.000	78.659	152.322	100.709	35.045	---- BETA <--> LIQUID ----		
700	78.659	154.718	102.294	36.697	−414.821	−319.100	23.812
800	78.659	165.221	109.518	44.563	−413.076	−305.545	19.950
900	78.659	174.486	116.232	52.429	−411.383	−292.206	16.959
1000	78.659	182.774	122.479	60.295	−409.763	−279.052	14.576
1100	78.659	190.271	128.306	68.161	−487.190	−261.446	12.415
1200	78.659	197.115	133.759	76.027	−484.716	−241.033	10.492
1300	78.659	203.411	138.878	83.893	−482.281	−220.825	8.873
1400	78.659	209.240	143.699	91.758	−479.883	−200.803	7.492
1500	78.659	214.667	148.251	99.624	−477.521	−180.952	6.301

PREVIOUS: March 1966 CURRENT: December 1970

$S°(298.15\ K) = [96.617]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 679\ K$

$\Delta_f H°(298.15\ K) = [-412.705]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 8\,619 \pm 0.63\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(KOH, l, 298 15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(679\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of the liquid phase is obtained from the high temperature enthalpy measurements of Powers and Blalock[1] The constant $C_p°$ is extrapolated below the melting point and up to 2000 K.

$S°(298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} = 1596 K for the process KOH(l) = KOH(g) is calculated as the temperature at which the fugacity of KOH(g) is 1 atm. The difference in the enthalpies of formation of KOH(l) and KOH(g) at T_{vap} is the enthalpy of vaporization. If $[KOH]_2$(g) is also considered a minor component in the vapor mixture (approximately 2% of the total vapor pressure at the boiling point) the calculated boiling point is unchanged.

Wartenberg and Albrecht[2] reported a boiling point of 1597 K for KOH from static vapor pressure measurements, while very recently Dubois and Millet[3] determined a boiling point of 1540 K from transpiration vapor pressure measurements.

References

[1]W.D Powers and G.C. Blalock, Oak Ridge Natl. Lab., ORNL 1653, (January 1954).
[2]H.von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 162 (1921).
[3]J. Dubois and J. Millet, Compt. Rend. 269, 1336 (1969).

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

	J·K⁻¹mol⁻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							
100							
200							
298 15	83.107	96.617	96.617	0.	−412.705	−372.166	65.202
300	83.107	97.131	96.618	0.154	−412.660	−371.915	64.756
400	83.107	121.039	99.878	8.464	−412.766	−358.234	46.781
500	83.107	139.584	106.034	16.775	−410.553	−344.856	36.027
600	83.107	154.736	112.926	25.086	−408.327	−331.926	28.897
679 000	83.107	165 016	118.401	31.651	---- BETA <--> LIQUID ----		
700	83.107	167.547	119.838	33.396	−406.108	−319.368	23.832
800	83.107	178.644	126.511	41.707	−403.919	−307.127	20.053
900	83.107	188.433	132.858	50 018	−401.781	−295.157	17.130
1000	83.107	197 189	138.861	58.328	−399.716	−283.421	14.804
1100	83.107	205.110	144.529	66.639	−476 698	−267.278	12.692
1200	83.107	212.341	149.883	74.950	−473.780	−248.368	10.811
1300	83.107	218.993	154 947	83.261	−470.900	−229 701	9.230
1400	83.107	225.152	159.744	91.571	−468.057	−211.254	7.882
1500	83.107	230.886	164.298	99.882	−465.250	−193.010	6.721
1600	83.107	236.250	168.629	108.193	−462.480	−174.951	5.712
1700	83.107	241.288	172.757	116.503	−459.744	−157.064	4.826
1800	83.107	246.038	176.697	124.814	−457.043	−139.338	4.043
1900	83.107	250.532	180.466	133.125	−454.378	−121.760	3.347
2000	83.107	254.794	184.077	141.435	−451.748	−104.322	2.725

PREVIOUS March 1966 CURRENT December 1970

0	to	516	K	crystal, alpha
516	to	679	K	crystal, beta
above		679	K	liquid

Refer to the individual tables for details.

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

	J·K⁻¹mol⁻¹			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	−12.163	−421.223	−421.223	INFINITE
100	34.100	23.857	130.178	−10.632	−424.377	−409.500	213.901
200	53.932	53.620	84.784	−6.233	−425.375	−394.110	102.931
298.15	64.894	78.907	78.907	0.	−424.718	−378.899	66.382
300	65.011	79.309	78.909	0.120	−424.706	−378.615	65.923
400	71.672	98.894	81.534	6.944	−426.299	−362.909	47.391
500	79.580	115.714	86.721	14.496	−424.845	−347.213	36.273
516.000	80.961	118.242	87.660	15.780	ALPHA <--> BETA		
516.000	78.659	130.729	87.660	22.224	TRANSITION		
600	78.659	142.593	94.541	28.831	−416.594	−332.908	28.982
679.000	78.659	152.322	100.709	35.045	BETA <--> LIQUID		
679.000	83.107	165.016	100.709	43.664	TRANSITION		
700	83.107	167.547	102.676	45.409	−406.108	−319.368	23.832
800	83.107	178.644	111.494	53.720	−403.919	−307.127	20.053
900	83.107	188.433	119.510	62.031	−401.781	−295.157	17.130
1000	83.107	197.189	126.848	70.342	−399.716	−283.421	14.804
1100	83.107	205.110	133.608	78.652	−476.698	−267.278	12.692
1200	83.107	212.341	139.872	86.963	−473.780	−248.369	10.811
1300	83.107	218.993	145.706	95.274	−470.900	−229.701	9.230
1400	83.107	225.152	151.164	103.584	−468.057	−211.254	7.882
1500	83.107	230.886	156.289	111.895	−465.251	−193.010	6.721
1600	83 107	236.250	161.121	120.206	−462.480	−174.951	5.712
1700	83.107	241.288	165.690	128.516	−459.744	−157.064	4.826
1800	83.107	246.038	170.023	136.827	−457.043	−139.338	4.043
1900	83.107	250.532	174.143	145.138	−454.378	−121.760	3.347
2000	83 107	254.794	178.070	153.448	−451.748	−104.322	2.725

PREVIOUS CURRENT: December 1970

$S°(298.15\ K) = [236.379 \pm 1.3]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -228.40 \pm 12.6\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -232.63 \pm 12.6\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
408 (1)
[340] (2)
[3610] (1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: $C_{\infty v}$
Bond Distances: K–O = 2.18 ± 0.01 Å O–H = [0.97 ± 0.05] Å
Bond Angle: K–O–H = 180°
Rotational Constant. $B_0 = 0.279902\ cm^{-1}$

Enthalpy of Formation

Mass spectrometric studies[1-5] of the equilibrium gases over pure KOH(cr, l) and mixed KOH–NaOH condensed phases have unequivocally identified the vapor species as monomer and dimer in the temperature range 600–700 K Absolute partial pressures for KOH(g) and $K_2(OH)_2$ (g) have been determined from peak intensity data by Porter and Schoonmaker[3] and Gusarov and Gorokhov.[5] These data are analyzed by the 3rd law method with JANAF Gibbs energy functions[6] in order to evaluate an enthalpy of dimerization at 298 K The adopted value is $\Delta_f H°(298.15\ K) = -45.3 \pm 3\ 0$ kcal mol^{-1} for the reaction 2 KOH(g) = $K_2(OH)_2$ (g).

Vapor pressures for liquid KOH have been determined by static (1443–1600 K)[7] and transpiration (873–1323 K)[8] methods. In order to evaluate $\Delta_{vap}H°$(KOH, l, 298.15 K) we have used a trial and error variation of $\Delta_{vap}H°$(298 15 K) for the monomer and dimer, such that these values are in accordance with the adopted enthalpy of dimerization given above, and the sum of the calculated partial pressures for KOH(g) and $[KOH]_2$(g) is in good agreement with the experimental vapor pressure data. Since the dimer to monomer ratio decreases with increasing temperature, more weight is given to the static data of Wartenberg and Albrecht.[7] The selected values are $\Delta_{vap}H°$(to monomer, 298.15 K) = 43.0 ± 3.0 kcal·mol^{-1} and $\Delta_{vap}H°$(to dimer, 298.15 K) = 40 8 ± 3.0 kcal·mol^{-1} From these results we derive $\Delta_f H°$(KOH, g, 298.15 K) = −55.6 ± 3.0 kcal·mol^{-1} with $\Delta_f H°$(KOH, l, 298.15 K) = −98.64 ± 0.50 kcal mol^{-1} [6] This value is adopted here and when used in combination with the enthalpy of dimerization results in $\Delta_f H°[KOH]_2$, g, 298.15 K) = −156 5 ± 3.0 kcal·mol^{-1}.

The bond dissociation energies of the alkali metal hydroxides have been determined by several workers from flame studies[9-11] and by mass spectrometry.[12] The data for KOH are summarized below.

Source	Method	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 3rd law	$D_0°$(K–OH) kcal·mol^{-1}
Smith and Sugden[9]	Flame	86 ± 1	
Jensen and Padley[10]	Flame	36.4	82 ± 2
Cotton and Jenkins[11]	Flame	32.5	86 ± 2
Gorokhov *et al.*[12]	Mass Spec.	80 ± 3	
	Reaction. K(g) + H_2O(g) = KOH(g) + H(g)		

Our adopted enthalpy of formation for KOH(g) leads to $D_0°$ = 85.4 ± 3.0 kcal mol^{-1}, which is in reasonable agreement with the results of the flame studies,[9-11] particularly when one considers the difficulties inherent in this method.

Heat Capacity and Entropy

Kuczkowski *et al.*[13] observed the microwave spectra of gaseous KOH and interpreted the results in terms of a linear geometry. Very recently, microwave studies of gaseous CsOH[14a] and RbOH,[14b] along with infrared spectra of matrix-isolated CsOH,[15a] RbOH[15b] and NaOH[15b] have been reported and interpreted in terms of linear structures for all these molecules. We adopt a linear configuration for KOH(g), along with the bond distances determined by Kuczkowski *et al.*[13] from their microwave studies.

Acquista and Abramowitz[15b] attempted to measure the infrared spectrum of matrix-isolated monomeric KOH but observed bands which could only be ascribable to polymeric species. Spinar and Margrave[16] investigated the infrared spectrum of the equilibrium gases over liquid KOH at temperatures up to 1000 K. An absorption band at 408 ± 10 cm^{-1} was assigned to the K–OH stretching by these workers, and this assignment is adopted here. The doubly degenerate bending and O–H stretching frequencies are estimates taken from the recent work of Jensen.[17]

Continued on page 1358

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	−11.423	−228.396	−228.396	INFINITE
100	32.946	191.442	275.830	−8.439	−230.096	−231.978	121.173
200	43.677	217.899	240.692	−4.559	−231.613	−233.204	60.907
250	46.658	227.990	237 169	−2.295	−232.150	−233.538	48.795
298.15	48.531	236.379	236.379	0.	−232.630	−233.762	40.954
300	48.589	236.679	236.380	0.090	−232.649	−233 769	40.703
350	49.880	244.273	236.977	2.554	−235.539	−233.819	34.896
400	50.776	250.995	238.317	5.071	−236.084	−233.535	30.497
450	51.424	257.015	240.066	7.627	−236.581	−233 186	27.068
500	51.913	262.460	242.037	10.211	−237.043	−232.784	24.319
600	52.628	271.992	246.258	15.440	−237.898	−231.850	20.184
700	53.187	280.147	250.531	20.732	−238.699	−230 779	17.221
800	53.704	287.283	254.688	26.076	−239 476	−229.594	14.991
900	54.220	293.638	258.669	31.473	−240.252	−228.312	13.251
1000	54 740	299.378	262.457	36.920	−241.050	−226.943	11.854
1100	55.257	304.620	266.056	42.420	−320.843	−220.882	10.489
1200	55.761	309.449	269.473	47.971	−320.684	−211.802	9.220
1300	56.244	313.932	272.723	53.572	−320.514	−202.735	8.146
1400	56.698	318.117	275.817	59.219	−320.335	−193.682	7.226
1500	57.122	322.043	278.769	64 911	−320 147	−184.642	6.430
1600	57.514	325.742	281.591	70.643	−319.955	−175.615	5.733
1700	57 874	329.240	284.292	76.412	−319.761	−166.599	5.119
1800	58.204	332.558	286.882	82.216	−319.567	−157.596	4.573
1900	58.504	335.713	289.369	88.052	−319.376	−148.603	4.085
2000	58.779	338.721	291 762	93.916	−319.192	−139.619	3.646
2100	59.028	341.595	294.067	99.807	−319.018	−130.645	3.250
2200	59 256	344.346	296.291	105.721	−318.858	−121.678	2.889
2300	59 464	346.985	298.438	111.657	−318.714	−112.719	2.560
2400	59.653	349.519	300.514	117.613	−318.591	−103.766	2.258
2500	59.826	351.958	302.523	123.588	−318.491	−94.817	1.981
2600	59.984	354.308	304.470	129.578	−318.418	−85.871	1.725
2700	60.129	356.574	306.358	135.584	−318.375	−76.928	1 488
2800	60.262	358 763	308.191	141.603	−318.366	−67.986	1.268
2900	60.383	360.880	309.971	147.636	−318.395	−59.043	1.063
3000	60.496	362.929	311.703	153.680	−318.465	−50 099	0.872
3100	60.599	364.915	313.387	159.735	−318.579	−41 151	0.693
3200	60.695	366.840	315.028	165.799	−318.743	−32.200	0.526
3300	60.783	368.709	316.626	171.873	−318.950	−23.243	0.368
3400	60.864	370.525	318.185	177.956	−319.220	−14.278	0.219
3500	60.940	372.290	319 706	184.046	−319.546	−5.305	0.079
3600	61.010	374.008	321.190	190.144	−319.939	3.679	−0.053
3700	61.076	375.681	322.641	196.248	−320.401	12.674	−0.179
3800	61 137	377.310	324.058	202.359	−320.935	21.684	−0.298
3900	61 193	378.899	325.444	208.475	−321.548	30.708	−0.411
4000	61.246	380.449	326.800	214.597	−322.237	39.748	−0.519
4100	61.296	381.962	328.127	220.724	−323.014	48.807	−0.622
4200	61.342	383.440	329.426	226.856	−323.886	57.886	−0.720
4300	61.386	384.883	330.699	232.993	−324.855	66.987	−0.814
4400	61.427	386.295	331.947	239.133	−325.648	76.084	−0.903
4500	61.465	387.676	333.170	245.278	−326.756	85.227	−0.989
4600	61.501	389.027	334.369	251.426	−327 963	94 395	−1.072
4700	61.535	390.350	335.547	257.578	−329.250	103.588	−1.151
4800	61.567	391.646	336.702	263.733	−330.531	112.799	−1.227
4900	61.598	392.916	337.836	269.892	−332.019	122.050	−1.301
5000	61.626	394 161	338.950	276.053	−333.611	131.333	−1.372
5100	61.653	395.381	340.045	282.217	−335.308	140.648	−1.441
5200	61.679	396.579	341.121	288.383	−337.111	149.998	−1.507
5300	61.703	397.754	342.178	294.553	−339.022	159.384	−1.571
5400	61 726	398.908	343.218	300.724	−341.039	168.806	−1.633
5500	61.748	400.040	344.241	306.898	−343.163	178.267	−1.693
5600	61.769	401.153	345.247	313.074	−345.392	187.768	−1.751
5700	61.788	402.247	346.238	319.251	−347.381	197.261	−1.808
5800	61.807	403.321	347.213	325 431	−349.774	206.838	−1.863
5900	61.825	404.378	348.173	331.613	−352.264	216.455	−1.916
6000	61.842	405.417	349 118	337.796	−354.849	226.116	−1.969

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

$S°(298.15\ K) = [250.331 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 495.60 \pm 41.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 497.896 \pm 41.8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Sigma^+$	[32000]	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[375](1)
[300](2)
[3600](1)

Point Group: $C_{\infty v}$ $\sigma = 1$
Bond Distance: K–O = [2.20] Å O–H = [1.03] Å
Bond Angle: K–O–H = [180]°
Rotational Constant: B_0 = [0.27367] cm^{-1}

Heat of Formation

Porter and Schoonmaker[1] obtained an appearance potential curve near threshold for KOH^+ which extrapolates to 7.8 eV at zero ion current. They presented evidence which indicated that a large fraction of KOH^+ was formed by dissociative ionization of the dimer. In a later study, these same workers[2] rejected their earlier results, since it was found that the presence of magnesia in their cell had reduced the activity of the hydroxide. Cusarov and Gorokhov[3] in a similar mass spectrometric study ofthe evaporation products of KOH have shown that KOH^+ is formed primarily from direct ionization of the hydroxide. Very recently, Gorokhov *et al.*[4] reported the appearance potential of KOH^+ from KOH as 7.5 ± 0.2 eV. We adopt this result as $\Delta_r H°$ for the process $e^- + KOH(g) \rightarrow KOH^+(g) + 2e^-$, since it is consistent with the expected mode of ionization. This value leads to $\Delta_f H°(KOH^+, g, 0\ K) = 118 \pm 10\ kcal \cdot mol^{-1}$ when used in conjunction with $\Delta_f H°(KOH, g, 0\ K) = -54.6 \pm 3.0\ kcal \cdot mol^{-1}$.[5]

Heat Capacity and Entropy

The configuration of KOH^+ is predicted to be linear by Walsh,[6] since it has seven valence electrons. The same correlation predicts that the unpaired electron is in a pi orbital, thus, the ground state of KOH^+ is $^2\Pi$. A first excited state is estimated at 32000 cm^{-1} to be $^2\Sigma$ by analogy with the isoelectronic molecules OH.[5] and SH[5] The vibrational frequencies are estimated from those for KOH with somewhat lower values to account for the effect of weaker bonding predicted for the positive ion. Similarly, the K–O and O–H bond distances are increased slightly over those for KOH.

References

[1]R. F. Porter and R. C. Schoonmaker, J. Phys. Chem. 62, 234 (1958).
[2]R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
[3]A. V. Gusarov and L. N. Gorokhov, Russ. J. Phys. Chem. 42, 449 (1968).
[4]L. N. Gorokhov, A. V. Gusarov, and I. G. Panchenkov, Russ. J. Phys. 44, 150 (1970).
[5]JANAF Thermochemical Tables: Chem. KOH(g), OH(g) 12–31–70; SH(g) 6–30–67.
[6]A. D. Walsh, J. Chem. Soc. 2288 (1953).

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	−11.760	495.596		
100	34.457	203.689	291.020	−8.733			
200	45.225	231.352	254.747	−4.679			
250	47.868	241.752	251.137	−2.346			
298.15	49.479	250.331	250.331	0.	497.896	486.350	−85.207
300	49.529	250.637	250.332	0.092	497.918	486.278	−84.669
350	50.620	258.359	250.939	2.597	496.108	484.390	−72.291
400	51.369	265.171	252.301	5.148	496.636	482.680	−63.032
450	51.908	271.254	254.075	7.731	497.205	480.902	−55.822
500	52.315	276.745	256.072	10.337	497.804	479.059	−50.047
600	52.917	286.339	260.339	15.600	499.062	475.192	−41.369
700	53.406	294.533	264.653	20.916	500.365	471.111	−35.155
800	53.877	301.696	268.845	26.280	501.686	466.842	−30.482
900	54.362	308.069	272.856	31.692	503.004	462.407	−26.837
1000	54.859	313.822	276.669	37.153	504.298	457.827	−23.914
1100	55.360	319.075	280.289	42.664	426.595	457.729	−21.736
1200	55.851	323.913	283.725	48.225	428.842	460.460	−20.043
1300	56.323	328.402	286.991	53.834	431.099	463.004	−18.604
1400	56.769	332.592	290.101	59.489	433.364	465.373	−17.363
1500	57.186	336.523	293.066	65.187	435.637	467.580	−16.283
1600	57.572	340.227	295.899	70.925	437.914	469.635	−15.332
1700	57.927	343.728	298.610	76.700	440.192	471.548	−14.489
1800	58.252	347.048	301.210	82.509	442.470	473.327	−13.736
1900	58.549	350.206	303.706	88.349	444.744	474.979	−13.058
2000	58.820	353.216	306.107	94.218	447.011	476.512	−12.445
2100	59.067	356.092	308.419	100.113	449.267	477.931	−11.888
2200	59.291	358.845	310.649	106.031	451.510	479.244	−11.379
2300	59.496	361.485	312.802	111.970	453.735	480.454	−10.911
2400	59.684	364.021	314.884	117.929	455.940	481.568	−10.481
2500	59.854	366.461	316.899	123.906	458.122	482.591	−10.083
2600	60.011	368.812	318.850	129.900	460.277	483.528	−9.714
2700	60.154	371.079	320.743	135.908	462.400	484.382	−9.371
2800	60.285	373.269	322.580	141.930	464.490	485.157	−9.051
2900	60.406	375.387	324.365	147.965	466.543	485.859	−8.751
3000	60.517	377.437	326.100	154.011	468.553	486.491	−8.471
3100	60.619	379.423	327.788	160.068	470.519	487.056	−8.207
3200	60.714	381.349	329.432	166.134	472.436	487.559	−7.959
3300	60.801	383.218	331.033	172.210	474.309	488.002	−7.724
3400	60.882	385.035	332.595	178.294	476.121	488.389	−7.503
3500	60.957	386.801	334.119	184.386	477.874	488.724	−7.294
3600	61.027	388.519	335.606	190.486	479.562	489.010	−7.095
3700	61.093	390.192	337.059	196.592	481.181	489.250	−6.907
3800	61.154	391.822	338.479	202.704	482.726	489.448	−6.728
3900	61.211	393.411	339.867	208.822	484.194	489.605	−6.558
4000	61.264	394.962	341.225	214.946	485.585	489.725	−6.395
4100	61.315	396.475	342.554	221.075	486.889	489.812	−6.240
4200	61.362	397.953	343.856	227.209	488.097	489.869	−6.092
4300	61.407	399.397	345.131	233.348	489.209	489.898	−5.951
4400	61.450	400.810	346.380	239.490	490.496	489.874	−5.816
4500	61.491	402.191	347.605	245.638	491.469	489.849	−5.686
4600	61.530	403.543	348.806	251.789	492.344	489.803	−5.562
4700	61.567	404.867	349.985	257.943	493.138	489.737	−5.443
4800	61.602	406.163	351.142	264.102	493.940	489.644	−5.328
4900	61.637	407.434	352.278	270.264	494.534	489.548	−5.219
5000	61.670	408.679	353.394	276.429	495.025	489.441	−5.113
5100	61.702	409.901	354.490	282.598	495.411	489.326	−5.012
5200	61.733	411.099	355.567	288.769	495.691	489.203	−4.914
5300	61.763	412.276	356.626	294.944	495.865	489.077	−4.820
5400	61.793	413.430	357.667	301.122	495.932	488.948	−4.730
5500	61.822	414.564	358.691	307.303	495.895	488.818	−4.642
5600	61.851	415.679	359.699	313.487	495.752	488.691	−4.558
5700	61.879	416.774	360.691	319.673	495.850	488.519	−4.477
5800	61.907	417.850	361.667	325.862	495.545	488.394	−4.398
5900	61.934	418.909	362.628	332.054	495.144	488.273	−4.323
6000	61.961	419.950	363.575	338.249	494 649	488.161	−4.250

PREVIOUS December 1971 (1 atm) CURRENT: December 1971 (1 bar)

$S°$(298 15 K) = 20.037 ± 0.13 J·K^{-1}·mol^{-1}
T_{fus} = 961.8 K

$\Delta_f H°$(0 K) = −85.548 ± 0.13 kJ mol^{-1}
$\Delta_f H°$(298.15 K) = −90.625 ± 0.13 kJ·mol^{-1}
$\Delta_{fus} H°$ = 22.594 ± 0.42 kJ·mol^{-1}

Enthalpy of Formation

The enthalpies of solution of Li(cr) and LiH(cr) in water have been measured by Guntz[1] and Moers[2] using an open Dewar flask calorimeter and by Messer[3] and Gunn[4] using closed bomb calorimetry Based on the reported values of the enthalpy changes ($\Delta_r H°$) for the reaction (A) Li(cr) + H_2O(l) = LiOH(aq) + 1/2 H_2(g), and (B) LiH(cr) + H_2O(l) = LiOH(aq) + H_2(g), the corresponding $\Delta_f H°$(298.15 K) for LiH(cr) are calculated. The results are presented in the table below.

The decomposition pressures of LiH(cr) have been determined by Hurd[5] at temperatures 782–926 K By use of the 2nd and 3rd law methods, the enthalpy changes for the decomposition reaction (C) LiH(cr) = Li(l) + 1/2 H_2(g) are evaluated as 21.87 ± 0.3 and 22.34 kcal·mol^{-1}, respectively. Based on the 3rd law $\Delta_r H°$(298.15 K) and $\Delta_f H°$(Li, l, 298.15 K) = 0 569 kcal mol^{-1}, we derive the value $\Delta_f H°$(LiH, cr, 298.15 K) = −21.77 ± 0.2 kcal·mol^{-1}, which is in good agreement with the values obtained by calorimetric method. Gunts[1] measured the decomposition pressure at 953 K for the same reaction. The 3rd law $\Delta_r H°$(298.15 K) and $\Delta_f H°$(LiH, cr, 298 15 K) are evaluated as 21.86 and 21 29 kcal·mol^{-1}, respectively.

Johnson[6] has determined the standard Gibbs energy of formation for LiH(cr) from emf measurements over the temperature range 675–885 K. The cell utilized an Armco iron flag over which H_2 was passed as the cathode and a molten Li anode LiCl, LiBr and LiI, each saturated with LiH were used as electrolytes. Using the reported emf values at different temperatures (47 data points) for reaction (C) we derive $\Delta_f H°$(298.15 K) = 21 81 kcal·mol^{-1} for LiH(cr).

The $\Delta_f H°$(LiH, cr, 298 15 K) value reported by Gunn[4] is adopted.

Source	$\Delta H°$(298.15 K), kcal·mol^{-1} Reaction A	Reaction B	Reaction C	Drift cal·K^{-1} mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Guntz[1]	−53.2	−31.6	–	–	21.6
	–	–	21.86	–	−21.29
Moers[2]	−52.7 ± 0.2	−31.1 ± 0.1	–	–	−21.6 ± 0.25
Messer[3]	−53.10 ± 0.11	−31.76 ± 0.10	–	–	−21.34 ± 0.15
Gunn[4]	−53.14 ± 0.02	−31 48 ± 0.02	–	–	−21.66 ± 0.03
Hurd[5]	–	–	22.34	0.5 ± 0.3	−21.77 ± 0.2
Johnson[6]	–	–	22.38	1 0 ± 0.2	−21.81 ± 0.15

Heat Capacity and Entropy

The low temperature heat capacities are obtained from the data of Kostyukov[7] 3.72–295.5 K. The $C_p°$ data reported by Gunther[8] are consistently lower than the adopted ones in the temperature range 74.0–90.5 K but considerably higher at 292.7 K The high temperature enthalpies have been determined by Fieldhouse[9] 413.2–914.3 K and Vogt[14] 878.15–953.15 K. The derived high temperature heat capacities are joined smoothly with the low temperature values and extrapolated smoothly above 953.15 K.

$S°$(298.15 K) is calculated based on the adopted low temperature heat capacities, using $S°$(7 K) = 0.0002 cal·K^{-1}·mol^{-1}.

Fusion Data

The value of T_{fus} has been reported as 953,[1] 961 ± 1,[10, 12] 959.6[11] and 961.8 ± 0.3.[13] The value reported by Messer[13] is adopted The heat of melting, $\Delta_{fus} H°$, has been determined as 5.095 ± 0.46[13] and 5.237 ± 0.040 kcal mol.[14] The first $\Delta_{fus} H°$ value was evaluated cryogenically from the lowering of melting point in the systems LiH–LiO_2O and LiH–CaH_2. The second value was derived from enthalpy data measured with copper block calorimeter. The adopted $\Delta_{fus} H°$ value is derived from the enthalpy data of Vogt[14] using the adopted heat capacities for LiH(cr) and LiH(l).

Sublimation Data

The value of $\Delta_{sub} H°$(298 15 K) is calculated as the difference between $\Delta_f H°$(298 15 K) for LiH(g) and LIH(cr).

References

[1]A. Guntz, Compt. Rend. 123, 694 (1896).
[2]K. Moers, Z. Anorg. Chem. 113, 179 (1920).
[3]C.E. Messer, L.G Fasolino and C.E. Thalmayer, J. Amer. Chem. Soc. 77, 4524 (1955).
[4]S.R. Gunn and L.G. Green, J. Amer. Chem. Soc. 80, 4782 (1958); UCRL 7992, Univ. of California, (July 29, 1964).
[5]C.B. Hurd and G.A. Moore, Jr., J. Amer. Chem. Soc. 57, 332 (1935).
[6]C.E. Johnson, R.R Heinrich and C E. Crouthamel, J. Phys. Chem. 70, 242 (1966).
[7]V.N. Kostryukov, Russ. J. Phys. Chem. 35, 865 (1961).
[8]P. Gunther, Ann. Physik 63, 476 (1920).

Continued on page 1358

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

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0	0.	INFINITE	−3.778	−85.548	−85.548	INFINITE
100	6.381	2.322	38.346	−3.602	−87.367	−81.828	42.743
200	18.778	10.715	22.326	−2.322	−89.275	−75.511	19.722
298.15	27.957	20.037	20.037	0	−90.625	−68.447	11.992
300	28.083	20.210	20.038	0.052	−90.646	−68.309	11.894
400	34.794	29.236	21.223	3.205	−91.546	−60.718	7.929
500	40.735	37.646	23.676	6.985	−95 160	−52 628	5.498
600	46.380	45.575	26.671	11.342	−95.251	−44 103	3.839
700	51.877	53.138	29.915	16.256	−94.731	−35.611	2.657
800	57.300	60.420	33.276	21.715	−93.644	−27.233	1.778
900	62.676	67.480	36.686	27.715	−92.024	−19.023	1.104
961.800	65.985	71.751	38.802	31 690	--- CRYSTAL <--> LIQUID ---		
1000	68.028	74.361	40.111	34.250	−89.876	−11.022	0.576
1100	73.362	81.095	43.531	41.320	−87.207	−3.261	0.155
1200	78.680	87.706	46.938	48.922	−84.020	4.233	−0.184
1300	83.994	94.214	50.325	57.056	−80.319	11.441	−0.460
1400	89.299	100.633	53.690	65.720	−76.103	18.345	−0.684
1500	94.600	106.974	57.031	74.915	−71.369	24.929	−0.868

PREVIOUS September 1962 CURRENT· September 1967

$S°(298.15\ K) = [22.227]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 961.8 \pm 0.3\ K$
$T_d = 1223\ K$

$\Delta_f H°(298.15\ K) = -[77.714]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 22.594 \pm 0.42\ kJ·mol^{-1}$

Heat of Formation

$\Delta_f H°(l, 298.15\ K)$ is obtained from $\Delta_f H°(cr, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference between $H°(961.8;298.15)$ for crystal and liquid.

The decomposition pressures of LiH(l) at different temperatures have been investigated by Hill,[1] Perlow,[2] Johnson, and Gibb[4] Based on their reported equilibrium pressures, the enthalpy changes for the reaction LiH(l) = Li(l) + 1/2H_2(g) are evaluated by the second and third law methods. The results are presented in the table below It should be noted that the measured decomposition pressures are highly sensitive to composition and change extremely rapidly between 99 and 100 percent purity. Therefore we give no weight to the equilibrium data.

Source	T/K	Data Points	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15K)$** kcal·mol^{-1}
Hill (1938)	973.2	1	–	16.93	–	−16.36
Perlow (1941)	1043–1098	2	20.10	17.69	−2.2	−17.12
Johnson*	1050–1090	–	24.69	18.36	−5.9	−17.79
Gibb (1951)	1073–1173	2	5.66	15.2	+8.5	−14.63

*The vapor pressure values are calculated from an equation quoted by Gibb[3] but derived from the vapor pressures measured by W.C. Johnson, University of Chicago.
**Based on the third law $\Delta_f H°(298.15\ K)$.

Heat Capacity and Entropy

The enthalpies of LiH(l) in the temperature range 975.15–1075.15 K have been measured by Vogt.[5] Using the reported enthalpy values, the heat capacity of LiH(l) is derived as 14.9 cal·K^{-1}·mol^{-1}. This $C_p°$ value is adopted and extrapolated above and below the measured range. $S°(298.15\ K)$ is obtained in a manner analogous to that of the enthalpy of formation.

Melting Data

Refer to crystal table for details.

Decomposition Data

T_{dcm} = 1223 K is calculated as the temperature at which LiH(l) decomposes into Li(l) and H_2(g) where the fugacity of H_2(g) equals one atmosphere.

References

[1]L. L. Hill, Ph. D. Thesis, University of Chicago, (1938).
[2]M. R. J. Perlow, Ph. D. Thesis, University of Chicago, (1941).
[3]T. R. P. Gibb, J. Electrochem. Soc. 93, 198 (1948).
[4]T. R. P. Gibb, NEPA 1841, (April 30, 1951).
[5]J. W. Vogt, Thompson Ramo Wooldridge Inc., Cleveland, Ohio, NASA N63 22167, (June 1962).

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

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	62.342	22.227	22.227	0.	−77.714	−56.189	9.844
300	62.342	22.613	22.228	0.115	−77.671	−56.055	9.760
400	62.342	40.547	24.673	6.349	−75.491	−49 187	6.423
500	62.342	54.458	29.291	12.584	−76.651	−42.525	4.443
600	62.342	65.825	34.462	18.818	−74.865	−35.866	3.122
700	62.342	75.435	39.646	25.052	−73.024	−29.511	2.202
800	62.342	83 759	44.651	31.286	−71.163	−23.422	1.529
900	62.342	91.102	49.413	37.520	−69.307	−17.566	1 020
961.800	62.342	95.242	52.226	41.373	--- CRYSTAL <--> LIQUID ---		
1000	62.342	97.670	53.916	43.754	−67.461	−11.916	0.622
1100	62.342	103.612	58.168	49.989	−65.627	−6.451	0.306
1200	62.342	109.036	62.184	56.223	−63.808	−1.151	0.050
1300	62.342	114.026	65.983	62.457	−62.007	3.997	−0.161
1400	62.342	118.646	69.581	68.691	−60.221	9.007	−0.336
1500	62.342	122.948	72.997	74.925	−58.448	13.890	−0.484
1600	62.342	126.971	76.246	81.159	−56.689	18.655	−0.609
1700	62.342	130.750	79.342	87.394	−200.179	30.487	−0.937
1800	62.342	134.314	82.298	93.628	−197.692	43.983	−1.276
1900	62.342	137.684	85.126	99.862	−195.226	57.342	−1.576
2000	62.342	140.882	87.834	106.096	−192.781	70.572	−1.843

PREVIOUS: September 1962 CURRENT: September 1967

0 to 961.8 K crystal
above 961 8 K liquid

Refer to the individual tables for details.

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

	J·K⁻¹mol⁻¹			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	−3.778	−85.548	−85.548	INFINITE
100	6.381	2.322	38.346	−3.602	−87.367	−81.828	42.743
200	18.778	10.715	22.326	−2.322	−89.275	−75.511	19.722
298.15	27.957	20.037	20.037	0.	−90.625	−68.447	11.992
300	28.083	20.210	20.038	0.052	−90.646	−68.309	11.894
400	34.794	29.236	21.223	3.205	−91.546	−60.718	7.929
500	40.735	37.646	23.676	6.985	−95.160	−52.628	5.498
600	46.380	45.575	26.671	11.342	−95.251	−44.103	3.839
700	51.877	53.138	29.915	16.256	−94.731	−35.611	2.657
800	57.300	60.420	33.276	21.715	−93.644	−27.233	1.778
900	62.676	67.480	36.686	27.715	−92.024	−19.023	1.104
961.800	65.985	71.751	38.802	31.690	CRYSTAL <---> LIQUID TRANSITION		
961.800	62.342	95.242	38.802	54.284			
1000	62.342	97.670	41.005	56.665	−67.461	−11.916	0.622
1100	62.342	103.612	46.431	62.900	−65.627	−6.451	0.306
1200	62.342	109.036	51.425	69.134	−63.808	−1.151	0.050
1300	62.342	114.026	56.051	75.368	−62.007	3.997	−0.161
1400	62.342	118.646	60.359	81.602	−60.221	9.007	−0.336
1500	62.342	122.948	64.390	87.836	−58 448	13.890	−0.484
1600	62.342	126.971	68.177	94.070	−56.689	18.655	−0.609
1700	62.342	130.750	71.748	100.305	−200.179	30.487	−0.937
1800	62.342	134.314	75.126	106.539	−197.692	43.983	−1.276
1900	62.342	137.684	78.330	112.773	−195.226	57.342	−1.576
2000	62.342	140.882	81.379	119.007	−192 781	70.572	−1.843

PREVIOUS: CURRENT September 1967

$S°(298.15\ K) = 170.909\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 140.794 \pm 0.04\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 140.624 \pm 0.04\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1
	26513.7	1
	34912.0	2

$\omega_e = 1406.73\ cm^{-1}$ $\omega_e x_e = 23.24\ cm^{-1}$ $\sigma = 1$
$B_e = 7.5247\ cm^{-1}$ $\alpha_e = 0.2137\ cm^{-1}$ $r_e = 1.595$ Å

Enthalpy of Formation

Velasco,[1] observed the absorption spectra of LiH(g) in the near ultraviolet with high dispersion and absorbing path lengths up to 16 meters. He found a new band system involving the ground state and a $^1\Pi$ excited state. Rotational and vibrational analyses of this system were carried out and the observed breaking off of the rotational structure of the bands was interpreted as due to predissociation by rotation. With this assumption very accurate dissociation limits of the $B^1\Pi$ state were obtained. From these dissociation limits the dissociation energy ($D°$) of the ground state of LiH was found to be 2.4288 ± 0.0002 eV. Based on this $D°$ value, we adopt $\Delta_f H°(2981.5\ K) = 33.61\ kcal·mol^{-1}$ for LiH(g)

Kemperer,[2] observed the infrared spectrum of LiH(g) in emission in the frequency region 1500 to 970 cm^{-1}, using a Perkin–Elmer double-pass monochromator with NaCl optics. Estimating the minimum LiH pressure as 10 mm and assuming the maximum possible Li pressure, he reported K = 0.005 (atm) at 1400 K for the reaction $2Li(g) + H_2(g) = 2LiH(g)$. We calculate the corresponding enthalpy change, $\Delta_r H°(1400\ K)$, to be −9.63 kcal·mol^{-1}, employing $\Delta_r S°(1400\ K) = -17.407\ cal·K^{-1}·mol^{-1}$. Incorporating this $\Delta_r H°(1400\ K)$ value with $\Delta_f H°(1400\ K) = 35.601\ kcal·mol^{-1}$ for Li(g), we obtain $\Delta_f H°(298\ 15\ K) \leq 33.92\ kcal·mol^{-1}$ for LiH(g), which is in good agreement with the adopted value.

Gaydon,[3] derived the value $D°(LiH) = 2.5 \pm 0.2$ eV from earlier spectroscopic data.

Heat Capacity and Entropy

The third electronic level and quantum weight are obtained from Velasco.[1] All the other constants are taken fro Herzberg,[4] and corrected to the average isotopic species.

References

[1]R. Velasco, Can. J. Phys. 35, 1204 (1957).
[2]W. Kemperer, J. Chem. Phys. 23, 2452 (1955).
[3]A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, (1953).
[4]G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York (1950).

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	−8.686	140.794	140.794	INFINITE
100	29.139	138.955	196.998	−5.804	141.681	133.556	−69.763
200	29.220	159.168	173.607	−2.888	141.409	125.482	−32.773
250	29.401	165.705	171.396	−1.423	141.048	121.540	−25.394
298.15	29.731	170.909	170.909	0.	140.624	117.820	−20.642
300	29.746	171.093	170.910	0.055	140.607	117.679	−20.490
350	30.235	175.714	171.273	1.554	140.119	113.896	−16.998
400	30.811	179.788	172.088	3.080	139.578	110.186	−14.389
450	31.422	183.452	173.150	4.636	138.981	106.547	−12.368
500	32.029	186.794	174.350	6.222	135.326	103.285	−10.790
600	33.144	192.735	176.931	9.482	134.138	96.991	−8.444
700	34.081	197.917	179.567	12.845	133.107	90.883	−6.782
800	34.848	202.519	182.154	16.293	132.182	84.915	−5.544
900	35.472	206.661	184.650	19.810	131.321	79.059	−4.588
1000	35.986	210.426	187.043	23.383	130.507	73.296	−3.829
1100	36.414	213.876	189.327	27.004	129.727	67.613	−3.211
1200	36.776	217.061	191.507	30.664	128.972	62.000	−2.699
1300	37.088	220.017	193.588	34.358	128.233	56.449	−2.268
1400	37.359	222.776	195.576	38.080	127.507	50.954	−1.901
1500	37.600	225.362	197.476	41.828	126.794	45.511	−1.585
1600	37.816	227.795	199.296	45.599	126.090	40.115	−1.310
1700	38.013	230.094	201.040	49.391	−19.843	41.939	−1.289
1800	38.193	232.272	202.715	53.201	−19.780	45.571	−1.322
1900	38.361	234.341	204.326	57.029	−19.720	49.200	−1.353
2000	38.517	236.313	205.876	60.873	−19.665	52.826	−1.380
2100	38.665	238.196	207.371	64.732	−19.615	56.450	−1.404
2200	38.806	239.998	208.813	68.606	−19.571	60.071	−1.426
2300	38.940	241.726	210.207	72.493	−19.534	63.690	−1 446
2400	39.069	243.386	211.555	76.394	−19.506	67.308	−1.465
2500	39.193	244.983	212.860	80.307	−19.486	70 925	−1.482
2600	39.314	246.523	214.126	84.232	−19.478	74.541	−1.498
2700	39.432	248.009	215.353	88.170	−19.481	78.157	−1.512
2800	39.546	249.445	216.545	92.119	−19.498	81.773	−1.526
2900	39.659	250.835	217.704	96.079	−19.530	85.391	−1.538
3000	39.770	252.181	218.831	100.050	−19.578	89.010	−1.550
3100	39.879	253.487	219.928	104.033	−19.644	92.630	−1.561
3200	39.988	254.755	220.996	108.026	−19.729	96.253	−1.571
3300	40.095	255.987	222.038	112.030	−19.835	99.879	−1.581
3400	40.202	257.185	223.054	116.045	−19.963	103.509	−1.590
3500	40.308	258.352	224.046	120.071	−20.114	107.142	−1.599
3600	40.415	259.489	225.015	124.107	−20.290	110.781	−1.607
3700	40.522	260.598	225.962	128.154	−20.492	114.424	−1.615
3800	40.630	261.680	226.888	132.211	−20.722	118.074	−1.623
3900	40.738	262.737	227.793	136.280	−20.980	121 730	−1.630
4000	40.847	263.770	228.680	140.359	−21.268	125.392	−1.637
4100	40.958	264.780	229.548	144.449	−21.587	129.063	−1.644
4200	41.070	265.768	230.399	148.550	−21.939	132.741	−1.651
4300	41.183	266.736	231.233	152.663	−22.324	136.429	−1.657
4400	41.299	267.684	232.050	156.787	−22.723	140.124	−1.663
4500	41.416	268.613	232.852	160.923	−23.169	143.830	−1.670
4600	41.536	269.525	233.640	165.070	−23.653	147.546	−1.675
4700	41.658	270.419	234.413	169.230	−24.173	151.273	−1.681
4800	41.782	271.298	235.172	173.402	−24.732	155.012	−1.687
4900	41.909	272.160	235.918	177.586	−25.329	158.763	−1.692
5000	42.039	273.008	236.652	181.784	−25.965	162.526	−1.698
5100	42.171	273.842	237.373	185.994	−26.637	166.302	−1.703
5200	42.306	274.662	238.082	190.218	−27.354	170.092	−1.709
5300	42.445	275.469	238.780	194.456	−28.114	173.896	−1.714
5400	42.586	276.264	239.467	198.707	−28.918	177 715	−1.719
5500	42.731	277.047	240.143	202.973	−29.766	181.549	−1.724
5600	42.878	277.818	240.809	207.253	−30.659	185.400	−1.729
5700	43.029	278.578	241.465	211.549	−31.598	189.266	−1.734
5800	43.182	279.328	242.111	215.859	−32.584	193.150	−1.740
5900	43.339	280 068	242.748	220.185	−33.618	197.050	−1.745
6000	43.499	280.797	243.376	224.527	−34.700	200.969	−1.750

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

$S°(298.15\ K) = 42.821 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -479.14 \pm 0.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -484.93 \pm 0.4\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of crystalline LiOH is determined from calorimetric studies on the enthalpy of hydrolysis of metallic lithium and the enthalpy of solution of the hydroxide in water.

Reshetnikov[1] determined the enthalpy of solution of LiOH(cr) in (aq, 400 H_2O) as -5.479 ± 0.007 kcal·mol^{-1} Combining this result with enthalpy of dilution data for LiOH tabulated by Parker[2] we derive $\Delta_{sol}H°$(LiOH, cr) = $-5\,632 \pm 0.020$ kcal·mol^{-1}, which is essentially the value recommended by Parker.[2] Lower values by some 600–650 cal·K^{-1}·mol^{-1} for the enthalpy of solution of LiOH(cr) are summarized by Parker[2] The discrepancy in these values probably arises from carbonate and water impurities in the LiOH samples Since their presence would tend to reduce the enthalpy of solution, we adopt the higher results of Reshetnikov.[1]

Gunn and Green[3a,3b] and Messer *et al.*[4] measured the enthalpy of hydrolysis of metallic lithium. Their results for the reaction Li(cr) + (n+1) $H_2O \rightarrow$ LiOHn H_2O + 0.5 H_2(g) are summarized below.

Source	Moles of H_2O	$\Delta_{hyd}H°(298.15\ K)$* kcal·mol^{-1}	$\Delta_f H°$(LiOH, aq, ∞, 298.15 K)** kcal·mol^{-1}	$\Delta_f H°$(298.15K) kcal·mol^{-1}
Gunn and Green[3a, 3b]	1000	-53.210 ± 0.040	-121.525 ± 0.040	-115.893 ± 0.060
Messer *et al.*[4]	70	-53.05 ± 0.20	-121.37 ± 0.20	-115.74 ± 0.20

*Dilution data from Parker[2]
*Based on $\Delta_f H°(H_2O, l, 298.15\ K) = -68.315$ kcal·mol^{-1} [5]

Combination of the $\Delta_f H°$(LiOH, aq, ∞, 298 15 K) values with the enthalpy of solution of LiOH(cr) given above results in the values for $\Delta_f H°$(LiOH, cr, 298.15 K) given in the last column. The adopted value is from the work of Gunn and Green[3a,3b] with minor adjustments in the uncertainty interval to include possible errors in some of the auxiliary data used in the calculations.

Heat Capacity and Entropy

Heat capacities for LiOH(cr) in the temperature range 15–300 K are those of Bauer *et al.*[6] Heat capacities above 300 K are calculated from the high temperature (418–879 K) enthalpy data of Shomate and Cohen.[7] Both sets of data were smoothed by computer and joined at 298.15 K. The rapid rise in the enthalpy data of Shomate and Cohen[7] near the melting point is attributed to premelting and data in the temperature range 725–732 K were not used in the fit. Powers and Blalock[8] also measured high temperature (397–1213 K) enthalpy data for LiOH(cr) in a Bunsen ice calorimeter. Although their results are less precise than those of Shomate and Cohen[7] the two sets of measurements are in reasonable agreement.

$S°(298.15\ K)$ is determined from the smoothed $C_p°$ data of Bauer *et al.*[6] and is based on an extrapolation of $S°(16\ K) = 0.027$ cal·K^{-1}·mol^{-1}.

Transition and Fusion Data

The adopted enthalpy of melting and melting point for LiOH are from the enthalpy measurements of Shomate and Cohen.[7] Powers and Blalock[8] reported $\Delta_{fus}H° = 5.029$ kcal·mol^{-1} at 746 K from their enthalpy measurements on LiOH. Very recently, Reshetnikov and Baranskaya[9] reported a slightly higher value of 5.29 kcal·mol^{-1} at 747 K which was determined by a thermographic method.

Sublimation Data

$\Delta_{sub}H°(298.15\ K)$ values for the monomer and dimer are calculated from the adopted enthalpies of formation for the gaseous species and the crystal.

References

[1]N. A. Reshetnikov, Zhur Neorg. Khim. 6, 682 (1961).
[2]V. B. Parker, NSRDS–NBS 2, (1965).
[3a]S. R. Gunn and L. G. Green, J Amer. Chem. Soc. 80, 4782 (1958).
[b]S. R. Gunn, J. Phys. Chem. 71, 1386 (1967).
[4]C. E. Messer, L. C. Fasolino, and C. E. Thalmayer, J. Amer. Chem. Soc. 77, 4524 (1955).
[5]U. S. Nat. Bur Stand. Tech. Note 270–3, (1968).
[6]T. W. Bauer, H. L. Johnston, and E. C. Kerr, J. Amer. Chem. Soc. 72, 5174 (1950).
[7]C. H Shomate and A. J. Cohen, J. Amer. Chem. Soc. 77, 285 (1955).
[8]W. D. Powers and G. C. Blalock, Oak Ridge Natl. Lab., ORNL 1653, (January 1954).
[9]N. A. Reshetnikov and E. V. Baranskaya, Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 10, 496 (1967).

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	−7.416	−479 144	−479 144	INFINITE
100	14.644	8.561	77.138	−6.858	−482.033	−468.453	244.695
200	35.977	25.632	46.982	−4.270	−484.089	−453.960	118.562
298.15	49.591	42.821	42.821	0.	−484.926	−438.958	76.904
300	49.761	43 128	42.822	0.092	−484.933	−438.672	76.380
400	58.053	58.678	44.886	5.517	−485.047	−423.222	55.267
500	63.647	72.260	49.032	11.614	−487.874	−407.475	42.569
600	68.208	84.277	53.924	18.212	−487.303	−391.441	34.078
700	72.279	95.101	59.045	25.239	−486.298	−375.538	28.023
744.300	73.970	99.588	61.326	28.479	--- CRYSTAL <--> LIQUID ---		
800	76.086	105.002	64.180	32.658	−484.920	−359.805	23.493
900	79.747	114.176	69.231	40 450	−483.208	−344.265	19.981
1000	83.308	122.763	74.159	48.604	−481.174	−328.933	17.182
1100	86.814	130.868	78.950	57.110	−478.823	−313 820	14.902
1200	90.274	138.570	83.600	65.965	−476.158	−298 935	13.012
1300	93.705	145.932	88.113	75.164	−473.183	−284.285	11.423
1400	97.115	153.001	92.497	84.705	−469.897	−269.876	10.069
1500	100.508	159.817	96.759	94.586	−466.298	−255.713	8.905

PREVIOUS March 1966 CURRENT June 1971

$S°(298.15\ K) = [47.969]\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{fus} = 744.3\ K$

$\Delta_f H°(298.15\ K) = [-474.422]\ kJ\cdot mol^{-1}$
$\Delta_{fus}H° = 20.878 \pm 0.21\ kJ\cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(LiOH, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(744.3\ K)-H°(298.15\ K)$, between the crysal and liquid.

Heat Capacity and Entropy

The heat capacity of the liquid phase is obtained from the high temperature enthalpy measurements (750–875 K) of Shomate and Cohen.[1] We derive a constant $C_p°$ of 20.814 $cal\cdot K^{-1}\cdot mol^{-1}$ for LiOH(l) from these enthalpy data. The average percent deviation of the linear fit of the data was 0.2%. Powers and Blalock[2] also determined a constant $C_p° = 22.03\ cal\cdot K^{-1}\ mol^{-1}$ for LiOH(l) from enthalpy data (746–1200 K) determined by dromp calorimetry.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

Dissociation pressures for LiOH(cr, l) have been measured by static,[4] effusion,[5-6] and transpiration[6] methods. These data are combined with the equilibrium studies of Berkowitz et al.[3] to give either $\Delta_{sub}H°(298.15\ K)$ or $\Delta_{vap}H°(298.15\ K)$ An analysis of the data is summerized below, and further discussion of these results is presented on the ideal gas table under Enthalpy of Formation.

Source	Reaction[a]	Method	T/K	Data Points	$\Delta_r H°(298.15\ K)$, $kcal\cdot mol^{-1}$ 2nd law	3rd law	Drift $cal\cdot K^{-1}\cdot mol^{-1}$	$\Delta_{sub}H°(298.15\ K)$ $kcal\cdot mol^{-1}$	$\Delta_{vap}H°(298\ 15\ K)$ $kcal\ mol^{-1}$
Berkowitz *et al.*	A	Mass. Spec.	11201450	18	82.3	82.9 ± 1.0	0.5 ± 2.6		
Johnston[4]	B	Static	793–1176	9[b]	34.7	25.9 ± 2.1	−8.5 ± 0.4		54.4 ± 5.0
Ditmars and	C	Effusion	648–736	11	37.8	39.5 ± 1.0	2.6 ± 5.4	61.2 ± 3.0	
Johnston[5]	B	Effusion	752–795	7	35.5	34.3 ± 0.9	−1.9 ± 12.9		58.6 ± 3.0
Gregory and Mohr[6]	C	Transpiration and Effusion	525–675	Equation	32.1	32.7 ± 0.1	0.9 ± 0.1	57.8 ± 2.0	

[a]A) $Li_2O(cr) + H_2O(g) = 2LiOH(g)$ B) $2LiOH(l) = Li_2O(cr) = H_2O(g)$ C) $2LiOH(cr) = Li_2O(cr) + H_2O(g)$
[b]One point rejected due to failure of a statistical test.

The boiling point, $T_{vap} = 1899\ K$, is determined as the temperature at which the fugacity of LiOH(g) becomes 1 atm for the process $LiOH(l) = LiOH(g)$. The difference in their enthalpies of formation at the boiling point is the enthalpy of vaporization, $\Delta_{vap}H° = 44.9\ kcal\cdot mol^{-1}$.

References

[1]C. H. Shomate and A. J. Cohen, J. Amer. Chem. Soc. 77, 285 (1955).
[2]W. D. Powers and G. C. Blalock, Oak Ridge Nat. Lab., ORNL 1653, (January 1954).
[3]J. Berkowitz, D. J. Meschi, and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).
[4]J. Johnston, Z. Phys. Chem. 62, 339 (1908).
[5]W. E. Ditmars and H. L. Johnston, J. Amer. Chem. Soc. 75, 1830 (1953).
[6]N. W. Gregory and R. H. Mohr, J. Amer. Chem. Soc. 77, 2142 (1955).

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

T/K	$C_p°$ ($J\cdot K^{-1}mol^{-1}$)	$S°$ ($J\cdot K^{-1}mol^{-1}$)	$-[G°-H°(T_r)]/T$ ($J\cdot K^{-1}mol^{-1}$)	$H°-H°(T_r)$ ($kJ\cdot mol^{-1}$)	$\Delta_f H°$ ($kJ\cdot mol^{-1}$)	$\Delta_f G°$ ($kJ\cdot mol^{-1}$)	log K_f
0							
100							
200							
298.15	87.086	47.969	47.969	0.	−474.422	−429.989	75.332
300	87.086	48.508	47.971	0.161	−474.360	−429.713	74.820
400	87.086	73.561	51.386	8.870	−471.191	−415.318	54.235
500	87.086	92.993	57.837	17.578	−471.406	−401.374	41.931
600	87.086	108.871	65.060	26.287	−468.725	−387.619	33.745
700	87.086	122.295	72.302	34.995	−466.038	−374.314	27.932
744.300	87.086	127.639	75.438	38.853	--- CRYSTAL <--> LIQUID ---		
800	87.086	133.924	79.294	43.704	−463.370	−361.393	23.597
900	87.086	144.181	85.945	52.413	−460.743	−348.804	20.244
1000	87.086	153.357	92.235	61.121	−458.153	−336.506	17.577
1100	87.086	161.657	98.175	69.830	−455.600	−324.465	15.408
1200	87.086	169.234	103.786	78.538	−453.081	−312.655	13.610
1300	87.086	176.205	109.092	87.247	−450.596	−301.054	12.096
1400	87.086	182.659	114.119	95.955	−448.142	−289.642	10.807
1500	87.086	188.667	118.891	104.664	−445.716	−278.406	9.695
1600	87.086	194.287	123.429	113.373	−443.316	−267.330	8.727
1700	87.086	199.567	127.754	122.081	−586.177	−249.228	7.658
1800	87.086	204.544	131.883	130.790	−583.074	−229.497	6.660
1900	87.086	209.253	135.833	139.498	−580.004	−209 938	5.772
2000	87.086	213.720	139.616	148.207	−576.965	−190.540	4.976
2100	87.086	217.969	143.247	156.916	−573.958	−171.292	4.261
2200	87.086	222.020	146.736	165.624	−570.983	−152.187	3.613
2300	87.086	225.891	150.094	174.333	−568.041	−133.217	3.025
2400	87.086	229.597	153.330	183.041	−565.130	−114.375	2.489
2500	87.086	233.152	156.453	191.750	−562.253	−95.652	1.999

PREVIOUS: March 1966 CURRENT June 1971

0 to 744.3 K crystal
above 744.3 K liquid

Refer to the individual tables for details.

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

	J·K⁻¹mol⁻¹			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	−7.416	−479.144	−479.144	INFINITE
100	14.644	8.561	77.138	−6.858	−482.033	−468.453	244.695
200	35.977	25.632	46.982	−4.270	−484.089	−453.960	118.562
298.15	49.591	42.821	42.821	0.	−484.926	−438.958	76.904
300	49.761	43.128	42.822	0.092	−484.933	−438.672	76.380
400	58.053	58.678	44.886	5.517	−485.047	−423.222	55.267
500	63.647	72.260	49.032	11.614	−487.874	−407.475	42.569
600	68.208	84.277	53.924	18.212	−487.303	−391.441	34.078
700	72.279	95.101	59.045	25.239	−486.298	−375.538	28.023
744.300	73.970	99.588	61.326	28.479	CRYSTAL <--> LIQUID TRANSITION		
744.300	87.086	127.639	61.326	49.357			
800	87.086	133.924	66.164	54.208	−463.370	−361.393	23.597
900	87.086	144.181	74.274	62.916	−460.743	−348.804	20.244
1000	87.086	153.357	81.732	71.625	−458.153	−336.506	17.577
1100	87.086	161.657	88.626	80.333	−455.600	−324.465	15.408
1200	87.086	169.234	95.032	89.042	−453.081	−312.655	13.610
1300	87.086	176.205	101.012	97.751	−450.596	−301.054	12.096
1400	87.086	182.659	106.616	106.459	−448.142	−289.642	10.807
1500	87.086	188.667	111.888	115.168	−445.716	−278.406	9.695
1600	87.086	194.287	116.864	123.876	−443.316	−267.330	8.727
1700	87.086	199.567	121.576	132.585	−586 177	−249.228	7.658
1800	87.086	204.544	126.048	141.294	−583.074	−229.497	6.660
1900	87.086	209.253	130.304	150.002	−580.003	−209.938	5.772
2000	87.086	213.720	134.365	158.711	−576.965	−190.540	4.976
2100	87.086	217.969	138.245	167.419	−573.958	−171.292	4.261
2200	87.086	222.020	141.962	176.128	−570.983	−152.187	3.613
2300	87.086	225.891	145.527	184.836	−568.041	−133.217	3.025
2400	87.086	229.597	148 954	193.545	−565.130	−114.375	2.489
2500	87.086	233.152	152.251	202.254	−562.253	−95.652	1.999

PREVIOUS: CURRENT June 1971

$S°(298.15\ K) = [210.659 \pm 2.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -231.99 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -234.30 \pm 6.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[630](1)
[362](2)
[3666](1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: C
Bond Distances: Li–O = 1.582 Å O–H = [0.97] Å
Bond Angle: Li–O–H = 180°
Rotational Constant: B_0 = [1.192055] cm^{-1}

Enthalpy of Formation

Smith and Sugden[1] provided the first information on the stability of gaseous LiOH by studying its formation in hydrogen–air flames. Very recently, other flame photometric studies[3-5] have been reported on LiOH(g), primarily in connection with establishing its bond dissociation energy. Mass spectrometry[6-7] has also provided additional information on the stability of this species. These investigations have resulted in a wealth of equilibrium data involving this compound. 2nd and 3rd law analyses of these data are presented in tabular form below. Vapor pressure data for LiOH(cr, l) are analyzed under Vaporization Data (see LiOH(l) table), these data lead to $\Delta_f H°$(LiOH, g, 298.15 K) values of −59.0, −54.7, −54.8 and −58.1 $kcal \cdot mol^{-1}$.

Source	Reaction*	Method	T/K	Data Points	$\Delta_r H°$(298.15 K), $kcal\ mol^{-1}$ 2nd law	3rd law	Drift $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°$(298.15 K) $kcal \cdot mol^{-1}$
Smith and Sugden[1]	A	Flame	2200	1		99.6		−51.7
James and Sugden[2]	A	Flame	2200	1		100.0		−53.2
Jensen and Padley[3]	B	Flame	2475	1		15.9		−55.6 ± 2.0
Cotton and Jenkins[4]	B	Flame	2370	1		15.1		−56.4 ± 1.5
McEwan and Phillips[5]	B	Flame	1400–2600	4	15.8	16.7 ± 0.6	0.5 ± 0.2	−54.8 ± 1.6

*Reactions: (A) LiOH(g) = Li(g) + OH(g) (B) Li(g) + H_2O(g) = LiOH(g) + H(g)

The equilibrium data of Sugden and co-workers[1,2] are likely to contain significant errors, since the dissociation constants were calculated with OH concentrations determined from measured flame temperatures and known gas compositions. It is now well established[8,9] that flame radical concentrations vary greatly with the distance from the reaction zone of the flame. The dissociation pressure data of Johnston and Ditmars and Johnston (refer to the LiOH(l) table) show excessive drifts which usually are indications of nonequilibrium measurements. However, even the remaining flame work[3-5] and vapor pressure data still show a scatter of over 3 $kcal \cdot mol^{-1}$ in $\Delta_f H°$(298.15 K) of LiOH(g). Cotton and Jenkins[4] investigated the other alkali metal hydroxides, and their data lead to $\Delta_f H°$(298 15 K) values for these compounds which are quite consistent with JANAF data.[10] On the other hand, the flame studies of McEwan and Phillips[5] as a function of temperature do not show significant drift; yet, the discrepancy between their $\Delta_f H°$(298.15 K) value and that of Cotton and Jenkins[4] is 1.6 $kcal \cdot mol^{-1}$. We choose to adopt for $\Delta_f H°$(LiOH, g, 298.15 K) a weighted average of the results from the flame work[3-5] and the vapor pressure data. The adopted value $\Delta_f H°$(LiOH, g, 298.15 K) = −56.0 ± 1.5 $kcal \cdot mol^{-1}$ corresponds to a bond dissociation energy of $D_0°$(Li–OH) = 102.8 ± 1.5 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Freund *et al.*[11] measured the molecular beam electric resonance spectra of LiOH and calculated molecular constants on the basis of a linear equilibrium structure. Linear structures for the other alkali metal hydroxides have been proposed from microwave and infrared studies on these molecules. (Refer to the respective tables for details.) We adopt a linear configuration for LiOH and calculate a Li–O bond length from the rotational constant given by Freund *et al.*[11] The O–H bond length is estimated to be the same as for H_2O.

Experimental vibrational frequencies for LiOH have not been reported in the literature at the present time. Acquista and Abramowitz[12] have made matrix-isolation studies of monomeric CsOH, RbOH, and NaOH and provided assignments for the metal–oxygen stretch (ν_1) and the bending modes (ν_2) of these molecules. A Valence Force Treatment of the frequencies by these workers led to metal–oxygen (F_{11}), O–H (F_{33}), and bending (F_{22}) force constants. We extrapolate their data to LiOH with the result; F_{11} = 1.15 mdyn/Å, F_{33} assumed equal to 7.5 mdyn/Å with the interaction constant F_{13} = 0, and F_{22} = 0.060 mdyn Å. These estimated force constants are used to calculate the adopted frequencies by the Valence Force Treatment. Our adopted frequencies when used in an analysis of the equilibrium data from McEwan and Phillips[5] and Berkowitz *et al.*[7] (refer to the LiOH(l) table) lead to reasonable agreement between the 2nd and 3rd law $\Delta_r H°$(298.15 K) values.

Continued on page 1358

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
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−9.879	−231.985	−231.985	INFINITE
100	31.674	168.451	247.699	−7.925	−232.478	−234.887	122.693
200	40.704	193.281	214.729	−4.289	−233.487	−236.888	61.869
250	43.897	202.726	211.407	−2.170	−233.923	−237.687	49.662
298.15	46.129	210.659	210.659	0.	−234.304	−238.377	41.763
300	46.201	210.945	210.660	0.085	−234.318	−238.402	41.510
350	47.864	218.198	211.229	2.439	−234.690	−239.053	35.677
400	49.081	224.673	212.512	4.864	−235.078	−239.651	31.295
450	49.993	230.509	214.193	7.342	−235.512	−240.197	27.881
500	50.696	235.814	216.094	9.860	−239.006	−240.384	25.113
600	51.719	245.154	220.180	14.984	−239.910	−240.573	20.944
700	52.479	253.185	224.335	20.196	−240.720	−240.619	17.955
800	53.130	260.236	228.391	25.477	−241.480	−240.552	15.706
900	53.737	266.529	232.285	30.820	−242.217	−240.392	13.952
1000	54.323	272.222	235.998	36.223	−242.933	−240.151	12.544
1100	54.889	277.426	239.531	41.684	−243.627	−239.838	11.389
1200	55.432	282.225	242.892	47.200	−244.301	−239.464	10.424
1300	55.945	286.683	246.091	52.769	−244.956	−239.034	9.605
1400	56.426	290.846	249.141	58.388	−245.592	−238.555	8.901
1500	56.873	294.755	252.053	64.054	−246.209	−238.031	8.289
1600	57.285	298.439	254.838	69.762	−246.809	−237.466	7.752
1700	57.662	301.923	257.506	75.509	−392.631	−229.688	7.057
1800	58.008	305.229	260.066	81.293	−392.453	−220.108	6.387
1900	58.322	308.374	262.527	87.110	−392.274	−210.538	5.788
2000	58.609	311.373	264.894	92.957	−392.097	−200.978	5.249
2100	58.871	314.239	267.176	98.831	−391.925	−191.426	4.761
2200	59.109	316.983	269.378	104.730	−391.760	−181.882	4.318
2300	59.326	319.615	271.506	110.652	−391.604	−172.346	3.914
2400	59.524	322.145	273.563	116.595	−391.459	−162.816	3.544
2500	59.705	324.578	275.556	122.556	−391.329	−153.292	3.203
2600	59.870	326.923	277.487	128.535	−391.215	−143.773	2.888
2700	60.022	329.186	279.360	134.530	−391.120	−134.258	2.597
2800	60.161	331.371	281.178	140.539	−391.045	−124.746	2.327
2900	60.289	333.484	282.946	146.562	−390.994	−115.236	2.076
3000	60.406	335.530	284.665	152.596	−390.967	−105.728	1.841
3100	60.514	337.513	286.338	158.643	−390.967	−96.220	1.621
3200	60.614	339 436	287.967	164.699	−390.996	−86.712	1.415
3300	60.706	341.302	289.555	170.765	−391.055	−77.202	1.222
3400	60.792	343.116	291.104	176.840	−391.147	−67.690	1.040
3500	60.871	344.879	292.615	182.923	−391.272	−58.175	0.868
3600	60.945	346.595	294.091	189.014	−391.433	−48.656	0.706
3700	61.013	348.266	295.533	195.112	−391.631	−39.132	0.552
3800	61.077	349.894	296.942	201.217	−391.868	−29.601	0.407
3900	61.137	351.481	298.320	207.327	−392.145	−20.064	0.269
4000	61.192	353.030	299.669	213.444	−392.463	−10.520	0.137
4100	61.244	354.541	300.989	219.566	−392.825	−0.967	0.012
4200	61.293	356.018	302.281	225.693	−393.232	8.596	−0.107
4300	61.338	357.460	303.548	231.824	−393.685	18.168	−0.221
4400	61.381	358.871	304.789	237.960	−394.165	27.750	−0.329
4500	61.422	360.251	306.006	244.100	−394.705	37.344	−0.433
4600	61.459	361.601	307.200	250.244	−395.298	46.952	−0.533
4700	61.495	362.923	308.372	256.392	−395.942	56.573	−0.629
4800	61.529	364.218	309.522	262.543	−396.639	66.209	−0.720
4900	61.560	365.487	310.651	268.698	−397.389	75.859	−0.809
5000	61.590	366.731	311.760	274.855	−398.196	85.525	−0.893
5100	61.619	367.951	312.850	281.016	−399.055	95.208	−0.975
5200	61.645	369.148	313.921	287.179	−399.977	104.908	−1.054
5300	61.671	370.323	314.975	293.345	−400.960	114.627	−1.130
5400	61.695	371.476	316.010	299.513	−402.006	124.364	−1.203
5500	61.718	372.608	317.029	305.684	−403.116	134.122	−1.274
5600	61.740	373.720	318.031	311.857	−404.293	143.901	−1.342
5700	61.760	374.813	319.018	318.032	−405.537	153.701	−1.409
5800	61.780	375.887	319.989	324.209	−406.850	163.524	−1.473
5900	61.799	376.944	320.946	330.388	−408.234	173.368	−1.535
6000	61.816	377.982	321.888	336.569	−409.692	183.239	−1.595

PREVIOUS: June 1971 (1 atm) CURRENT June 1971 (1 bar)

Lithium Hydroxide, Ion (LiOH⁺) — IDEAL GAS — M_r = 23.947791

$S°(298.15\ K) = [221.685 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [774.1 \pm 105]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [778.2 \pm 105]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Sigma^+$	[32000]	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[600](1)
[325](2)
[3600](1)

Point Group: [$C_{\infty v}$] $\sigma = 1$
Bond Distances: Li–O = [1.60] Å O–H = [1.03] Å
Bond Angle: Li–O–H = [180]°
Rotational Constant: B_0 = [1.154155] cm^{-1}

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(LiOH⁺, g, 298.15 K) = 186 ± 25 kcal·mol^{-1}, is calculated from the ionization potential for LiOH and $\Delta_f H°$(LiOH, g, 298.15 K) = −56.0 ± 1.5 kcal·mol^{-1}.[1] The ionization potential is estimated to be 10.5 ± 1.0 eV for LiOH by comparison with similar data[2] for the isoelectronic molecules LiF and LiCl. We note that this estimated value is in accord with the ionization potential of LiO (IP = 9.0 eV),[3] which should be less than LiOH since the electron in the monoxide is unpaired.

Heat Capacity and Entropy

The correlation diagram of Walsh[4] for HAB molecules predicts a linear configuration for LiOH⁺ (seven valence electrons) with the unpaired electron in a pi orbital. Therefore, the electronic ground state of LiOH⁺ should be $^2\Pi$. A first excited state ($^2\Sigma$) is estimated at 32000 cm^{-1} by analogy with the isoelectronic molecules OH[1] and SH.[1] The ionization of LiOH is assumed to lead to weaker bonding in LiOH⁺, since the electron lost is a bonding one. The Li–O and O–H bond distances are increased slightly over those for LiOH to account for this weaker bonding. Similarly, the vibrational frequencies are estimated from those for LiOH with somewhat lower values.

References

[1] JANAF Thermochemical Tables: LiOH(g), 6–30–71; OH(g), 12–31–70, SH(g), 6–30–67.
[2] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, NSRDS–NBS 26, (1969).
[3] C. W. Beckett and E. C. Cassidy, U. S. Nat. Bur. Stand. Report 8628, (1965).
[4] A. D. Walsh, J. Chem. Soc. 2288 (1953).

Lithium Hydroxide, Ion (LiOH⁺) — $H_1Li_1O_1^+(g)$

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	−11 137	774.087		
90	32.662	178.163	259.751	−8.159			
200	41 973	203.872	225.848	−4.395			
250	44.971	213.579	222.449	−2.217			
298.15	47.019	221.685	221.685	0.	778.224	764.609	−133.956
300	47.085	221.976	221.686	0.087	778.250	764.524	−133.116
350	48.589	229.354	222.265	2.481	778.958	762.181	−113.749
400	49.681	235.917	223.569	4.939	779.642	759.737	−99.211
450	50 495	241.818	225.274	7.444	780.274	757.210	−87.895
500	51 121	247.172	227.201	9.985	777.843	754 923	−78.866
600	52.040	256.578	231.334	15.146	779.055	750.227	−65.313
700	52.739	264.655	235.531	20.386	780.352	745.321	−55.617
800	53.355	271.738	239.623	25.691	781.695	740.225	−48.332
900	53.943	278.056	243.549	31.057	783.057	734.960	−42.656
1000	54.516	283.769	247.290	36.480	784.440	729.542	−38.107
1100	55.074	288.992	250.847	41.959	785.843	723.984	−34.379
1200	55.609	293.807	254.229	47.494	787.267	718.298	−31.267
1300	56.116	298.278	257.447	53.080	788.708	712.492	−28.628
1400	56.590	302.454	260.514	58.716	790.167	706.575	−26.363
1500	57.030	306.374	263.442	64.397	791.645	700.553	−24.395
1600	57.434	310.068	266.242	70.121	793.138	694.431	−22.671
1700	57.805	313.561	268.924	75.883	649.409	695.392	−21.367
1800	58.143	316.875	271.497	81.681	651.680	698.031	−20.256
1900	58.451	320.027	273.968	87.510	653.951	700.544	−19.259
2000	58 731	323.032	276.347	93.370	656.218	702.938	−18.359
2100	58.986	325.904	278.639	99.256	658.481	705.218	−17.541
2200	59.218	328.653	280.850	105.166	660.736	707.391	−16.796
2300	59 429	331.290	282.986	111.099	662.982	709.461	−16.112
2400	59.622	333.824	285.052	117.051	665.215	711.434	−15.484
2500	59.797	336.261	287.052	123.022	667.433	713.314	−14 904
2600	59.958	338.610	288.990	129.010	669.634	715.106	−14.367
2700	60 105	340.875	290.870	135.014	671.817	716.814	−13.868
2800	60.240	343.064	292.695	141.031	673.978	718.441	−13.403
2900	60.363	345.180	294.469	147.061	676.116	719.991	−12.968
3000	60.477	347.228	296.194	153.103	678.228	721.468	−12.562
3100	60.582	349.213	297.872	159.156	680.314	722.875	−12.180
3200	60.679	351.138	299.507	165.219	682.370	724.214	−11.822
3300	60.768	353.006	301.100	171.292	684.396	725.491	−11.484
3400	60.851	354.822	302.653	177.373	686.389	726.706	−11.164
3500	60.928	356.587	304.169	183.462	688.348	727.863	−10.863
3600	61.000	358.304	305.649	189.558	690.271	728.965	−10.577
3700	61.066	359.976	307.095	195.661	692.157	730.013	−10.306
3800	61.129	361.606	308.508	201.771	694 004	731.012	−10.048
3900	61.187	363.194	309.890	207.887	695.811	731.963	−9.804
4000	61.242	364.744	311.242	214.009	697.576	732.867	−9.570
4100	61.294	366.257	312.565	220.135	699.298	733.728	−9.348
4200	61.342	367.735	313.861	226.267	700.975	734.547	−9.135
4300	61.388	369.179	315.131	232.404	702.605	735.327	−8.932
4400	61.432	370.590	316.376	238.545	704.209	736 068	−8.738
4500	61.473	371.971	317.596	244.690	705.752	736.774	−8.552
4600	61.513	373.323	318.793	250.839	707.243	737.447	−8.374
4700	61.550	374.646	319.967	256.992	708.683	738.088	−8.203
4800	61.587	375.942	321.120	263.149	710.071	738.699	−8.039
4900	61.622	377.213	322.252	269.310	711.405	739.281	−7.881
5000	61.655	378.458	323.363	275.474	712.683	739.838	−7 729
5100	61.688	379.679	324.456	281.641	713.909	740.368	−7.583
5200	61.720	380.877	325.529	287.811	715.073	740.875	−7.442
5300	61 751	382.053	326.585	293.985	716.176	741.361	−7.307
5400	61.781	383.208	327.622	300.161	717.217	741.826	−7.176
5500	61.810	384.342	328.643	306.341	718.194	742.272	−7.050
5600	61.839	385.456	329.648	312.523	719.106	742.702	−6.928
5700	61.868	386.551	330.637	318.709	719.951	743 116	−6.810
5800	61.896	387.627	331.610	324.897	720.728	743.516	−6.696
5900	61.924	388.685	332.569	331.088	721.434	743.901	−6.586
6000	61.951	389.726	333.512	337.282	722.068	744.277	−6.480

PREVIOUS: December 1971 (1 atm) CURRENT December 1971 (1 bar)

Lithium Hydroxide, Ion (LiOH⁺) — $H_1Li_1O_1^+(g)$

$S°(298.15\ K) = 193.200\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 169.58 \pm 48.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 169.03 \pm 48.1\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights					
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	2	35400	2	42070	2
19221.2	2	[38730]	2	48000	4
19224.7	2	41120	4		

$\omega_e = 1495.7\ cm^{-1}$ $\omega_e x_e = 31.5\ cm^{-1}$ $\sigma = 1$
$B_e = 5.8181\ cm^{-1}$ $\alpha_e = 0.1668\ cm^{-1}$ $r_e = 1.73$ Å

Enthalpy of Formation

The enthalpy of formation is calculated using $D_0^\circ = 2.0 \pm 0.5$ eV derived from a graphical extrapolation of the (0–3) energy levels of the $X^2\Sigma^+$ state reported by Gaydon.[1] Herzberg[2] reported $D_0^\circ \leq 2.49$ eV assuming predissociation of the C^2 state of MgH into Mg(^{3}P) and H(^{2}S).

Heat Capacity and Entropy

The molecular constants and electronic levels are obtained from Herzberg[2] except for the electronic levels 35400 and 48000 obtained from Khan.[3]

References

[1]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Edition, Chapman and Hall Ltd., London, (1953).
[2]G. Herzberg, "Spectra of Diatomic Molecules," 2nd Edition, D. Van Nostrand Co., Inc., New York, (1950).
[3]M. A. Khan, Proc. Phys. Soc. (London) 80, 209–21 (1962).

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	−8.682	169.583	169.583	INFINITE
100	29.127	161.292	219.230	−5.794	170.330	160.188	−83.673
200	29.181	181.492	195.889	−2.879	169.890	150.162	−39.218
250	29.316	188.016	193.685	−1.417	169.483	145.275	−30.354
298.15	29.583	193.200	193.200	0.	169.034	140.653	−24.642
300	29.596	193.383	193.201	0.055	169.016	140.477	−24.459
350	30.016	197.975	193.562	1.545	168.519	135.759	−20.261
400	30.535	202.016	194.371	3.058	168.011	131.114	−17.122
450	31.103	205.645	195.426	4.599	167.501	126.533	−14.688
500	31.683	208.952	196.615	6.169	166.993	122.008	−12.746
600	32.778	214.828	199.173	9.393	165.986	113.106	−9.847
700	33.724	219.954	201.783	12.719	164.971	104.372	−7.788
800	34.510	224.510	204.345	16.132	163.919	95.786	−6.254
900	35.158	228.613	206.817	19.616	162.798	87.336	−5.069
1000	35.694	232.346	209.186	23.160	152.983	79.728	−4.165
1100	36.141	235.770	211.449	26.752	151.625	72.469	−3.441
1200	36.519	238.931	213.609	30.386	150.289	65.332	−2.844
1300	36.844	241.867	215.671	34 054	148.966	58.306	−2.343
1400	37.127	244.608	217.642	37.753	20.243	54.549	−2.035
1500	37.376	247.178	219.526	41.479	20.286	56.998	−1.985
1600	37.599	249.598	221.330	45.228	20.330	59.443	−1.941
1700	37.800	251.883	223.061	48.998	20.375	61.887	−1.902
1800	37.985	254.049	224.723	52.787	20.419	64.327	−1.867
1900	38.155	256.108	226.321	56.594	20.461	66.765	−1.836
2000	38.314	258.069	227.860	60.418	20.501	69.202	−1.807
2100	38.465	259.942	229.343	64.257	20.538	71.636	−1.782
2200	38.608	261 734	230.775	68.110	20.573	74.068	−1.759
2300	38.746	263.454	232.159	71.978	20.605	76.499	−1.737
2400	38.881	265.106	233.497	75.860	20.636	78.928	−1.718
2500	39.013	266.695	234.794	79.754	20.663	81.357	−1.700
2600	39.144	268.228	236.050	83.662	20.689	83.784	−1 683
2700	39.275	269.708	237.270	87.583	20.712	86.210	−1.668
2800	39.407	271.139	238.454	91.517	20.732	88.636	−1.654
2900	39.541	272.524	239.605	95.464	20.749	91.060	−1.640
3000	39.678	273.867	240.725	99.425	20.763	93.485	−1.628
3100	39.818	275.170	241.815	103.400	20.773	95.909	−1.616
3200	39.962	276.436	242.877	107.389	20.778	98.332	−1.605
3300	40.110	277.668	243.913	111.393	20.778	100.756	−1.595
3400	40.264	278.868	244.923	115.411	20.771	103.179	−1.585
3500	40.423	280.037	245.910	119.445	20.756	105.603	−1.576
3600	40.587	281.178	246.874	123.496	20.733	108.028	−1.567
3700	40.757	282.293	247.816	127.563	20.699	110.453	−1.559
3800	40.933	283.382	248.738	131.648	20.653	112.880	−1.552
3900	41.114	284.448	249.640	135.750	20.595	115.307	−1.544
4000	41.301	285.491	250.523	139.871	20.521	117.737	−1.537
4100	41.494	286.513	251.389	144.010	20.431	120.168	−1.531
4200	41.693	287.515	252.237	148.170	20.323	122.602	−1.525
4300	41.897	288.499	253.069	152.349	20.195	125.039	−1.519
4400	42.106	289.464	253.885	156.549	20.046	127.479	−1.513
4500	42.320	290.413	254.686	160.770	19.874	129.922	−1.508
4600	42.538	291.345	255.473	165.013	19 678	132.370	−1.503
4700	42.761	292.263	256.246	169.278	19.455	134.822	−1.498
4800	42.989	293.165	257.006	173.566	19.205	137.279	−1.494
4900	43.220	294.054	257.753	177.876	18.926	139.742	−1.490
5000	43.455	294.930	258.488	182.210	18.617	142.211	−1.486
5100	43.694	295.792	259.211	186.567	18.277	144.686	−1.482
5200	43.936	296.643	259.922	190.949	17.903	147.168	−1.478
5300	44.181	297.482	260.623	195.355	17.497	149.658	−1.475
5400	44.428	298.311	261.313	199.785	17.056	152.155	−1.472
5500	44.678	299.128	261.994	204.240	16.579	154.661	−1.469
5600	44.931	299.935	262.664	208.721	16.066	157.177	−1.466
5700	45.185	300.733	263.325	213.226	15.516	159.701	−1.463
5800	45.441	301.521	263.977	217.758	14.928	162.236	−1.461
5900	45.699	302.300	264.620	222.315	14.301	164.781	−1.459
6000	45.958	303.070	265.254	226.898	13.636	167.337	−1.457

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

Magnesium Hydroxide (MgOH) — IDEAL GAS — M_r = 41.31234

$S°(298.15\ K) = [226.458 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-161.34 \pm 37.7]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-164.75 \pm 37.7]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights ϵ_i, cm^{-1}	g_i
0	2
[27000]	[4]

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[718](1)
[492](2)
[3650](1)

Point Group: $[C_{\infty v}]$ $\sigma = 1$
Bond Distances: Mg–O = [1.77] Å O–H = [0.96] Å
Bond Angle: Mg–O–H = [180]°
Rotational Constant: B_0 = [0.491925] cm^{-1}

Enthalpy of Formation

From observations made during a flame spectra study of the bond dissociation energy of magnesium oxide, Cotton and Jenkins[1] concluded that $D_0°$(Mg–OH) is less than 90 kcal·mol^{-1}. The analogy between gaseous monohydroxides and monohalides has been recognized.[2-5] Hildenbrand[6] has found that the ratio of $D_0°$(Mg–F)/$D_0°$(F–Mg–F) is 0 45, current JANAF values[7] give 0.448. From the latter ratio and current JANAF data,[7] $D_0°$(Mg–OH) = 84.49 kcal·mol^{-1} is derived. Adding the difference, −16.1 kcal mol^{-1}, between $D_0°$(Mg–F) and $D_0°$(Ca–F)[7] to $D_0°$(Ca–OH) = 97.5 kcal·mol^{-1}[17] gives $D_0°$(Mg–OH) = 81.4 kcal·mol^{-1}. The average $D_0°$(Mg–OH) = 82.9 ± 5 kcal·mol^{-1} is adopted from which $\Delta_f H°$(MgOH, g, 0 K) = −38.56 ± 9 kcal·mol^{-1} is derived.

The value of $D_0°$(Mg–OH) = 56 ± 5 kcal·mol^{-1} derived by Bulewicz and Sugden[8] from flame spectra studies appears to be too low.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear in accordance with the prediction of Walsh,[9] the evidence that the alkali metal monohydroxides are linear,[10-13] and the ESR spectrum study of MgOH in argon and neon matrices from which Brom and Weltner[13] concluded that MgOH is probably linear with a $^2\Sigma$ ground state. The analogy with MgF and MgCl[7] also indicates a $^2\Sigma^+$ ground state, which is assumed.

Ultraviolet emission spectra near 3800 Å were observed from MgOH and MgOD by Pesic and Gaydon[14] and by Brewer and Trajmar.[15] Brom and Weltner[13] observed absorption spectra of MgOH in an argon matrix in the 3100–3700 Å range. From these observations and from the comparison with MgF and MgCl, the first excited state at 27000 cm^{-1} is estimated.

The Mg–O bond distance is estimated to be slightly larger, 0.02 Å, than the MgF bond distances[7] after noting the close similarity in bond distance of the alkali metal fluorides and hydroxides. The O–H bond distance is that in water.[7]

The Mg–O stretching frequency, 718 cm^{-1}, is estimated to be the same as in MgF.[5,7] The O–H stretching frequency, 3650 cm^{-1}, is estimated from the alkali hydroxide series. The bending frequency, 492 cm^{-1}, is estimated by assuming that the ratio of the bending force constant to the stretching force constant is 0.022, which is the average ratio found in the alkali metal monohydroxides by Acquista and Abramowitz.[5,12]

The entropy in the present table is lower by 0.20 cal·K^{-1} mol^{-1} at 298 K and 0.25 cal·K^{-1}·mol^{-1} at 1000 K than that proposed by Jackson;[5] the data relevant to the calculation are nearly the same.

References

[1] D. H. Cotton and D. R. Jenkins, Trans. Faraday Soc. 65, 376 (1969).
[2] R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
[3] J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).
[4] F. E. Stafford and J. Berkowitz, J. Chem. Phys. 40, 2963 (1964).
[5] D. D. Jackson, Lawrence Livermore Laboratory, Univ. of Calif., UCRL–51137, (1971).
[6] D. L. Hildenbrand, personal communication, Stanford Research Institute, (July 2, 1974).
[7] JANAF Thermochemical Tables: $Mg(OH)_2$(g), CaOH(g), 12–31–75; MgF_2(g), 6–30–75; Mg(g), 9–30–62; OH(g), 12–31–70; CaF(g), 12–31–68; H_2O(g), 3–31–61.
[8] E. M. Bulewicz and T. M. Sugden, Trans. Faraday Soc. 55, 720 (1959).
[9] A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).
[10] N. Acquista, S. Abramowitz, and R. Lide, J. Chem. Phys. 49, 780 (1968).
[11] R. L. Kuczkowski and R. Lide, J. Chem. Phys. 44, 3131 (1966).
[12] N. Acquista and S. Abramowitz, U. S. Nat. Bur. Stand. Report 9905, (July 1968).
[13] J. M. Brom, Jr., and W. Weltner, Jr., J. Chem. Phys. 58, 5322 (1973).
[14] D. Pesic and A. G. Gaydon, Proc. Phys. Soc. (London) 73, 244 (1959).
[15] L. Brewer and S. Trajmar, J. Chem. Phys. 36, 1585 (1962).

Magnesium Hydroxide (MgOH) — $H_1Mg_1O_1$(g)

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	−10.160	−161.341	−161.341	INFINITE
100	29.833	187.913	260.329	−7.242	−162.017	−166.156	86.791
200	36.797	210.512	230.214	−3.940	−163.525	−169.709	44.323
250	40.324	219.114	227.152	−2.010	−164.192	−171.176	35.765
298 15	43.036	226 458	226.458	0.	−164.755	−172.469	30.216
300	43.127	226.725	226.459	0.080	−164.775	−172.517	30.038
350	45.270	233.541	226.992	2.292	−165.287	−173.766	25.933
400	46.900	239.698	228.202	4.598	−165.750	−174.945	22.845
450	48.151	245.297	229.795	6.976	−166.182	−176.068	20.437
500	49.130	250.423	231.605	9.409	−166.597	−177.144	18.506
600	50.561	259.515	235.519	14.398	−167.419	−179.177	15.599
700	51.597	267.390	239.522	19.508	−168.278	−181.069	13.512
800	52 441	274.337	243.448	24.711	−169.208	−182.834	11.938
900	53.189	280.557	247.232	29.993	−170.234	−184.477	10.707
1000	53.879	286.197	250.851	35.347	−179.969	−185.287	9.678
1100	54.524	291.363	254.302	40.767	−181.254	−185.756	8.821
1200	55.128	296 134	257.592	46.250	−182.515	−186.109	8.101
1300	55 690	300.569	260.729	51.792	−183.757	−186.358	7.488
1400	56.209	304 715	263.724	57.387	−312.390	−183.345	6.841
1500	56 686	308.610	266.588	63.032	−312.249	−174.133	6.064
1600	57.123	312.282	269.330	68.723	−312.096	−164.930	5.384
1700	57.521	315.757	271.960	74.455	−311.934	−155.737	4 785
1800	57.883	319.055	274.486	80.226	−311.767	−146.554	4.253
1900	58.212	322.194	276.915	86.031	−311.597	−137.380	3 777
2000	58.511	325.188	279.254	91.867	−311.426	−128.215	3.349
2100	58 783	328.049	281.510	97.732	−311.255	−119.059	2.961
2200	59.030	330.789	283.688	103.623	−311.088	−109.910	2.610
2300	59.254	333.418	285.794	109.537	−310.924	−100.770	2.289
2400	59 459	335.945	287.831	115.473	−310.766	−91.636	1.994
2500	59.646	338.376	289.804	121.428	−310.615	−82.509	1.724
2600	59 817	340.718	291.718	127.401	−310.472	−73.388	1.474
2700	59.973	342.979	293.575	133.391	−310.339	−64.271	1.243
2800	60 117	345.163	295.378	139.396	−310.217	−55.160	1.029
2900	60.250	347.275	297.132	145.414	−310.107	−46.053	0.830
3000	60.373	349.319	298.837	151.445	−310.012	−36.949	0.643
3100	60.486	351.301	300.498	157.488	−309.931	−27.848	0.469
3200	60.592	353.223	302.116	163.542	−309.868	−18.750	0.306
3300	60.692	355.089	303.693	169.607	−309.823	−9.654	0.153
3400	60 785	356 902	305.231	175.681	−309.799	−0.558	0.009
3500	60.874	358.665	306.733	181.764	−309.797	8.537	−0.127
3600	60.958	360.381	308.199	187.855	−309.819	17.633	−0.256
3700	61.038	362.053	309.632	193.955	−309.867	26.729	−0.377
3800	61 116	363.682	311.033	200.063	−309.943	35.828	−0.492
3900	61.192	365.270	312.404	206 178	−310.050	44.929	−0.602
4000	61.266	366.820	313.745	212.301	−310.189	54.032	−0.706
4100	61.338	368.334	315.058	218.431	−310.363	63.140	−0.804
4200	61 410	369.813	316.344	224.569	−310.574	72.252	−0.899
4300	61 482	371.259	317.605	230.713	−310.823	81.370	−0.988
4400	61.553	372.673	318.840	236.865	−311.114	90.494	−1.074
4500	61.625	374.057	320.052	243.024	−311.447	99.624	−1.156
4600	61.698	375.412	321.241	249.190	−311.825	108.763	−1.235
4700	61.772	376.740	322.407	255.364	−312.250	117.911	−1.310
4800	61.846	378.041	323.553	261.544	−312.724	127.069	−1.383
4900	61.923	379.317	324.678	267.733	−313.249	136.236	−1.452
5000	62.000	380.569	325.783	273.929	−313.826	145.416	−1.519
5100	62.079	381.798	326.870	280.133	−314.457	154.607	−1.583
5200	62.160	383.004	327.938	286.345	−315.144	163.810	−1.645
5300	62.243	384.189	328.988	292.565	−315.888	173.028	−1.705
5400	62.328	385.353	330.021	298.794	−316.690	182.260	−1.763
5500	62.415	386.497	331.037	305.031	−317.552	191.507	−1.819
5600	62.503	387.623	332.038	311.277	−318.475	200.772	−1.873
5700	62.593	388.730	333.023	317.531	−319.461	210.053	−1.925
5800	62.686	389.819	333.993	323.795	−320.510	219.352	−1.975
5900	62.780	390.892	334.948	330.069	−321.624	228.668	−2.024
6000	62.876	391.948	335.889	336.351	−322.804	238.006	−2.072

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

Magnesium Hydroxide (MgOH) $H_1Mg_1O_1$(g)

$S°(298.15\ K)$ = [220.824 ± 8.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [581.61 ± 62.8] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [584.42 ± 62.8] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[700](1)
[490](2)
[3650](1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: [$C_{\infty v}$]
Bond Distances: Mg–O = [1.77] Å O–H = [0.96] Å
Bond Angle: Mg–O–H = [180]°
Rotational Constant: B_0 = [0.491933] cm^{-1}

Enthalpy of Formation

The enthalpy of formation of $MgOH^+(g)$ is estimated based on trends suggested by the alkaline earth monohydroxide unipositive ions. The estimate is based on the close agreement of the appearance potentials of the alkaline earth monohydroxides and the corresponding monofluoride.[1] In addition, the ionization potentials of the alkaline earth elements are fairly close to the appearance potential of the monohydroxide. We adopt, as the ionization potential for MgOH(g), a value of 7.7 eV (177.57 $kcal·mol^{-1}$). This value is identical to the appearance potential of MgF(g).[1] The ionization potential of Mg(g) is 7.65 eV,[1] which is very close to our adopted value.

The adopted ionization potential of 7.7 eV refers to the process $MgOH(g) + e^- = MgOH^+(g) + 2\ e^-$. Using auxiliary data,[1] we calculate $\Delta_f H°(0\ K)$ = 139.01 ± 15 $kcal·mol^{-1}$ for $MgOH^+(g)$. This leads to $\Delta_f H°(298.15\ K)$ = 139.68 ± 15.0 $kcal·mol^{-1}$.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the gaseous alkali metal hydroxides are linear.[1-4] In addition, Walsh[5] had predicted that BAH molecules (H = hydrogen atom) with ten or less valence electrons ($MgOH^+$ has 8 valence electrons) will be linear in their ground state. The molecule $MgOH^+$ is isoelectronic with NaOH.

The bond dissociation energy for $MgOH^+$ (81.7 $kcal·mol^{-1}$)[1] for the process $MgOH^+(g) = Mg^+(g) + OH(g)$ is essentially identical to that for MgOH (82.0 $kcal·mol^{-1}$)[1]. This suggests a similar bonding in these two molecules. Thus, the bond distances are assumed to be the same as those adopted for MgOH(g).[1] The vibrational frequencies are assumed to be similar to those adopted for MgOH(g).[1] The ground state quantum weight is assumed to be the same as that of NaOH(g).[1]

References

[1]JANAF Thermochemical Tables: e^-, 3–31–65; NaOH(g) and $Mg^+(g)$, 12–31–70; MgOH(g) and $MgF^+(g)$, 12–31–75.
[2]N. Acquista, S. Abramowitz, and D. R. Lide, J. Chem. Phys. 49, 780 (1968).
[3]R. L. Kuczkowski and D. R. Lide, J. Chem. Phys. 44, 313 (1966).
[4]N. Acquista and S. Abramowitz, U. S. Nat. Bur. Stand. Report 9905, (July 1968).
[5]A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).

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	−9.186	581.611		
100	29.854	182.153	254.830	−7.268			
200	36.949	204.808	224.596	−3.958			
250	40.503	213.448	221.522	−2.018			
298.15	43.216	220.824	220.824	0.	584.421	572.132	−100.235
300	43.306	221.092	220.825	0.080	584.440	572.055	−99.604
350	45.437	227.935	221.361	2.301	584.975	569.950	−85.060
400	47.050	234.113	222.575	4.615	585.560	567.764	−74.142
450	48.284	239.729	224.174	7.000	586.174	565.503	−65.642
500	49.246	244.868	225.990	9.439	586.805	563.172	−58.834
600	50.651	253.979	229.915	14.438	588.071	558.327	−48.607
700	51.668	261.867	233.929	19.557	589.299	553.271	−41.286
800	52.498	268.822	237.864	24.766	590.455	548.044	−35.784
900	53.235	275.048	241.656	30.053	591.512	542.679	−31.496
1000	53.917	280.693	245.282	35.411	583.859	537.914	−28.098
1100	54.556	285.862	248.739	40.835	584.657	533.281	−25.323
1200	55.155	290.635	252.034	46.321	585.477	528.574	−23.008
1300	55.713	295.072	255.176	51.865	586.317	523.798	−21.046
1400	56.229	299.220	258.175	57.462	459.764	522.124	−19.481
1500	56.704	303.116	261.043	63.109	461.986	526.501	−18.334
1600	57.138	306.789	263.788	68.802	464.219	530.729	−17.327
1700	57.535	310.266	266.421	74.536	466.461	534.818	−16.433
1800	57 895	313.564	268.949	80.308	468.708	538.774	−15.635
1900	58.223	316 704	271.381	86.114	470.958	542.605	−14.917
2000	58.521	319.698	273.722	91.951	473.209	546.318	−14.268
2100	58.792	322.560	275.980	97.817	475.459	549.918	−13.678
2200	59.038	325.301	278.160	103.709	477.706	553.411	−13.140
2300	59.262	327.930	280.267	109.624	479.949	556.802	−12.645
2400	59.466	330.456	282.306	115.560	482.187	560.095	−12.190
2500	59.652	332.888	284.281	121.516	484.417	563.295	−11.769
2600	59.822	335.231	286.196	127.490	486.639	566.406	−11.379
2700	59.977	337.491	288.054	133.480	488.851	569.432	−11.016
2800	60.120	339.675	289.859	139.485	491.052	572.377	−10.678
2900	60.250	341.787	291.613	145.504	493.240	575.242	−10.361
3000	60.371	343.832	293.320	151.535	495.414	578.033	−10.064
3100	60.481	345.813	294.982	157.578	497.573	580.752	−9.786
3200	60.583	347.735	296.600	163.631	499.714	583.400	−9.523
3300	60.678	349.601	298.178	169.694	501.837	585.982	−9.275
3400	60.765	351.413	299.717	175.766	503.938	588.501	−9.041
3500	60.846	353.176	301.220	181.847	506.016	590.957	−8.820
3600	60.921	354.891	302.687	187.935	508.070	593.355	−8.609
3700	60.991	356.561	304.121	194.031	510.096	595.696	−8.410
3800	61.056	358.189	305.522	200.133	512.093	597.983	−8.220
3900	61.117	359.775	306.893	206.242	514.058	600.218	−8.039
4000	61.173	361.324	308.234	212.357	515.989	602.402	−7.867
4100	61.226	362.835	309.548	218.477	517.883	604.539	−7.702
4200	61.276	364.311	310.834	224.602	519.739	606.630	−7.545
4300	61.322	365.753	312.095	230.732	521.553	608.678	−7.394
4400	61.366	367.163	313.330	236.866	523.324	610.683	−7.250
4500	61.407	368.543	314.542	243.005	525.050	612.649	−7.111
4600	61.445	369.893	315.731	249.147	526.726	614.577	−6.979
4700	61.482	371.215	316.897	255.294	528.353	616.469	−6.851
4800	61.516	372.510	318.042	261.444	529.926	618.327	−6.729
4900	61.548	373.778	319.167	267.597	531.445	620.153	−6.611
5000	61.579	375.022	320.272	273.753	532.906	621.949	−6.497
5100	61.607	376.242	321.357	279.912	534.309	623.716	−6.388
5200	61.635	377.438	322.424	286.075	535.651	625.455	−6.283
5300	61.660	378.613	323.473	292.239	536.931	627.170	−6.181
5400	61.685	379.765	324.505	298.407	538.146	628.861	−6.083
5500	61.708	380.898	325.520	304.576	539.295	630.530	−5.988
5600	61.730	382.010	326.519	310.748	540.376	632.180	−5.897
5700	61.751	383.102	327.502	316.922	541.389	633.810	−5.808
5800	61.771	384.177	328.470	323.098	542.330	635.423	−5.723
5900	61.790	385.233	329.423	329.276	543.200	637.020	−5.640
6000	61.808	386.271	330.362	335.456	543.996	638.603	−5.560

PREVIOUS: December 1975 (1 atm) CURRENT. December 1975 (1 bar)

$S°(298.15\ K) = 181.253 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 376.51 \pm 16.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 376.56 \pm 16.7\ kJ \cdot mol^{-1}$

Electronic States and Molecular Constants ($\sigma = 1$)

Source	State	ϵ_e, cm^{-1}	g_e	r_e, A	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
13,15	$X^3\Sigma^-$	0.0	3	1.038	16.666	0.648	3282.09	78.3
13,14	$a^1\Sigma$	12590	2	1.041	16.439	[0.7]	3303	55
13,16	$b^1\Sigma^+$	21240	1	1.035	16.7326	0.6049	3347	70.7
13,15	$A^3\Pi$	29777	6	1.036	16.6901	0.7440	3231.0	98.5
16,17	$C^1\Pi$	43345	2	1.1005	14.7985	1.267	2503	194
16,17	$d^1\Sigma^+$	82856	1	1.1165	14.3809	0.6119	2665	71.0

Enthalpy of Formation

The electron impact appearance potential of N_2^+ from HN_3 determined by Franklin *et al.*,[1] leads to a value $\Delta_f H°$(NH, g, 298.15 K) = 81 7 ± 0.5 kcal·mol^{-1}. Reed and Snedden[2] determined the electron impact appearance potential of NH^+ from NH_3. This, combined with the directly measured electron impact ionization potential of NH, 13.1 eV, gives $\Delta_f H°$ = 82.9 kcal·mol^{-1}. This value of the ionization potential of NH has also been obtained by Foner and Hudson.[3] However, all of these electron impact experiments are subject to errors of several tenths of an electron volt or more.

More recently, Seal and Gaydon[4] measured the concentration of NH in reflected shock waves in nitrogen–hydrogen–krypton and ammonia–krypton mixtures. These led to $D_0°$(NH) = 3.21 ± 0.16 eV, corresponding to $\Delta_f H°$(NH, g) = 90 13 ± 3 kcal·mol^{-1}. Kaskan and Nadler[5] determined NH, NH_3, and OH concentrations in a flat NH_3–D_2–N_2 flame and concluded $\Delta_f H°$(NH, g) = 90 ± 4 kcal·mol^{-1}. Stedman[6] studied the NH emission spectrum obtained by collision of metastable rare gas atoms with HN_3. Taking the highest level of NH as observed in emission as a limit, he concluded that $\Delta_f H°$(NH, g) > 80 kcal·mol^{-1}. From analogous consideration on N_2 emission observed by collision of metastable argon atoms with HN_3 he concluded that $\Delta_f H°$(NH, g) ≤ 94 kcal·mol^{-1}.

Quantum chemical calculation of the dissociation energy of small molecules is possible with estimated accuracies of 0.1 to 0.2 eV. A theoretical calculation of the dissociation energy of NH($X^3\Sigma^-$), applying the techniques of Wahl and Das[7] has been determined by Stevens[8] to yield D_e = 3.4 eV. This result corroborates the results of Seal and Gaydon and would support $\Delta_f H°$(NH, g) = 90 ± 4 kcal mol^{-1}. Theoretical calculations of this type can be used to distinquish between disparate experimental results that differ by more than 0.2 eV.

Heat Capacity and Entropy

The vibrational and rotational constants for the ground and excited states are taken from the sources indicated. The splitting between the $X^3\Sigma^-$ and $a^1\Delta$ states is based on the work of Gilles *et al.*[14] who observed the $b^1\Sigma^+$–$X^3\Sigma^-$ band in emission.

The thermodynamic functions are calculated using first-order anharmonic corrections to Q_r' and Q_v' in the partition function $Q = Q_n \Sigma Q_r' Q_v' g_e \exp(-c_2\epsilon_e/T)$. The National Bureau of Standards prepared this table[9] by critical analysis of data existing in 1972 using only the ground electronic state Using the molecular constants selected here and $\Delta_f H°$ selected by NBS,[9] we recalculate the table in terms of 1973 fundamental constants,[10] 1975 atomic weights[11] and current JANAF reference states for the elements.

References

[1] J. L. Franklin, V. H. Dibeler, R. M. Reese, and M. Krauss, J. Amer. Chem. Soc. 80, 298 (1958).
[2] R. I. Reed and W. Snedden, J. Chem. Soc. 4132 (1959).
[3] S N. Foner and R. L. Hudson, J. Chem. Phys. 45, 40 (1966).
[4] K. E. Seal and A. G. Gaydon, Proc. Phys. Soc 89, 459 (1966).
[5] W. E. Kaskan and M. P. Nadler, J. Chem. Phys. 56, 2220 (1972).
[6] D. H. Stedman, J Chem. Phys. 52, 3966 (1970).
[7] A. C. Wahl and G. Das, Advan. Quantum Chem. 5, 261 (1970).
[8] W. J. Stevens, J. Chem. Phys. 58, 1264 (1973).
[9] S. Abramowitz *et al.*, U. S. Nat. Bur. Stand. Report 10904, 239, (July 1972).
[10] CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, (December 1973).
[11] IUPAC Commission on Atomic Weights, Pure Appl. Chem. 47, 75 (1976); 37, 589 (1974).
[12] JANAF Thermochemical Tables, 2nd ed., NSRDS–NBS 37, (1971).
[13] B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, Oxford, (1970).
[14] A. Gilles, C. Vermeil, and J. Masanet, J. Photochem. 3, 417 (1974/75).
[15] J. Malicet, J. Brain, and H Guenebaut, J. Chim. Phys. 67, 25 (1970).
[16] F. L. Whittaker, J. Phys. B1, 977 (1968); Can. J. Phys. 47, 1291 (1969).
[17] N. A. Narasimham and G. Krishnamurty, Proc. Indian Acad. Sci. 64A, 97 (1966).

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	−8.617	376.511	376.511	INFINITE
100	29.126	149.428	207.157	−5.773	376.405	374.489	−195.613
200	29.133	169.618	183.918	−2.860	376.516	372.532	−97.295
250	29.140	176.119	181.732	−1.403	376.547	371.532	−77.627
298.15	29.147	181.253	181.253	0.	376.560	370.565	−64.921
300	29.147	181.433	181.253	0.054	376.560	370.528	−64.515
350	29.158	185.927	181.608	1.512	376.565	369.522	−55.148
400	29 175	189.821	182.397	2.970	376.565	368.515	−48.123
450	29.208	193.259	183.416	4.429	376.561	367.509	−42.659
500	29.263	196.339	184.557	5.891	376.555	366.504	−38.288
600	29.461	201.690	186.980	8.826	376.534	364 496	−31.732
700	29.787	206.254	189.415	11.787	376.505	362.492	−27.049
800	30.219	210.259	191.775	14.787	376.473	360.492	−23.538
900	30.722	213.847	194.032	17.834	376 444	358.496	−20.807
1000	31.258	217.111	196.179	20.933	376.421	356.503	−18.622
1100	31 798	220.116	198.220	24.085	376.406	354.512	−16 834
1200	32.325	222.906	200.162	27.292	376.399	352.522	−15.345
1300	32.825	225.513	202.013	30.549	376.399	350.532	−14.085
1400	33.294	227.963	203.780	33.856	376.407	348.542	−13 004
1500	33.730	230.275	205.470	37.207	376.420	346.552	−12.068
1600	34.134	232.465	207.089	40.601	376.438	344.560	−11.249
1700	34.507	234.546	208.644	44.033	376.461	342.567	−10.526
1800	34.852	236.528	210.138	47.501	376.488	340.572	−9.883
1900	35.173	238.421	211.577	51.003	376.518	338.576	−9.308
2000	35.473	240.233	212.965	54.535	376.551	336.578	−8.791
2100	35.755	241.970	214.305	58.097	376.587	334.579	−8.322
2200	36.021	243.640	215.601	61.685	376.627	332.578	−7.896
2300	36.274	245.247	216.855	65.300	376.670	330.574	−7.508
2400	36.516	246.796	218.071	68.940	376.716	328.569	−7.151
2500	36.749	248.291	219.250	72.603	376.766	326.562	−6.823
2600	36.975	249.737	220.395	76.290	376.820	324.553	−6.520
2700	37 194	251.136	221.508	79.998	376.879	322.541	−6.240
2800	37.407	252.493	222.590	83.728	376.942	320.528	−5.980
2900	37.616	253.809	223.644	87.479	377.010	318.512	−5.737
3000	37.821	255.088	224.671	91.251	377.084	316.493	−5.511
3100	38.022	256.331	225.672	95.043	377.163	314.472	−5.299
3200	38.220	257.542	226.649	98.855	377.247	312.449	−5.100
3300	38.416	258.721	227.603	102.687	377.338	310.423	−4.914
3400	38.609	259.870	228.536	106.538	377.435	308.393	−4.738
3500	38.799	260.992	229.447	110.409	377.538	306.361	−4.572
3600	38.988	262.088	230.339	114.298	377.648	304.326	−4 416
3700	39.175	263.159	231.211	118.206	377.764	302.288	−4.268
3800	39.360	264.206	232.066	122.133	377.886	300.246	−4.127
3900	39.543	265.231	232.903	126.078	378.015	298.201	−3.994
4000	39.725	266.234	233 724	130.042	378.151	296.153	−3.867
4100	39.905	267.217	234.529	134.023	378.294	294.102	−3.747
4200	40.084	268.181	235.319	138.023	378.443	292.046	−3.632
4300	40.262	269.126	236.094	142.040	378.599	289.987	−3.523
4400	40.439	270.054	236.855	146.075	378.763	287 925	−3.418
4500	40.615	270.965	237.603	150.128	378.933	285.858	−3.318
4600	40.789	271.859	238.338	154.198	379.110	283 788	−3.223
4700	40.963	272.738	239.061	158.286	379.295	281.714	−3.131
4800	41.136	273.603	239.771	162.391	379.486	279.636	−3 043
4900	41.309	274.453	240.470	166.513	379.686	277.553	−2.959
5000	41.480	275.289	241.158	170.652	379.893	275.467	−2.878
5100	41.652	276.112	241.836	174.809	380.108	273.376	−2.800
5200	41.823	276.922	242.503	178.983	380.331	271.281	−2.725
5300	41.993	277.721	243.160	183.173	380.563	269.182	−2.653
5400	42.164	278.507	243.807	187.381	380.803	267.078	−2.583
5500	42.334	279.283	244.445	191.606	381.053	264 970	−2.516
5600	42.504	280.047	245.074	195.848	381.312	262.857	−2.452
5700	42.674	280.801	245.694	200.107	381.581	260.740	−2.389
5800	42 844	281.544	246.306	204.383	381.861	258.617	−2.329
5900	43.015	282.278	246.909	208.676	382.151	256 490	−2.271
6000	43.185	283.003	247.505	212.986	382.451	254.357	−2.214

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

$S°(298.15\ K) = 220.722\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 102.501\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 99.579\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
2854.17(1)
1570 (1)
1110 (1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: C_s
Bond Distances: H–N = 1.020 ± 0.02 Å N=O = 1.239 ± 0.005 Å
Bond Angle. H–N=O = 114° 25' ± 2°
Product of the Moments of Inertia: $I_A I_B I_C = 5.939 \times 10^{-118}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°$(HNO, g, 298.15 K) is calculated from $D_0°$(H–NO) = 48.6 kcal·mol^{-1} reported by Clement and Ramsay.[1]

Heat Capacity and Entropy

Vibrational frequencies were assigned by Bancroft *et al.*[2] and Brown and Pimentel[3]. Bond distances and bond angles were taken from Bancroft *et al.*[2] The molecular constants given by Dalby[4] were: r(N=O) = 1.211$_6$ Å; r(N–H) = 1.0628 Å, and a H–N=O bond angle of 108.5$_8$°. The principal moments of inertia are: $I_A = 0.1262 \times 10^{-39}$, $I_B = 2.1070 \times 10^{-39}$, and $I_C = 2.2332 \times 10^{-39}$ g·cm^2.

References

[1]M. J. Y. Clement and D A. Ramsay, Can. J. Phys. 39, 205 (1961).
[2]J. L. Bancroft, J. M Hollas and D. A. Ramsay, Can. J. Phys. 40, 322 (1962).
[3]H. Brown and G. Pimentel, J. Chem. Phys. 29, 883 (1958).
[4]F. W. Dalby, Can. J. Phys. 36, 1336 (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	−9.988	102.501	102.501	INFINITE
100	33.258	184.104	250.730	−6.663	101.424	104.706	−54.693
200	33.451	207.183	223.843	−3.332	100.497	108.348	−28.298
250	33.911	214.691	221.288	−1.649	100.025	110.366	−23.060
298.15	34.640	220.722	220.722	0.	99.579	112.398	−19.692
300	34.673	220.937	220.723	0.064	99.562	112 478	−19.584
350	35.658	226.353	221.148	1.822	99.129	114 665	−17.113
400	36.768	231.186	222.106	3.632	98.733	116.912	−15.267
450	37.928	235.584	223.363	5.499	98.379	119.206	−13.837
500	39.085	239.640	224.790	7.425	98.065	121.538	−12.697
600	41.289	246.964	227.889	11.445	97.550	126.283	−10.994
700	43.281	253.481	231.087	15.675	97.162	131.104	−9.783
800	45.042	259.378	234.261	20.093	96.881	135.973	−8.878
900	46.583	264.774	237.356	24 676	96.686	140.872	−8.176
1000	47.922	269.753	240.350	29.403	96.560	145.789	−7.615
1100	49.081	274.376	243.235	34.255	96.489	150.716	−7.157
1200	50.083	278.691	246.012	39.214	96.460	155.647	−6.775
1300	50.948	282.734	248.683	44.267	96.464	160.580	−6.452
1400	51.697	286.538	251.252	49.400	96.491	165.511	−6.175
1500	52.346	290.128	253.726	54.603	96.535	170.439	−5.935
1600	52.911	293.524	256.108	59.866	96.590	175.364	−5.725
1700	53.403	296.747	258 404	65.183	96.651	180.286	−5.540
1800	53.834	299.812	260.620	70.545	96 714	185.204	−5.374
1900	54.213	302.733	262.761	75.948	96.776	190.118	−5.227
2000	54.548	305.523	264.829	81.386	96.834	195.029	−5.094
2100	54.843	308.191	266.831	86.856	96.886	199.938	−4.973
2200	55.106	310.749	268.770	92.354	96.930	204.844	−4.864
2300	55.341	313.204	270.649	97.876	96.965	209.748	−4.764
2400	55.550	315.563	272.471	103.421	96.990	214.651	−4.672
2500	55 739	317.835	274.241	108.986	97.004	219.553	−4.587
2600	55.908	320.024	275.960	114.568	97.006	224.455	−4.509
2700	56.061	322.137	277.631	120.167	96.996	229.358	−4.437
2800	56.200	324.179	279.257	125.780	96.974	234.260	−4.370
2900	56.326	326.153	280.840	131.406	96.938	239.164	−4.308
3000	56.440	328.064	282.383	137.045	96.890	244.069	−4.250
3100	56.545	329.917	283.887	142.694	96.828	248.976	−4.195
3200	56.641	331.714	285.353	148.353	96.753	253.885	−4.144
3300	56.729	333.458	286.785	154.022	96.665	258.797	−4.096
3400	56.809	335.153	288.182	159.699	96.564	263.711	−4.051
3500	56.884	336.801	289.548	165.384	96.449	268.629	−4.009
3600	56.953	338.404	290.883	171.075	96.322	273.550	−3.969
3700	57.016	339.965	292.189	176.774	96.181	278.475	−3.931
3800	57.075	341.487	293.466	182.478	96.027	283.404	−3.896
3900	57.130	342.970	294.716	188.189	95.860	288.337	−3.862
4000	57.180	344.417	295.941	193.904	95.681	293.275	−3.830
4100	57.228	345.829	297.140	199.625	95.488	298.217	−3.799
4200	57.272	347.209	298.316	205.350	95.282	303.164	−3.770
4300	57.313	348.557	299.469	211.079	95.063	308.116	−3.743
4400	57.352	349.875	300.600	216.812	94.832	313.073	−3.717
4500	57.388	351.164	301.709	222.549	94.587	318.036	−3 692
4600	57.422	352.426	302.798	228.290	94.330	323.004	−3.668
4700	57.454	353.661	303.867	234.034	94.059	327.978	−3.645
4800	57.484	354.871	304.917	239.780	93.775	332.959	−3.623
4900	57.512	356.057	305.949	245.530	93.478	337.945	−3.603
5000	57.539	357.219	306.963	251.283	93.168	342.937	−3.583
5100	57.564	358.359	307.959	257.038	92.844	347.936	−3.564
5200	57.587	359.477	308.939	262.796	92.507	352.940	−3.545
5300	57.610	360.574	309.903	268.555	92.157	357.953	−3.528
5400	57.631	361.651	310.851	274.317	91.792	362.971	−3.511
5500	57.651	362.709	311.785	280.082	91.414	367.996	−3.495
5600	57.670	363.748	312.703	285.848	91.022	373.028	−3.479
5700	57.688	364.768	313.608	291.616	90.615	378.068	−3.465
5800	57.705	365.772	314.499	297.385	90.195	383.115	−3.450
5900	57.722	366.759	315.376	303.157	89.759	388.168	−3.437
6000	57.737	367.729	316.241	308.930	89.309	393.230	−3.423

PREVIOUS. March 1963 (1 atm) CURRENT: March 1963 (1 bar)

Nitrous Acid, Cis (HNO_2) — IDEAL GAS — M_r = 47.01344 — Nitrous Acid, Cis (HONO) — $H_1N_1O_2$(g)

$S°(298.15\ K) = 249.416\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -70.509 \pm 1.34\ kJ·mol^{-1}$
$\Delta_f H°(298\ 15\ K) = -76.735 \pm 1.34\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
3462(1)	855(1)
1639(1)	525(1)
1330(1)	638(1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: C_s
Bond Distances: O–N = 1.20 Å N–O' = 1.46 Å O–H = 0.98 Å
Bond Angles: O–N–O' = 114° N–O'–H = 103°
Product of the Moments of Inertia: $I_A I_B I_C = 5.51348 \times 10^{-116}\ g^3·cm^6$

Enthalpy of Formation

Ashmore and Tyler[1] reported $\Delta_f H°(298.15\ K) = -9.06 \pm 0.32\ kcal·mol^{-1}$ for the reaction. $NO(g) + NO_2(g) + H_2O(g) = 2\ HNO_2(g)$, yielding $\Delta_f H°(298\ 15\ K) = -18.57 \pm 0.20\ kcal·mol^{-1}$ for $HNO_2(g)$. Jones *et al* [2] estimated the difference in energy of cis– and trans– $HNO_2(g)$ to be $506 \pm 250\ cal·K^{-1}·mol^{-1}$. Hence the value of $\Delta_f H°(298.15\ K)$ for cis–$HNO_2(g)$ was calculated.

The heat of reaction and the equilibrium constants for the formation of $HNO_2(g)$ have been calculated by Karavaev and Skvortsov.[3] The value of $\Delta_f H°(298.15\ K)$ reported is $-18.8\ kcal·mol^{-1}$. However, based on the enthalpy of formation of liquid HNO_2, Ashmore and Levitt[4] give $\Delta_f H° = -13.7\ kcal·mol^{-1}$ The corresponding value reported by Rosser and Wise[5] is $-20.0\ kcal\ mol^{-1}$, based on the experimental data of Wayne and Yost,[6] and the entropy of the equilibrium mixture of the trans– and cis– $HNO_2(g)$ calculated by Jones, *et al.*[2]

Heat Capacity and Entropy

Vibrational frequencies, bond distances, and bond angles were obtained from Dor and Tarte[7] and Jones *et al.*[2] The principal moments of inertia are: $I_A = 1\ 0282 \times 10^{-39}$, $I_B = 6.8267 \times 10^{-39}$, and $I_C = 7.8549 \times 10^{-39}\ g·cm^2$.

References

[1]P. G. Ashmore and B. J. Tyler, J. Chem. Soc. 1017 (1961).
[2]L. H. Jones, R. M. Badger and G. E. Moore, J. Chem. Phys. 19, 1599 (1951).
[3]M M. Karavaev and G. A. Skvortsov, Russ. J. Phys. Chem. 36, 566 (1962).
[4]P. G. Ashmore and B. P. Levitt, Trans. Faraday Soc. 53, 945 (1957).
[5]W. A. Rosser and H. Wise, J. Chem. Phys. 26, 571 (1957).
[6]L. G. Wayne and D. M. Yost, J. Chem. Phys. 19, 41 (1951).
[7]L. Dor and P. Tarte, Bull. Soc. Roy. Sci. Lg. 478 (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	−11.026	−70.509	−70.509	INFINITE
100	33.585	208.174	285.140	−7.697	−73.034	−63.494	33.166
200	38.653	232.718	253.350	−4.126	−75.178	−53.084	13.864
250	42.127	241.717	250.144	−2.107	−76.042	−47.458	9.916
298.15	45.354	249.416	249.416	0	−76.735	−41.888	7.339
300	45.473	249.696	249.416	0.084	−76.759	−41.672	7.256
350	48.560	256.942	249.982	2.436	−77.336	−35.776	5.339
400	51.357	263.612	251.274	4.935	−77.790	−29.807	3.892
450	53.870	269.809	252.993	7.567	−78.138	−23.787	2.761
500	56.115	275 603	254.967	10.318	−78.398	−17.733	1.853
600	59.904	286.182	259.305	16.126	−78.705	−5.568	0.485
700	62.943	295.652	263.833	22.273	−78.802	6.632	−0.495
800	65.424	304.225	268.355	28.696	−78.748	18.835	−1.230
900	67.490	312.053	272.782	35.344	−78.580	31.024	−1.801
1000	69.236	319.257	277.074	42.183	−78.326	43.189	−2.256
1100	70.730	325.928	281.215	49.183	−78.003	55.325	−2.627
1200	72.017	332.138	285.203	56.322	−77.626	67.430	−2.935
1300	73 133	337.948	289.039	63.581	−77.208	79.501	−3.194
1400	74.105	343.404	292.730	70.944	−76.757	91.539	−3.415
1500	74.955	348.546	296.281	78.398	−76.283	103.543	−3.606
1600	75.700	353.408	299.701	85.931	−75.791	115.516	−3.771
1700	76.356	358.018	302.997	93.535	−75.289	127.457	−3.916
1800	76.935	362.399	306.176	101.200	−74.781	139.369	−4.044
1900	77.448	366.572	309.246	108.920	−74.272	151.252	−4.158
2000	77.904	370.557	312.213	116.688	−73.766	163.109	−4.260
2100	78.311	374.368	315.083	124.499	−73.266	174.940	−4.351
2200	78.675	378.019	317.861	132.349	−72.774	186.749	−4.434
2300	79.001	381.524	320.553	140.233	−72.292	198.534	−4.509
2400	79.294	384.892	323.164	148.148	−71.823	210.298	−4.577
2500	79.558	388.135	325.699	156.091	−71.369	222.044	−4.639
2600	79.797	391.260	328.160	164.059	−70.929	233.772	−4.697
2700	80.014	394.276	330.554	172.049	−70.506	245.483	−4.749
2800	80.212	397.189	332.882	180.061	−70.099	257.179	−4.798
2900	80.391	400.007	335.148	188.091	−69.709	268.860	−4.843
3000	80.556	402.735	337.356	196.139	−69.337	280.529	−4.884
3100	80.706	405.379	339.508	204.202	−68.983	292.186	−4.923
3200	80.844	407.944	341.606	212.279	−68.646	303.830	−4.960
3300	80.971	410.433	343.655	220.370	−68.327	315.465	−4.993
3400	81.088	412.852	345.654	228.473	−68.026	327.091	−5.025
3500	81.196	415.204	347.608	236.587	−67.743	338.707	−5.055
3600	81.296	417.493	349.518	244.712	−67.478	350.317	−5.083
3700	81.388	419 722	351.385	252.846	−67.230	361.918	−5.109
3800	81.474	421.894	353.212	260.990	−66.999	373.515	−5.134
3900	81.554	424.011	355.000	269.141	−66.786	385.105	−5.158
4000	81.628	426.077	356.752	277.300	−66.590	396.688	−5.180
4100	81.698	428.093	358.467	285.466	−66.411	408.268	−5.201
4200	81.762	430.063	360.149	293.640	−66.249	419.844	−5.222
4300	81.823	431.987	361.797	301.819	−66.105	431.416	−5.241
4400	81.880	433.869	363.414	310.004	−65.977	442.984	−5.259
4500	81.933	435.710	365.000	318.195	−65.867	454.550	−5.276
4600	81.983	437.511	366.557	326.391	−65.775	466.113	−5.293
4700	82.030	439.275	368.085	334.591	−65.700	477.676	−5.309
4800	82.074	441.002	369.586	342.796	−65.643	489.236	−5.324
4900	82.116	442.695	371.061	351.006	−65.604	500.796	−5.339
5000	82.155	444.354	372.510	359.220	−65.583	512.355	−5.353
5100	82.192	445.982	373.935	367.437	−65.582	523.914	−5.366
5200	82.227	447.578	375.336	375.658	−65.600	535.472	−5.379
5300	82.261	449.145	376.714	383.882	−65.637	547.033	−5.391
5400	82.292	450.682	378.069	392.110	−65.696	558.592	−5.403
5500	82.322	452.193	379.403	400.341	−65.774	570.153	−5.415
5600	82.350	453.676	380.717	408.574	−65.874	581.718	−5.426
5700	82.377	455.134	382.009	416.811	−65.997	593.282	−5.437
5800	82.403	456.567	383.283	425.050	−66.142	604.851	−5.447
5900	82.427	457.976	384.537	433.291	−66.311	616.419	−5.457
6000	82.450	459.361	385.772	441.535	−66.504	627.993	−5.467

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

$S°(298.15\ K) = 249.261\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -72.674 \pm 1.34\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -78.827 \pm 1.34\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
3590(1)	794(1)
1696(1)	598(1)
1260(1)	543(1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: C_s
Bond Distances: O–N = 1.20 Å N–O' = 1.46 Å O'–H = 0.98 Å
Bond Angles: O–N–O' = 118° N–O'–H = 105°
Product of the Moments of Inertia: $I_A I_B I_C = 4.91660 \times 10^{-116}\ g^3·cm^6$

Enthalpy of Formation

Ashmore and Tyler[1] reported $\Delta_f H°(298.15\ K) = -9.06 \pm 0.32\ kcal·mol^{-1}$ for the reaction $NO(g) + NO_2(g) + H_2O(g) \rightarrow 2HNO_2\ (g)$, yielding $\Delta_f H°(298.15\ K) = -18.57 \pm 0.20\ kcal·mol^{-1}$ for HNO_2(g). Jones *et al.*[2] estimated the difference in energy of cis– and trans–HNO_2(g) to be 506 ± 250 $cal·K^{-1}·mol^{-1}$. Hence the value of $\Delta_f H°(298.15\ K)$ for trans–HNO_2(g) was calculated.

The heat of reaction and the equilibrium constants for the formation of HNO_2(g) have been calculated by Karavaev and Skvortsov.[3] The value of $\Delta_f H°(298.15\ K)$ reported is $-18.8\ kcal·mol^{-1}$. However, based on the enthalpy of formation of liquid HNO_2, Ashmore and Levitt[4] give $\Delta_f H° = -13.7\ kcal·mol^{-1}$. The corresponding value reported by Rosser and Wise[5] is $-20.0\ kcal·mol^{-1}$, based on the experimental data of Wayne and Yost[6] and the entropy of the equilibrium mixture of the trans– and cis– HNO_2(g) calculated by Jones *et al.*[2]

Heat Capacity and Entropy

Vibrational frequencies, bond distances, and bond angles were taken from Jones *et al.*[2] The values of vibrational frequencies were in good agreement to those reported by Dor and Tarte.[7] The principal moments of inertia are: $I_A = 0.7855 \times 10^{-39}$, $I_B = 7.5286 \times 10^{-39}$, and $I_C = 8.3141 \times 10^{-39}\ g·cm^2$.

References

[1]P. G. Ashmore and B. J. Tyler, J. Chem. Soc. 1017 (1961).
[2]L. H. Jones, R. M. Badger and G. E. Moore, J. Chem. Phys. 19, 1599 (1951).
[3]M. M. Karavaev and G. A. Skvortsov, Russ. J. Phys. Chem. 36, 566 (1962).
[4]P. G. Ashmore and B. P. Levitt, Trans. Faraday Soc. 53, 945 (1957).
[5]W. A. Rosser and H. Wise, J. Chem. Phys. 26, 571 (1957).
[6]L. G. Wayne and D. M. Yost, J. Chem. Phys. 19, 41 (1951).
[7]L. Dor and P. Tarte, Bull. Soc. Roy. Sci. Lg. 478 (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	−11.099	−72.674	−72.674	INFINITE
100	33.588	207.696	285.389	−7.769	−75.199	−65.611	34.272
200	39.045	232.339	253.252	−4.183	−77.326	−55.157	14.405
250	42.718	241.447	250.001	−2.138	−78.165	−49.514	10.345
298.15	46.051	249.261	249.261	0.	−78.827	−43.934	7.697
300	46.173	249.546	249.262	0.085	−78.849	−43.717	7.612
350	49.290	256.902	249.835	2.473	−79.391	−37.817	5.644
400	52.066	263.669	251.147	5.009	−79.809	−31.848	4.159
450	54.528	269.946	252.891	7.675	−80.123	−25.833	2.999
500	56.707	275.807	254.893	10.457	−80.351	−19.788	2.067
600	60.354	286.481	259.286	16.317	−80.606	−7.648	0.666
700	63.260	296.011	263.864	22.503	−80.665	4.519	−0.337
800	65.628	304.618	268.429	28.951	−80.585	16.683	−1.089
900	67.601	312.465	272.892	35.615	−80.402	28.832	−1.673
1000	69.275	319.676	277.215	42.461	−80.139	40.956	−2.139
1100	70.713	326.348	281.382	49.462	−79.816	53.050	−2.519
1200	71.959	332.555	285.391	56.597	−79.443	65.113	−2.834
1300	73.046	338.359	289.245	63.849	−79.032	77.143	−3.100
1400	73.998	343.808	292.949	71.202	−78.591	89.140	−3.326
1500	74.835	348.943	296.513	78.645	−78.128	101.104	−3.521
1600	75.572	353.796	299.943	86.166	−77.649	113.037	−3.690
1700	76.224	358.398	303.247	93.756	−77.160	124.940	−3.839
1800	76.802	362.771	306.433	101.408	−76.665	136.814	−3.970
1900	77.316	366.938	309.509	109.115	−76.170	148.661	−4.087
2000	77.774	370.916	312.481	116.870	−75.676	160.481	−4.191
2100	78.184	374.720	315.355	124.668	−75.189	172.277	−4.285
2200	78.551	378.366	318.136	132.505	−74.709	184.050	−4.370
2300	78.881	381.865	320.832	140.377	−74.240	195.801	−4.447
2400	79.179	385.229	323.445	148.280	−73.783	207.532	−4.517
2500	79.448	388.466	325.982	156.212	−73.340	219.244	−4.581
2600	79.692	391.587	328 445	164.169	−72.911	230.939	−4.640
2700	79.913	394.599	330.840	172.149	−72.498	242.618	−4.694
2800	80.115	397.509	333.169	180.151	−72.101	254.282	−4.744
2900	80.298	400.324	335.437	188.172	−71.720	265.931	−4.790
3000	80.467	403.049	337.645	196.210	−71.358	277.568	−4.833
3100	80.621	405.690	339.798	204.264	−71.012	289.194	−4.873
3200	80 763	408.252	341.897	212.334	−70.684	300.807	−4.910
3300	80.893	410.739	343.946	220.417	−70.373	312.411	−4.945
3400	81.013	413.156	345.946	228.512	−70.080	324.007	−4.978
3500	81.124	415.506	347.900	236.619	−69.804	335.593	−5.008
3600	81.227	417.792	349.810	244.737	−69.545	347.172	−5.037
3700	81.323	420.019	351.678	252.864	−69.304	358.744	−5.065
3800	81.411	422.189	353.505	261.001	−69.080	370.311	−5.090
3900	81.494	424.305	355.293	269.146	−68.873	381.871	−5.115
4000	81.570	426.369	357.044	277.299	−68.683	393.426	−5.138
4100	81.642	428.384	358.760	285.460	−68.509	404.976	−5.159
4200	81.709	430.352	360.441	293.628	−68.353	416.523	−5.180
4300	81.772	432.276	362.089	301.802	−68.214	428.066	−5.200
4400	81.830	434.156	363.706	309.982	−68.092	439.606	−5.219
4500	81.885	435.996	365.292	318.168	−67.986	451.143	−5.237
4600	81.937	437.796	366.849	326.359	−67.898	462.677	−5.254
4700	81.986	439.559	368.377	334.555	−67.828	474.211	−5.270
4800	82.032	441.286	369.878	342.756	−67.775	485.744	−5.286
4900	82.075	442.977	371.353	350.961	−67.740	497.275	−5.301
5000	82.115	444.636	372.802	359.171	−67.724	508.806	−5.315
5100	82.154	446.262	374.226	367.384	−67.727	520.337	−5.329
5200	82.190	447.858	375.627	375.602	−67.748	531.867	−5.343
5300	82.225	449.424	377.005	383.822	−67.789	543.399	−5.356
5400	82.257	450.961	378.360	392.046	−67.851	554.931	−5.368
5500	82.288	452.471	379.694	400.274	−67.933	566.464	−5.380
5600	82.318	453.954	381.007	408.504	−68.037	578.001	−5.391
5700	82.346	455.411	382.299	416.737	−68.162	589.538	−5.403
5800	82.372	456.843	383.572	424.973	−68.311	601.078	−5.413
5900	82.397	458.252	384.826	433.212	−68.482	612.619	−5.424
6000	82.421	459.637	386.061	441.453	−68.679	624.166	−5.434

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

$S°(298.15\ K) = 266.400\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -124.492 \pm 0.42\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -134.306 \pm 0.42\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1320(1)	765(1)
886(1)	3560(1)
680(1)	1335(1)
1710(1)	465(1)
583(1)	

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: C_s
Bond Distances: O–N = 1.206 ± 0.005 N–O' = 1.405 ± 0.005 O–H = [0.96]
Bond Angles. O–N–O = 130° ± 20' N–O' H = 102° ± 30'
Product of the Moments of Inertia: $I_A I_B I_C = 5.988123 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was taken from.[1] Equilibria involving HNO_3 were measured by Jones,[2] Feick,[3] and Abel, *et al.*,[4] yielding $\Delta_f H° = -32.06$, -32.02, and -32.09 kcal·mol$^-$, respectively. Becker and Roth[5] and Thomsen[6] measured the enthalpy of neutralization of HNO_3(aq) with NH_3, combining these values with the data for NH_4NO_3 yields $\Delta_f H° = -32.27$ and $-32\ 07$ kcal·mol^{-1}. Berthelot[7] measured the enthalpy of reaction of N_2O_4(g) and Cl_2(g), obtaining $\Delta_f H° = -32.10$ kcal·mol^{-1} The value of $\Delta_f H°(298.15\ K)$ reported by Forsythe and Giauque[8] was -31.994 kcal·mol^{-1}. The value adopted is the weighted average of these six values.

Heat Capacity and Entropy

Vibrational frequencies were obtained from Palm and Kilpatrick.[9] Bond distances and bond angles were taken from Millen and Morton.[10] The basic parameters of HNO_3(g) reported by Akishin *et al.*[1] were. r(N=O) = 1.22 ± 0.01 ; r(N–O) = 1.40 ± 0.01 A, and the bond angle (O–N–O) = 135° ± 2.5°. Forsythe and Giauque[8] have calculated the absolute entropy of pure nitric acid (g) from calorimetric data. The value obtained was $S°(298\ 15\ K) = 63.62$ cal·K^{-1}·mol^{-1}. The entropy of nitric acid vapor at 298.15 K has also been computed by Cohn *et al.*[9] to be 63 70 cal·K^{-1}·mol^{-1}. The prinicpal moments of inertia are $I_A = 6.3868 \times 10^{-39}$, $I_B = 7.0025 \times 10^{-39}$, and $I_C = 13.3893 \times 10^{-39}$ g·cm^2.

References

[1]D. D. Wagman, U. S. Nat. Bur Stand. Report 7437, Chapter B4, 83, (January 1, 1962).
[2]E. J. Jones, J Amer. Chem. Soc. 65, 2274 (1943).
[3]G. Feick, J. Amer. Chem. Soc. 76, 5858 (1954).
[4]H. E. Abel, H. Schmid, and M. Stein Wien, Z. Elektrochem. 36, 692 (1930).
[5]G. Becker and W A. Roth, Z. Elektrochem. 40, 836 (1934).
[6]J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipsiz, 1882–1886.
[7]M. Berthelot, "Sur la Force des Matieres Explosives," 3rd ed., Paris, (1883).
[8]W. R. Forsythe and W. F. Giauque, J Amer. Chem. Soc. 64, 48 (1942).
[9]A. Palm and M. Kilpatrick, J Chem. Phys. 23, 1562 (1955).
[10]D. J. Millen and J R Morton, J Chem. Soc. 1523 (1960).
[11]P. A. Akishin, L. V. Vilkov and V. Y. Rosolovskii, Zhur Strukt. Khim. 1, 1 (1960).
[12]H Cohn, C. K. Ingold, and H. G. Poole, J. Chem. Soc 4272 (1952).

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	−11.780	−124.492	−124.492	INFINITE
100	33.920	221.800	306.248	−8.445	−128.465	−111.622	58.305
200	42.298	247.433	270.926	−4.699	−131.888	−93.389	24.391
250	48.008	257.484	267.248	−2.441	−133.243	−83.602	17.468
298.15	53.336	266.400	266.400	0.	−134.306	−73.941	12.954
300	53.534	266.730	266.401	0.099	−134.343	−73.567	12.809
350	58.618	275.371	267.072	2.905	−135.205	−63.366	9.457
400	63.190	283.502	268.622	5.952	−135.858	−53.057	6.928
450	67.252	291.185	270.706	9.215	−136.333	−42.676	4.954
500	70.836	298.460	273.121	12.669	−136.660	−32.251	3.369
600	76.765	311.922	278.485	20.062	−136.963	−11.334	0.987
700	81.382	324 116	284.147	27.979	−136.918	9.605	−0.717
800	85.039	335.231	289.848	36.306	−136.627	30.519	−1.993
900	87.994	345.424	295.465	44.963	−136.154	51.386	−2.982
1000	90.425	354.824	300.937	53.888	−135.544	72.192	−3.771
1100	92.455	363.541	306.237	63.035	−134.829	92.932	−4.413
1200	94.172	371 661	311.354	72.368	−134.032	113.603	−4.945
1300	95.636	379.258	316.289	81.861	−133.172	134.204	−5.392
1400	96.895	386.393	321.044	91.489	−132.263	154.738	−5.773
1500	97.984	393.116	325.627	101.234	−131.318	175.205	−6.101
1600	98.931	399.471	330.045	111.081	−130.347	195.608	−6.386
1700	99.758	405.494	334.308	121.016	−129.358	215.950	−6.635
1800	100.485	411.217	338.423	131.029	−128.361	236.233	−6.855
1900	101.125	416.667	342.399	141.110	−127.360	256.461	−7.051
2000	101.692	421.869	346.243	151.252	−126.362	276.637	−7.225
2100	102.196	426.843	349.964	161.447	−125.370	296.762	−7.382
2200	102.645	431.608	353.567	171.689	−124.389	316.842	−7.523
2300	103.047	436.179	357.060	181.974	−123.423	336.875	−7.651
2400	103.407	440.573	360.449	192.297	−122.472	356.867	−7.767
2500	103.732	444.801	363.739	202.654	−121.541	376.821	−7.873
2600	104.025	448.875	366.936	213.042	−120.629	396.737	−7.971
2700	104.291	452.806	370.044	223.458	−119.739	416.619	−8.060
2800	104.532	456.603	373.068	233.900	−118.871	436.469	−8.142
2900	104.751	460.275	376.012	244.364	−118.026	456.286	−8.219
3000	104.952	463.830	378.880	254.849	−117.205	476.076	−8.289
3100	105.135	467.274	381.676	265.354	−116.407	495.840	−8.355
3200	105.303	470.615	384.404	275.876	−115.633	515.576	−8.416
3300	105.457	473.858	387.066	286.414	−114.882	535.290	−8.473
3400	105.599	477.008	389.665	296.967	−114.155	554.982	−8.526
3500	105.731	480.071	392.204	307.534	−113.452	574.651	−8.576
3600	105.852	483.051	394.687	318.113	−112.771	594.302	−8.623
3700	105.964	485 953	397.114	328.704	−112.114	613.933	−8.667
3800	106.069	488.780	399.489	339.305	−111.479	633.549	−8.709
3900	106.165	491.537	401.814	349.917	−110.866	653.147	−8.748
4000	106.256	494.226	404.091	360.538	−110.276	672.729	−8.785
4100	106.340	496.851	406.322	371.168	−109.708	692.297	−8.820
4200	106.418	499.414	408.508	381.806	−109.162	711.851	−8.853
4300	106.492	501.919	410.651	392.451	−108.638	731.394	−8.885
4400	106.560	504.368	412.753	403.104	−108.136	750.923	−8.915
4500	106.625	506.763	414.816	413.763	−107.657	770.441	−8.943
4600	106.685	509.108	416.840	424.429	−107.199	789.948	−8.970
4700	106.742	511.403	418.828	435.100	−106.765	809.447	−8.996
4800	106.796	513.650	420.780	445.777	−106.354	828.937	−9.021
4900	106.846	515.853	422.698	456.459	−105.966	848.419	−9.044
5000	106.894	518.012	424.583	467.146	−105.603	867.893	−9.067
5100	106.938	520.129	426.436	477.838	−105.264	887.360	−9.088
5200	106.981	522.206	428.257	488.534	−104.951	906.818	−9.109
5300	107.021	524.244	430.049	499.234	−104.665	926.274	−9.129
5400	107.059	526.245	431.812	509.938	−104.406	945.722	−9.148
5500	107.095	528.210	433.547	520.646	−104.174	965.166	−9.166
5600	107.129	530.140	435.255	531.357	−103.973	984.608	−9.184
5700	107 162	532.036	436.936	542.072	−103.801	1004.045	−9.201
5800	107.193	533.900	438.592	552.789	−103.662	1023.481	−9.217
5900	107.222	535 733	440.223	563.510	−103.555	1042.911	−9.233
6000	107.250	537.535	441.830	574.234	−103.482	1062.343	−9.249

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

$\Delta_f H°(0\ K) = -52\ 021 \pm 0\ 08\ kJ·mol^{-1}$

$S°(298.15\ K) = 40.016\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298\ 15\ K) = -56.442 \pm 0.08\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was obtained from Gunn and Green.[1] The value of $\Delta_f H°(298.15\ K)$ reported by Messer *et al.*[2] was 13.60 ± 0.27 kcal·mol^{-1} which is in excellent agreement with the value given by Gunn and Green.[1] The results of the previous investigations were also reviewed by Messer, *et al.*[2]

Heat Capacity and Entropy

$C_p°$ below 350 K were measured by Westrum, *et al.*[3] $C_p°$ above 350 K were estimated by comparison with those for LiH(cr). $C_p°$ (59.94–91 84 K) were also measured by Sayre and Beaver.[4] $S°(T)$ at 100, 200, and 298.15 K were taken from Westrum *et al.*[3] using the extrapolated value $S°(10\ K) = 0.008\ cal·K^{-1}·mol^{-1}$.

Decomposition Data

T_{dcm} was estimated from the value of $\Delta_f G°$ in the table. The table of T_{dcm} given by Banus *et al.*[5] was 940 K. It was assumed that NaH would behave similarly to LiH and that decomposition pressures would be purity dependent, and this would produce apparently high decomposition temperatures.

References

[1]S. R Gunn and L G. Green, J Amer. Chem. Soc. 80, 4782 (1958).
[2]C E. Messer, L. G. Fasolino and C E. Thalmayer, J Amer. Chem. Soc. 77, 4524 (1955).
[3]E. F. Westrum, *et al.*, University of Michigan, Ann Arbor, Michigan, personal communication, (May 19, 1960).
[4]E. V. Sayre and J J. Beaver, J Chem. Phys. 18, 584 (1950).
[5]D M. Banus, J J McSharry and E. A. Sullivan, J Amer. Chem. Soc 77, 2007 (1955).

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	−6.259	−52.021	−52.021	INFINITE
100	17.497	11.560	66.580	−5.502	−54.103	−47.841	24.990
200	28.234	27.125	43.108	−3.197	−55.600	−40.945	10.694
298.15	36.392	40.016	40.016	0.	−56.442	−33.551	5.878
300	36.535	40.241	40.016	0.067	−56.454	−33.408	5.817
400	42.468	51 636	41.530	4.043	−59.553	−25.444	3.323
500	47.154	61.637	44.571	8.533	−59.625	−16.897	1.765
600	50.710	70.557	48.172	13.431	−59.208	−8.384	0.730
700	53.723	78.609	51.955	18.658	−58.402	0.028	−0.002
800	56.066	85.940	55.751	24.151	−57.294	8 303	−0.542
900	57.948	92.657	59.484	29.855	−55.965	16.425	−0.953
1000	59.413	98.840	63.115	35.725	−54.484	24.390	−1.274
1100	60 668	104.563	66.626	41.731	−52.906	32.201	−1.529
1200	61.641	109.885	70.012	47.848	−148.038	42.307	−1.842
1300	62.425	114.851	73.272	54.053	−145.472	58.065	−2.333
1400	63.021	119.501	76.410	60.327	−142.859	73.624	−2.747
1500	63.429	123.864	79.430	66.651	−140.218	88.995	−3.099

PREVIOUS: CURRENT: March 1963

Sodium Hydride (NaH) IDEAL GAS M_r = 23.99771 Sodium Hydride (NaH) $H_1Na_1(g)$

$S°(298\ 15\ K) = 188.387\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 126.21 \pm 19.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 124.26 \pm 19.2\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 1172.2\ cm^{-1}$ $\omega_e x_e = 19.72\ cm^{-1}$ $\alpha = 1$
$B_e = 4.9012\ cm^{-1}$ $\alpha_e = 0.1353\ cm^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from $D_0° = 2.05 \pm 0.2$ eV reported by Gaydon.[1]

Heat Capacity and Entropy

All molecular and spectroscopic constants were obtained from Herzberg.[2]

References

[1]A. G Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall Ltd., London, (1953).
[2]G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand, Inc., New York, (1950).

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	−8.731	126.214	126.214	INFINITE
100	29 136	156.294	214.684	−5.839	126.267	118.055	−61 666
200	29.333	176.522	191.121	−2.920	125.384	110.160	−28 771
250	29.724	183.105	188.882	−1 444	124.836	106.416	−22.234
298.15	30.293	188.387	188.387	0.	124.265	102.919	−18.031
300	30.318	188.575	188.388	0.056	124.242	102.787	−17.897
350	31.023	193.300	188.759	1.589	123.598	99.261	−14.814
400	31.753	197.490	189.594	3.159	120.270	96.037	−12.541
450	32.453	201.271	190.684	4.764	119.583	93.050	−10.801
500	33.098	204.725	191.918	6.403	118.952	90.136	−9.416
600	34.191	210.860	194.577	9.770	117.838	84.481	−7.355
700	35.047	216.197	197.292	13.233	116.880	78.999	−5.895
800	35.716	220.923	199.956	16.773	116.035	73.646	−4.809
900	36.249	225.161	202.525	20.372	115.259	68.395	−3.970
1000	36.681	229.003	204.984	24.019	114.517	63.227	−3.303
1100	37.039	232.517	207.330	27.706	113.776	58.134	−2.761
1200	37.344	235.753	209.565	31.425	16.246	55.549	−2.418
1300	37.608	238.753	211.696	35.173	16.355	58.820	−2.363
1400	37.840	241.549	213.730	38.946	16.467	62.083	−2.316
1500	38.049	244.166	215.673	42.741	16.579	65.337	−2.275
1600	38.239	246.628	217.531	46.555	16.689	68.584	−2.239
1700	38.414	248.952	219.312	50.388	16.796	71.824	−2.207
1800	38.577	251.152	221.020	54.237	16.900	75.058	−2.178
1900	38.730	253.242	222.662	58.103	16.999	78.286	−2.152
2000	38.876	255.232	224.241	61.983	17.094	81.510	−2.129
2100	39.015	257.132	225.762	65.878	17.185	84.728	−2.107
2200	39.148	258.950	227.230	69.786	17.272	87.942	−2.088
2300	39.277	260.694	228.647	73.707	17.353	91.153	−2.070
2400	39.402	262.368	230.017	77.641	17.430	94.360	−2.054
2500	39.524	263.979	231.344	81.588	17.500	97.564	−2.038
2600	39.644	265.531	232.629	85.546	17.565	100.765	−2.024
2700	39.760	267.030	233.876	89.516	17.623	103.964	−2.011
2800	39.875	268.478	235.086	93.498	17.674	107.161	−1.999
2900	39.988	269.879	236.261	97.491	17.715	110.356	−1.988
3000	40.099	271.237	237.405	101.496	17.747	113.550	−1.977
3100	40.209	272.553	238.517	105.511	17.768	116.743	−1.967
3200	40.318	273.831	239.601	109.537	17.777	119.935	−1.958
3300	40.426	275.074	240.657	113.575	17.772	123.128	−1.949
3400	40.533	276.282	241.687	117.623	17.752	126.321	−1.941
3500	40.639	277.459	242.693	121.681	17 715	129.514	−1.933
3600	40.744	278.605	243.674	125.750	17.658	132.709	−1.926
3700	40.848	279.723	244.634	129.830	17.581	135.906	−1.919
3800	40.952	280.814	245.571	133.920	17.481	139.106	−1.912
3900	41.056	281.879	246.489	138.020	17.355	142.308	−1.906
4000	41.158	282.919	247.387	142.131	17.202	145.513	−1.900
4100	41.261	283.937	248.266	146.252	17.019	148.724	−1.895
4200	41.363	284.932	249.127	150.383	16.805	151.938	−1.890
4300	41.464	285.907	249.971	154.525	16.555	155.159	−1.885
4400	41.566	286.861	250.799	158.676	16.309	158.382	−1.880
4500	41.667	287.797	251.610	162.838	16.003	161.613	−1.876
4600	41.768	288.713	252.407	167.009	15.649	164.853	−1.872
4700	41.868	289.613	253.189	171.191	15.253	168.101	−1.868
4800	41.968	290.495	253.957	175.383	14.811	171.357	−1.865
4900	42.068	291.362	254.712	179.585	14.322	174.624	−1.862
5000	42.168	292.213	255.453	183.797	13.791	177.900	−1.859
5100	42.268	293.049	256.182	188.018	13.201	181.188	−1.856
5200	42.367	293.870	256.899	192.250	12.556	184.488	−1.853
5300	42.466	294.678	257.604	196.492	11.854	187.801	−1.851
5400	42.566	295.473	258.298	200.743	11.093	191.128	−1.849
5500	42.665	296.255	258.981	205.005	10.271	194.469	−1.847
5600	42.764	297.025	259.654	209.276	9.385	197.826	−1.845
5700	42.862	297.782	260.316	213.558	8.434	201.199	−1.844
5800	42.961	298.529	260.968	217.849	7.416	204.590	−1.843
5900	43.060	299.264	261.611	222.150	6.328	207.999	−1.841
6000	43.158	299.988	262.245	226.461	5.329	211.408	−1.840

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

Sodium Hydride (NaH) $H_1Na_1(g)$

$S°(298.15\ K) = 64.445 \pm 0.84\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 572\ K$
$T_{fus} = 596\ K$

$\Delta_f H°(0\ K) = -421.40 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -425.93 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 7.196 \pm 0.84\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 6.611 \pm 0.84\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of NaOH(cr) is obtained from its enthalpy of solution in water, the enthalpy of hydrolysis of metallic sodium, and appropriate auxiliary data.

Reshetnikov[1] determined calorimetrically the enthalpy of solution of NaOH in aq, 400 H_2O as $-10.445 \pm 0.015\ kcal \cdot mol^{-1}$. Combining this result with enthalpy of dilution data for aqueous sodium hydroxide solutions tabulated by Parker[2] we derive $\Delta_{sln} H°$(NaOH, cr) = $-10.56 \pm 0.02\ kcal \cdot mol^{-1}$. Murch and Giauque[3] measured the heats of solution in water of a series of solids which contained various amounts of water in the range NaOH·(0.1 to 1) H_2O. Their data indicated a linear relationship between the heat of solution and the ratio of the moles of water to the moles of sodium hydroxide. Upon extrapolation their data gave $\Delta_{sln} H°$(NaOH, cr) = $-10.637 \pm 0.010\ kcal \cdot mol^{-1}$.[2] This latter value is adopted here, since the extrapolation to zero moles of water tends to eliminate its effect on the heat of solution.

The enthalpy of hydrolysis of metallic sodium has been determined by various investigators.[4–6] For the reaction $Na(cr) + (n+1)H_2O \rightarrow NaOH \cdot n H_2O + 0.5\ H_2(g)$ data are summarized below.

Source	n moles of H_2O	$\Delta_h H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°$(NaOH·aq, ∞)* kcal·mol^{-1}	$\Delta_f H°$(NaOH, cr, 298.15 K) kcal·mol^{-1}
Gunn and Green[4a,4b]	∞	−44.124 ± 0.015	−112.439	−101.80
Messer *et al.*[5]	∞	−44.22 ± 0.20	−112.53	−101.88
Ketchen and Wallace[6]	∞	−44.05 ± 0.20	−112.37	−101.72

*Based on $\Delta_f H°(H_2O, l, 298.15\ K) = 68.315\ kcal \cdot mol^{-1}$.[7]

Combination of the $\Delta_f H°$(NaOH·aq,∞, 298 15 K) values with the enthalpy of solution of NaOH(cr) at infinite dilution given above, results in the $\Delta_f H°$(NaOH, cr, 298.15 K) values given in the last column. The value determined from the work of Gunn and Green[4] is adopted. Earlier determinations of $\Delta_f H°$(NaOH, cr, 298.15 K) have been summarized by Bichowsky and Rossini[8] and are not listed here.

Heat Capacity and Entropy

Murch and Giauque[3] determined low temperature heat capacities for NaOH·O 04014 H_2O and NaOH·0.97776 H_2O from 15 to 320 K. From these data heat capacities for anhydrous NaOH(cr) were calculated and joined smoothly at 298 15 K with the high temperature (273–973 K) enthalpy data of Douglas and Dever.[9] These smoothed heat capacities given by Murch and Giauque are adopted. Low temperature heat capacity data for NaOH(cr) in the temperature range 60 to 300 K have also been reported by Kelley and Snyder.[10] The deviations of their data from the adopted values range from a few tenths of a percent (150–300 K) to up to about 30% at the lowest temperatures investigated (60 K). Popov and Ginzburg[11] also determined high temperture enthalpy data (293–1016 K) for NaOH by drop calorimetry. Their reported value $H°(500\ K) - H°(298.15\ K) = 3.112\ kcal \cdot mol^{-1}$ [11] is in very good agreement with the tabulated value of 3.176 kcal mol^{-1}.

$S°(298.15\ K)$ is based upon the extrapolated value of 0.020 cal·K^{-1} mol^{-1} at 15 K.

Transition and Fusion Data

The adopted enthalpies of the polymorphic transformation and fusion of NaOH are mean values from the work of Douglas and Dever[9] Popov and Ginzburg[11] and Reshetnikov and Baranskaya.[12] T_{trs} and T_{fus} are from Reshetnikov and Baranskaya.[12]

Sublimation Data

$\Delta_{sub} H°$(298 15 K) for the monomer and dimer are calculated from the adopted enthalpies of formation of the crystal and the respective gaseous species.

References

[1]N. A. Reshetnikov, Zhur Neorg. Khim. 6, 682 (1961).
[2]V. B. Parker, NSRDS NBS 2, (1965).
[3]L. E. Murch and W. F. Giauque, J. Phys. Chem. 66, 2052 (1962).
[4]a) S. R. Gunn and L. G. Green, J. Amer. Chem. Soc. 80, 4782 (1958); b) S. R. Gunn, J. Phys. Chem. 71, 1386 (1967).
[5]C. E. Messer, L. G. Fasolino, and C. E. Thalmayer, J. Amer Chem. Soc. 77, 4524 (1965).
[6]E. E. Ketchen and W. E. Wallace, J. Amer. Chem. Soc. 76, 4736 (1954).
[7]U. S. Nat. Bur. Stand. Tech. Note 270 3, (1968).
[8]F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York,(1936).
[9]T. B. Douglas and J. L. Dever, J. Res. Nat. Bur. Stand. 53, 81 (1954).
[10]a) J. C. R. Kelley and P. E. Snyder, J. Amer. Chem. Soc. 73, 4114 (1951); b) J. C. R Kelley and P. E. Snyder, J. Amer. Chem. Soc. 73, 5933 (1951).
[11]a) M. M. Popov and D M. Ginzburg, Zhur. Obshchei Khim. 26, 971 (1956), b) D. M. Ginzburg, Zhur. Obschchei Khim. 26, 968 (1956).
[12]N. A. Reshetnikov and E. V. Baranskaya, Izv. Vyssh. Ucheb. Zaved., Khim. Tekhnol. 10, 496 (1967), C.A. 67 94551.

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	−10.487	−421.396	−421.396	INFINITE
100	27.744	15.513	109.879	−9.437	−424.637	−410.105	214.217
200	49.580	42.588	69.615	−5.406	−425.864	−394.953	103.151
298.15	59.530	64.445	64.445	0.	−425.931	−379.741	66.529
300	59.664	64.814	64.447	0.110	−425.927	−379.454	66.069
400	64.936	82.739	66.856	6.353	−428.244	−363.802	47.508
500	75.157	98.172	71.595	13.288	−427.401	−347.767	36.331
572.000	85.887	108.971	75.620	19.077	I <--> II		
572.000	86.023	121.574	75.620	26.286	TRANSITION		
596.000	86.023	125.110	77.542	28.350	----- II <--> LIQUID -----		
600	86.023	125.685	77.861	28.694	−418.055	−332.373	28.936
700	86.023	138.946	85.665	37.297	−415.502	−318.294	23.751
800	86.023	150.433	93.059	45.899	−412.953	−304.581	19.887
900	86.023	160.565	100.008	54.501	−410.428	−291.187	16.900
1000	86.023	169.628	106.525	63.104	−407.946	−278.071	14.525
1100	86.023	177.827	112.640	71.706	−405.526	−265.202	12.593
1200	86.023	185.312	118.388	80.308	−499.948	−250.109	10.887
1300	86.023	192.198	123.805	88.911	−496.776	−229.418	9.218
1400	86.023	198.573	128.921	97.513	−493.641	−208.970	7.797
1500	86.023	204.508	133.764	106.115	−490.542	−188.745	6.573

PREVIOUS March 1966 CURRENT: December 1970

$S°(298\ 15\ K) = [75\ 891]\ J·K^{-1}\ mol^{-1}$
$T_{fus} = 596\ K$

$\Delta_f H°(298\ 15\ K) = [-416.878]\ kJ\ mol^{-1}$
$\Delta_{fus}H° = 6\ 611 \pm 0.84\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(NaOH, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(596\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The adopted heat capacities for NaOH(l) in the temperature range 596 to 1000 K are from the enthalpy measurements of Douglas and Dever [1] The heat capacities below the melting point and above 1000 K are extrapolated from the experimental heat capacity curve. Powers and Blalock[2] reported $C_p°(l) = 19.6\ cal·K^{-1}·mol^{-1}$ from enthalpy measurements, in a short temperature range, by drop calorimetry. The smoothed enthalpy data for NaOH(l) reported by Popov and Ginzburg[3a,3b] are from 0 2 to 0 5 kcal·mol^{-1} less than the adopted values in the temperature range 700 to 1000 K.

$S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

$T_{vap} = 1830\ K$ (for monomer) is calculated as the temperature at which the fugacity of NaOH(g) is 1 atm for the process NaOH(l) = NaOH(g). The difference in the enthalpies of formation of NaOH(l) and NaOH(g) at the T_{vap} is the enthalpy of vaporization, $\Delta_{vap}H° = 175.310\ kJ\ mol^{-1}$.

Wartenberg and Albrecht[4] reported a boiling point of 1661 K from their static vapor pressure data. However, these workers observed the presence of water after each experiment which may indicate some decomposition of the sample. See the ideal gas table for further discussion.

References

[1]T. B. Douglas and J. L. Dever, J. Res. Nat. Bur Stand 53, 81 (1954).
[2]W. D. Powers and G. C. Blalock, Oak Ridge Nat. Lab , ORNL 1653, (1954).
[3]a.M. M. Popov and D. M Ginzburg, Zhur Obshchei Khim. 26, 971 (1956).
b D. M. Ginzburg, Zhur Obshchei Khim. 26, 968 (1956).
[4]H von Wartenberg and P Albrecht, Z. Elektrochem. 27, 162 (1921).

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							
100							
200							
298 15	87.822	75.891	75.891	0.	−416.878	−374 100	65.541
300	87.814	76 434	75.892	0.162	−416.821	−373.835	65 090
400	87.211	101.613	79.329	8.913	−416.631	−359.738	46 977
500	86.651	121.013	85.800	17.606	−414.030	−345 816	36.127
596.000	86.111	136.202	92.791	25.873	----- II <--> LIQUID -----		
600	86.065	136 778	93.024	26.252	−411.445	−332 417	28.939
700	85.479	150.001	100.245	34.829	−408.916	−319 446	23.837
800	84.893	161.377	107.192	43.348	−406.451	−306.834	20.034
900	84.308	171.342	113.777	51.808	−404.068	−294.526	17.094
1000	83.722	180.194	119.985	60.209	−401 787	−282.478	14.755
1100	83.136	188.146	125.826	68.552	−399.626	−270 653	12.852
1200	82.550	195.355	131.324	76.837	−494.366	−256.579	11.169
1300	81.965	201.939	136.507	85.062	−491.571	−236.877	9.518
1400	81.379	207.992	141.400	93.230	−488.871	−217.387	8.111
1500	80.793	213.587	146.028	101.338	−486.266	−198.087	6.898
1600	80.207	218 782	150 415	109.388	−483 754	−178.957	5.842
1700	79.622	223.627	154.580	117.379	−481.334	−159.982	4.916
1800	79.119	228 164	158.544	125.316	−479.001	−141.147	4.096
1900	78.638	232.428	162.321	133.203	−476.749	−122.439	3.366
2000	78.199	236.450	165.928	141.045	−474.574	−103.848	2.712
2100	77.801	240.256	169.378	148.844	−472.471	−85.363	2.123
2200	77.467	243.867	172.682	156.607	−470 434	−66.977	1.590
2300	77.182	247.304	175.853	164.339	−468.457	−48.683	1 106
2400	76.956	250.584	178.899	172.046	−466.535	−30.474	0 663
2500	76.760	253.722	181.829	179.731	−464.662	−12.343	0.258

PREVIOUS March 1966 CURRENT· December 1970

0	to	572	K crystal, alpha
572	to	596	K crystal, beta
above		596	K liquid

Refer to the individual tables for details.

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⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−10.487	−421.396	−421.396	INFINITE
100	27.744	15.513	109.879	−9.437	−424 637	−410.105	214.217
200	49.580	42.588	69.615	−5.406	−425.864	−394.953	103.151
298.15	59.530	64 445	64.445	0.	−425.931	−379.741	66.529
300	59.664	64.814	64.447	0.110	−425.927	−379 454	66.069
400	64.936	82 739	66.856	6.353	−428.244	−363.802	47.508
500	75 157	98.172	71.595	13.288	−427.401	−347 767	36.331
572.000	85.887	108.971	75.620	19.077	I <--> II		
572 000	86.023	121.574	75.620	26.286	TRANSITION		
596.000	86.023	125.110	77.542	28.350	II <--> LIQUID		
596.000	86.111	136.202	77.542	34.961	TRANSITION		
600	86.065	136.778	77.935	35.305	−411.445	−332.417	28.939
700	85 479	150.001	87.311	43.883	−408.916	−319.446	23.837
800	84.893	161.377	95.875	52.401	−406.451	−306.834	20.034
900	84.308	171.342	103.718	60.861	−404.068	−294.526	17.094
1000	83.722	180.194	110.931	69.263	−401.787	−282.478	14.755
1100	83.136	188.146	117.596	77.606	−399.626	−270.653	12.852
1200	82.550	195.355	123.780	85.890	−494.366	−256.579	11.169
1300	81.965	201.939	129.543	94.116	−491.571	−236.877	9.518
1400	81.379	207.992	134.933	102.283	−488.871	−217.387	8.111
1500	80.793	213.587	139.992	110.392	−486.266	−198.087	6.898
1600	80.207	218.782	144.756	118.442	−483.754	−178.957	5.842
1700	79.622	223.627	149.255	126.432	−481.334	−159.982	4.916
1800	79 119	228.164	153.514	134.369	−479.001	−141.147	4.096
1900	78.638	232.428	157.556	142.257	−476.749	−122.439	3.366
2000	78.199	236.450	161.401	150.098	−474.574	−103.848	2.712
2100	77 801	240.256	165.067	157.898	−472.471	−85.363	2.123
2200	77.467	243.867	168.567	165.661	−470.434	−66.977	1.590
2300	77 182	247.304	171.916	173.393	−468.457	−48.683	1.106
2400	76.956	250.584	175.126	181.099	−466.535	−30.474	0.663
2500	76.760	253.722	178.208	188.785	−464.662	−12.343	0.258

PREVIOUS: CURRENT December 1970

$S°(298.15\ K) = 228.443 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -194.12 \pm 12.6\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -197.76 \pm 12.6\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
431 (1)
337 (2)
[3650] (1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: $C_{\infty v}$
Bond Distance: Na–O = [1.93] Å, O–H = [0.97] Å
Bond Angle. Na–O–H = 180°
Rotational Constant: $B_0 = 0.426703\ cm^{-1}$

Enthalpy of Formation

The bond dissociation energies of the alkali metal hydroxides have been the subject of a number of investigations[1-4] in recent years. The majority of this work has involved equilibrium studies on the reaction A(g) + H_2O(g) = AOH(g) + H(g), where A is an alkali metal, in hydrogen oxygen nitrogen flames containing water. In the case of NaOH, data are summarized below:

Source	Method	Reaction*	Data Points	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 3rd law	$D°$(Na–OH, 0 K) kcal·mol^{-1}
Jensen and Padley[2a]	Flames	A	1	2475	40.5	77.9
Cotton and Jenkins[4]	Flames	A	1	2030	36.6	81.8

*(A) Na(g) + H_2O(g) = NaOH(g) + H(g)

We note that Cotton and Jenkins[4] in the same paper reported bond dissociation energies for LiOH(g) and KOH(g) which are in reasonable agreement with JANAF values[5] for the enthalpy of formation of these two compounds. Furthermore, bond dissociation data for the alkali metal halides[6] clearly establish the sodium compound as the least stable within each halide series. The potuccirctassium and sodium compounds differ by from 4.3 kcal·mol^{-1} for the fluorides and bromides to 3.6 kcal mol^{-1} for the chlorides. It seems most likely that this same trend in the bond dissociation energies would apply to the hydroxides as well. Based upon these correlations, we adopt $D_0°$(Na–OH) = 81.5 ± 3.0 kcal·mol^{-1} with $D_0°$(K–OH)–$D_0°$(Na–OH) = 3.9 kcal·mol^{-1}. This value corresponds to $\Delta_f H°$(NaOH, g, 298.15 K) = −47.3 ± 3.0 kcal·mol^{-1}.

Wartenberg and Albrecht[7] determined vapor pressures for NaOH(l) in the temperature range 1283–1681 K by a static method. In order to evaluate $\Delta_{vap}H°$(NaOH, l, 298.15 K), we have used a trial and error variation of $\Delta_{vap}H°$(298.15 K) for the monomer and dimer, such that these values are in accordance with the adopted enthalpy of dimerization (refer to the $Na_2(OH)_2$(g) table), and the sum of the calculated partial pressures for NaOH(g) and $Na_2(OH)_2$(g) in good agreement with the experimental vapor pressure data. The resulting values are: $\Delta_{vap}H°$(to monomer) = 48.25 kcal·mol^{-1} and $\Delta_{vap}H°$(to dimer) = 48.8 kcal·mol^{-1}. From the enthalpy of vaporization of the monomer, we derive $\Delta_f H°$(NaOH, g, 298.15 K) = −51.4 kcal·mol^{-1}. This value corresponds to a bond dissociation energy for NaOH(g) that is slightly greater than the adopted value for KOH(g),[5] and thus not in line with the established trends in $D_0°$ discussed above Buchler and Berkowitz Mattuck[8] in their review on gaseous ternary compounds of the alkali metals point to the decomposition of NaOH in the condensed phase with a resulting change in composition as the major problem in the interpretation of thermodynamic measurements on this system. Until the nature of the condensed phase and the relationship between the vapor and condensed phase composition for NaOH(l) are established, an accurate enthalpy of vaporization will remain undetermined.

Heat Capacity and Entropy

The infrared spectra of matrix isolated NaOH and NaOD have been recently observed by Acquista and Abramowitz.[9] The alkali–metal–oxygen stretching frequency, ν_1, and the bending mode, ν_2, for NaOH were assigned as 431 and 337 cm^{-1}, respectively, by these workers. The isotope shift of ν_2 was consistent with a linear structure for NaOH having bond lengths of 1.93 and 0.97 Å for the Na–O and O–H bonds. We have adopted a linear configuration for NaOH with the bond lengths and frequencies given above. Spinar and Margrave[10] assigned ν_1 as 437 ± 10 cm^{-1} for NaOH which is in good agreement with the adopted value. The O–H stretching frequency, ν_3, was estimated by Jensen.[2b]

References

[1]H. Smith and T. M. Sugden, Proc. Roy. Soc. A **219**, 204 (1953).
[2]a) D. E. Jensen and P. J. Padley, Trans. Faraday Soc. **62**, 2132 (1966); b) D. E. Jensen, J. Phys. Chem. **74**, 207 (1970).
[3]M. J. McEwan and L. F. Phillips, Combustion and Flame **11**, 63 (1967).
[4]D. H. Cotton and D. R. Jenkins, Trans. Faraday Soc. **65**, 1537 (1969).
[5]JANAF Thermochemical Tables: LiOH(g), 3–31–66; KOH(g), 12–31–70.

Continued on page 1358

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	−11.385	−194.119	−194.119	INFINITE
100	32.864	183.702	267.723	−8.402	−195.428	−197.715	103.276
200	43.462	210.040	232.739	−4.540	−196.824	−199.403	52.079
250	46.468	220.085	229.230	−2.286	−197.322	−199.989	41.785
298.15	48.371	228.443	228.443	0.	−197.757	−200.463	35.120
300	48.431	228.743	228.444	0.090	−197.773	−200.479	34.907
350	49.750	236.314	229.039	2.546	−198.232	−200.895	29.982
400	50.669	243.021	230.376	5.058	−201.365	−201.036	26.253
450	51.334	249.029	232.120	7.609	−201.866	−200.964	23.327
500	51.836	254.465	234.087	10.189	−202.326	−200.839	20.981
600	52.566	263.984	238.299	15.411	−203.165	−200.461	17.452
700	53.130	272.131	242.564	20.696	−203.928	−199.949	14.920
800	53.646	279.259	246.715	26.035	−204.642	−199.332	13.015
900	54.158	285.607	250.690	31.426	−205.329	−198.626	11.528
1000	54.674	291.340	254.473	36.867	−206.008	−197.845	10.334
1100	55.188	296.575	258.066	42.360	−206.697	−196.996	9.355
1200	55.690	301.399	261.478	47.904	−304.177	−193.642	8.429
1300	56.171	305.875	264.723	53.498	−304.014	−184.438	7.411
1400	56.626	310.055	267.814	59.138	−303.842	−175.246	6.539
1500	57.051	313.976	270.762	64.822	−303.661	−166.067	5.783
1600	57.444	317.671	273.579	70.547	−303.474	−156.900	5.122
1700	57.806	321.165	276.277	76.310	−303.282	−147.745	4.540
1800	58.138	324.478	278.863	82.107	−303.089	−138.601	4.022
1900	58.441	327.630	281.348	87.936	−302.895	−129.468	3.559
2000	58.718	330.635	283.738	93.795	−302.703	−120.346	3.143
2100	58.971	333.506	286.040	99.679	−302.515	−111.232	2.767
2200	59.201	336.255	288.260	105.588	−302.332	−102.128	2.425
2300	59.411	338.891	290.405	111.519	−302.157	−93.032	2.113
2400	59.603	341.424	292.478	117.470	−301.990	−83.943	1.827
2500	59.779	343.860	294.485	123.439	−301.834	−74.861	1.564
2600	59.939	346.208	296.429	129.425	−301.689	−65.785	1.322
2700	60.086	348.473	298.315	135.426	−301.559	−56.714	1.097
2800	60.221	350.661	300.146	141.442	−301.444	−47.648	0.889
2900	60.345	352.776	301.924	147.470	−301.346	−38.586	0.695
3000	60.459	354.824	303.654	153.510	−301.266	−29.526	0.514
3100	60.564	356.808	305.336	159.561	−301.207	−20.469	0.345
3200	60.661	358.732	306.975	165.623	−301.171	−11.414	0.186
3300	60.751	360.600	308.572	171.693	−301.157	−2.360	0.037
3400	60.834	362.415	310.129	177.773	−301.170	6.695	−0.103
3500	60.911	364.180	311.648	183.860	−301.211	15.750	−0.235
3600	60.983	365.897	313.131	189.955	−301.281	24.807	−0.360
3700	61.049	367.568	314.580	196.056	−301.383	33.867	−0.478
3800	61.111	369.197	315.996	202.164	−301.520	42.930	−0.590
3900	61.169	370.785	317.381	208.278	−301.693	51.996	−0.696
4000	61.223	372.335	318.735	214.398	−301.905	61.068	−0.797
4100	61.274	373.847	320.061	220.523	−302.159	70.145	−0.894
4200	61.321	375.324	321.359	226.653	−302.454	79.229	−0.985
4300	61.365	376.768	322.631	232.787	−302.798	88.321	−1.073
4400	61.407	378.179	323.878	238.926	−303.150	97.417	−1.156
4500	61.446	379.559	325.100	245.068	−303.574	106.525	−1.237
4600	61.483	380.910	326.298	251.215	−304.058	115.643	−1.313
4700	61.518	382.233	327.475	257.365	−304.597	124.773	−1.387
4800	61.550	383.529	328.629	263.518	−305.195	133.915	−1.457
4900	61.581	384.798	329.762	269.675	−305.853	143.070	−1.525
5000	61.610	386.042	330.875	275.834	−306.567	152.238	−1.590
5100	61.638	387.263	331.969	281.997	−307.354	161.422	−1.653
5200	61.664	388.460	333.044	288.162	−308.209	170.622	−1.714
5300	61.689	389.635	334.101	294.330	−309.137	179.839	−1.772
5400	61.712	390.788	335.140	300.500	−310.138	189.074	−1.829
5500	61.735	391.921	336.162	306.672	−311.217	198.328	−1.884
5600	61.756	393.033	337.168	312.847	−312.375	207.604	−1.936
5700	61.776	394.126	338.157	319.023	−313.616	216.900	−1.988
5800	61.795	395.201	339.132	325.202	−314.940	226.219	−2.037
5900	61.813	396.257	340.091	331.382	−316.352	235.560	−2.085
6000	61.831	397.296	341.036	337.564	−317.694	244.909	−2.132

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

$S°(298.15\ K) = [242.626 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [674.9 \pm 105]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [677.8 \pm 105]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ν_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Sigma^+$	[32000]	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[400](1)
[300](2)
[3600](1)

Point Group: $[C_{\infty v}]$ $\sigma = 1$
BondDistances: Na–O = [2.00]Å; O–H = [1.03] Å
Bond Angle: Na–O–H = [180]°
Rotational Constant: B_0 = [0.396362] cm^{-1}

Enthalpy of Formation

Beckett and Cassidy[1] selected the ionization potential of NaOH as 9.0 ± 1.0 eV (207 6 ± 23 kcal·mol^{-1}). A measured value of roughly 9 eV has been reported by Schoonmaker and Porter.[2] Combining this result with JANAF auxiliary data,[3] we derive $\Delta_f H°$(NaOH⁺, g, 0 K) = 161 ± 25 kcal·mol^{-1}, which is tentatively adopted.

Heat Capacity and Entropy

NaOH⁺ has seven valence electrons. According to the correlation diagram of Walsh[4] for HAB type molecules, NaOH + should be linear with the unpaired electron in a pi orbital. Therefore, we assume the ground state to be $^2\Sigma$ A first excited state is estimated at 32000 cm^{-1} to be $^2\Sigma$ by analogy with the isoelectronic molecules OH[3] and SH.[3] The removal of a bonding electron from NaOH to form NaOH⁺ should lead to weaker bonding in the positive ion. Consequently, the vibrational frequencies are estimated to be somewhat lower than those for NaOH. Similarly, the Na–O and O–H bond distances are increased slightly over those for NaOH.

References

[1]C. W. Beckett and E. C. Cassidy, U. S. Nat. Bur. Stand. Report 8628, (1965).
[2]R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 28, 454 (1958).
[3]JANAF Thermochemical Tables: NaOH(g), 12–31–70; OH(g), 12–31–70; SH(g), 6–30–67.
[4]A. D. Walsh, J. Chem. Soc. 2288 (1953).

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	−11.693	674.940		
100	34.226	196.325	283.048	−8.672			
200	44.889	223.761	247.019	−4.652			
250	47.591	234.091	243.429	−2.334			
298.15	49.257	242.626	242.626	0.	677.808	664.619	−116.438
300	49.308	242.931	242.627	0.091	677.832	664.537	−115.706
350	50.443	250.623	243.232	2.587	678.451	662.271	−98.839
400	51.226	257.413	244.589	5.130	676.389	660.126	−86.204
450	51.790	263.481	246.357	7.706	676.953	658.060	−76.386
500	52.216	268.960	248.348	10.306	677.552	655.929	−68.524
600	52.846	278.539	252.604	15.561	678.825	651.486	−56.717
700	53.352	286.724	256.908	20.872	680.165	646.825	−48.267
800	53.836	293.880	261.091	26.231	681.550	641.968	−41.916
900	54.328	300.249	265.095	31.639	682.959	636.935	−36.967
1000	54.832	305.999	268.902	37.097	684.375	631.746	−32.999
1100	55.337	311.249	272.517	42.606	685.780	626.415	−29.746
1200	55.832	316.085	275.949	48.164	590.393	623.397	−27.136
1300	56.307	320.573	279.211	53.771	592.648	626.056	−25.155
1400	56.755	324.763	282.316	59.425	594.913	628.541	−23.451
1500	57.174	328.693	285.279	65.121	597.185	630.863	−21.969
1600	57.561	332.395	288.109	70.858	599.463	633.034	−20.666
1700	57.918	335.896	290.818	76.633	601.744	635.062	−19.513
1800	58.244	339.216	293.415	82.441	604.027	636.956	−18.484
1900	58.541	342.373	295.909	88.280	606.310	638.723	−17.560
2000	58.813	345.383	298.308	94.148	608.590	640.371	−16.725
2100	59.060	348.258	300.619	100.042	610.866	641 904	−15 966
2200	59.286	351.011	302.847	105.960	613.136	643.329	−15.275
2300	59 491	353.651	304.999	111.899	615.399	644.650	−14.640
2400	59.679	356.187	307.080	117.857	617.652	645.873	−14.057
2500	59.850	358.627	309.093	123.834	619.894	647.003	−13.518
2600	60.007	360.977	311.044	129.827	622.124	648.043	−13.019
2700	60.150	363.244	312.935	135.835	624.339	648.998	−12.556
2800	60.282	365.434	314.771	141.856	626.539	649 872	−12.124
2900	60.402	367.552	316.555	147.891	628.722	650 666	−11.720
3000	60.514	369.602	318.289	153.937	630.886	651.386	−11.342
3100	60.616	371.587	319.977	159.993	633.029	652.034	−10.987
3200	60.711	373.513	321.620	166.060	635.149	652.613	−10.653
3300	60.798	375.383	323.221	172.135	637.246	653.126	−10.338
3400	60.880	377.199	324.782	178.219	639.316	653.576	−10.041
3500	60.955	378.965	326.305	184.311	641.359	653.966	−9.760
3600	61.025	380.683	327.792	190.410	643.371	654.297	−9 494
3700	61.091	382.356	329.244	196.516	645.352	654.573	−9.241
3800	61.152	383.986	330.663	202.628	647.298	654.797	−9.001
3900	61.209	385.575	332.051	208.746	649.208	654.970	−8.772
4000	61.263	387.126	333.408	214.870	651.078	655.093	−8.555
4100	61.313	388.639	334.737	220.998	652.907	655.171	−8.347
4200	61.361	390.117	336.038	227.132	654.694	655.204	−8.149
4300	61.406	391.562	337.313	233.270	656.432	655.196	−7.959
4400	61.449	392.974	338.562	239.413	658.163	655.144	−7.778
4500	61.489	394.355	339.786	245.560	659.823	655.055	−7 604
4600	61.528	395 707	340.987	251.711	661.421	654 931	−7.437
4700	61.565	397.031	342.166	257.866	662.965	654.774	−7.277
4800	61.601	398.327	343.322	264.024	664.451	654.584	−7.123
4900	61.635	399.598	344.458	270.186	665.877	654.364	−6.976
5000	61.669	400.843	345.573	276.351	667.247	654.114	−6.833
5100	61.701	402.065	346.669	282.520	668.545	653.838	−6.697
5200	61.732	403.263	347.746	288.691	669 775	653.538	−6.565
5300	61.762	404 439	348.804	294.866	670.933	653.215	−6.438
5400	61.792	405.594	349.845	301.044	672.018	652.870	−6.315
5500	61.821	406.728	350.869	307.224	673.026	652.505	−6.197
5600	61.850	407.842	351.877	313.408	673.955	652.124	−6.083
5700	61.878	408.937	352.868	319.594	674.803	651.727	−5.972
5800	61.906	410.014	353.844	325.784	675.568	651.316	−5.866
5900	61.933	411.072	354.805	331.975	676.246	650.890	−5.763
6000	61.961	412 113	355.752	338.170	676 996	650.438	−5.663

PREVIOUS: December 1971 (1 atm) CURRENT: December 1971 (1 bar)

$S°(298.15\ K) = 183\ 708 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 38\ 390 \pm 1.21\ kJ\ mol^{-1}$
$\Delta_f H°(298\ 15\ K) = 38\ 987 \pm 1.21\ kJ \cdot mol^{-1}$

Electronic States and Molecular Constants ($\sigma = 1$)

State	ϵ_e, cm^{-1}	g_e	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Pi_i$	0	2	3735.21	82.81	18.871	0.714	0.9706
	139.7	2					
$A^2\Sigma^+$	32403	2	3184.28	97.84	17.355	0.807	1.0121
$B^2\Sigma^+$	68372	2	940	105	5.54	0.65	1.80
$C^2\Sigma^+$	89420	2	2339	32	4.20	0.16	2.16

Enthalpy of Formation

$\Delta_f H°$(OH, g, 0 K) is calculated from the relation $\Delta H°$(OH, g, 0 K) = 1/2 $D_0°(O_2)$ + 1/2 $D_0°(H_2) - D_0°$(OH). are as follows $D_0°(O_2) = 117.967 \pm 0.042$ kcal·mol^{-1} and $D_0°(H_2) = 103\ 267 \pm 0.003$ kcal·mol^{-1} were taken from the CODATA[1] selection. Barrow[2] in a refinement of the work of Barrow and Downie[3] obtains a value of $D_0°$ for OH($X^2\Pi_{3/2}$) → O($^3P_2$) + H($^2S_{1/2}$) of 35427 cm^{-1} from an extrapolation of $\Delta_{vap}G$ versus v, it was increased to 35450 ± 100 cm^{-1} to account for the fact that $\Delta_{vap}G$ yields slightly low values at high v Fehlenbok[4] obtains a value of D_e for OH($B^2\Sigma^+$) of 1315 cm^{-1} and G(O) for this state of 441 cm^{-1}. Using $T_e(B^2\Sigma^+)$ given by Rosen[5] and the zero point energy of HO (including the Dunham correction, see Herzberg)[6] of 847 0 cm^{-1}, this yields $D_0°$(OH) = 35451 cm^{-1} with an estimated uncertainty of 100 cm^{-1}. A value of $D_0°$(OH) = 35450 ± 100 cm^{-1} = 101 356 ± 0.29 kcal mol^{-1} was adopted. Combining the above values, one obtains $\Delta_f H°$(OH, g, 0 K) = 9 261 ± 0.29 kcal mol^{-1} which is in good agreement with the last JANAF[7] 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 $H°(0\ K)-H°(298.15\ K)$, $S°(298.15\ K)$ and $C_p°(298.15\ K)$ be taken as −2.107 kcal·mol^{-1}, 43 890 kJ·mol^{-1}, and 7.144 kJ 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_v^i and Q_v^i in the partition function $Q = Q_i \Sigma Q_v^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$ The National Bureau of Standards prepared this table[11] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[11] we recalculate the table in terms of 1973 fundamental constants,[12] 1975 atomic weights[13] and current JANAF reference states for the elements.

References

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

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	−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)

$S°(298.15\ K) = 182.776 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1310.88 \pm 0.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 1317.12 \pm 10.5\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^3\Sigma^-$	0	3
$a^1\Delta$	[17700]	2
$A^3\Pi$	22949	6
$b^1\Sigma^+$	29150	1

$\omega_e = [3135 \pm 100]\ cm^{-1}$ $\omega_e x_e = [89.3 \pm 50]\ cm^{-1}$ $\sigma = 1$
$B_e = 16.776\ cm^{-1}$ $\alpha_e = 0.728\ cm^{-1}$ $r_e = 1.0289$ Å

Enthalpy of Formation

The ionization potential of hydroxyl has been determined by Mann *et al.*[1] as 13.6 eV and by Foner and Hudson[2] as 13.18 ± 0.1 eV, both by electron impact methods These values correspond to $\Delta_f H°(OH^+, g, 0\ K) = 322.97\ kcal \cdot mol^{-1}$ and 313.28 ± 2.5 kcal mol^{-1}, respectively. Metzger and Cook[3] have reported the photoionization onset of the process $H_2O(g) + h\nu \rightarrow OH^+ + H + e^-$ as 18.3 eV, with JANAF auxiliary data[4] this gives $\Delta_f H°(OH^+, g, 0\ K) = 313.3\ kcal \cdot mol^{-1}$, which is adopted.

Heat Capacity and Entropy

The measured electronic levels are those reported by Merer *et al*,[5] the rotational constants are derived from this analysis also. The estimated electronic level is from the Hartree–Fock calculations of Cade.[6]

The vibrational constants are estimated so that $\Delta G_{1/2}$ is equal to that reported by Merer *et al*[5] The anharmonicity, $\omega_e x_e$, is estimated by comparison with OH and NH. Calculations of $\omega_e x_e$ based on the Morse potential curve and the relation $\omega_{e2} = 4B_{e3}/D_e$, or $\omega_{o2} = 4\omega_o x_o D_0^{97}$ do not appear to yield values which are preferable to our estimates, this is due to the inexactness of the potential for ionic molecules.

References

[1]M. M. Mann, A. Hustrulid and J. T. Tate, Phys. Rev. 58, 340 (1940).
[2]S. F. Foner and R. L. Hudson, J. Chem. Phys. 25, 602 (1956).
[3]P. H. Metzger and G. R. Cook, J. Chem. Phys. 41, 642 (1964).
[4]JANAF Thermochemical Tables: $H_2O(g)$, 3–31–61, H(g), 9–30–65.
[5]A. J. Merer, E. K. Achter, M. Horani and J Rostas, Can. J. Phys. 47, 1723 (1969).
[6]P. E. Cade, Can. J. Phys. 46, 1989 (1968).
[7]V. S. Yungman, Russ. J. Phys. Chem. 8, 147 (1960).

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
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−8.618	1310.883		
100	29.127	150.948	208.684	−5.774			
200	29.136	171.140	185.442	−2.860			
250	29.144	177.642	183.256	−1.403			
298.15	29.153	182.776	182.776	0.	1317.123	1306.437	−228.882
300	29.153	182.956	182.777	0.054	1317.162	1306.371	−227.459
350	29.167	187.451	183.132	1.512	1318.196	1304.490	−194.685
400	29.192	191.347	183.920	2.971	1319.219	1302 462	−170.084
450	29.237	194.788	184.940	4.431	1320.230	1300.307	−150.936
500	29.311	197.872	186.082	5.895	1321.231	1298.040	−135.605
600	29.566	203.236	188.507	8.838	1323.208	1293.215	−112.584
700	29.959	207.822	190.946	11.813	1325.165	1288.062	−96.116
800	30.456	211.854	193.313	14.833	1327.119	1282.628	−83.747
900	31.013	215.473	195.577	17.906	1329.081	1276.949	−74 112
1000	31.590	218.770	197.734	21.036	1331.057	1271.050	−66.393
1100	32.160	221.808	199.786	24.224	1333.049	1264.954	−60.068
1200	32.706	224.630	201.740	27.467	1335.057	1258.675	−54.789
1300	33 217	227.268	203.604	30.764	1337.081	1252.227	−50.315
1400	33.691	229.747	205.383	34.110	1339.116	1245.624	−46.475
1500	34.127	232.087	207.086	37.501	1341.161	1238.874	−43.141
1600	34.526	234.302	208.719	40.934	1343.214	1231.988	−40.220
1700	34.891	236.407	210.286	44 405	1345.271	1224.974	−37.639
1800	35.226	238.411	211.793	47 911	1347.331	1217.838	−35.341
1900	35.532	240.324	213.245	51 449	1349.391	1210.588	−33.281
2000	35.814	242.153	214.645	55.017	1351.451	1203.229	−31.425
2100	36.074	243.907	215.997	58.611	1353.509	1195.767	−29.743
2200	36.315	245.591	217.304	62.231	1355.563	1188.208	−28.212
2300	36.539	247.210	218.569	65.874	1357.614	1180.555	−26.811
2400	36 749	248.770	219 795	69.538	1359.660	1172.813	−25.526
2500	36.946	250.274	220.985	73.223	1361 701	1164.985	−24.341
2600	37.133	251.727	222.139	76.927	1363.737	1157.076	−23.246
2700	37.311	253.131	223.261	80 649	1365.767	1149.090	−22.230
2800	37.482	254.491	224.352	84.389	1367.792	1141.028	−21.286
2900	37.647	255.810	225.415	88 146	1369.811	1132.893	−20.406
3000	37.806	257.089	226.449	91.918	1371.825	1124 689	−19.583
3100	37.962	258.331	227.458	95 707	1373.834	1116.418	−18.812
3200	38.114	259.538	228.441	99.510	1375.839	1108.082	−18.088
3300	38.265	260.714	229 402	103.329	1377.839	1099.684	−17 407
3400	38.413	261.858	230.340	107.163	1379.836	1091.225	−16.765
3500	38.562	262.974	231.256	111.012	1381.829	1082.707	−16.159
3600	38.709	264.062	232.152	114.876	1383.819	1074.133	−15.585
3700	38.857	265.125	233.029	118.754	1385.806	1065.503	−15.042
3800	39.006	266.163	233.887	122.647	1387.792	1056.820	−14.527
3900	39.156	267.178	234.728	126.555	1389.776	1048.084	−14.038
4000	39.307	268.171	235.552	130.478	1391.759	1039.298	−13.572
4100	39.460	269.144	236.359	134.417	1393.741	1030.462	−13.128
4200	39.615	270.097	237.151	138.371	1395.723	1021.577	−12.705
4300	39 773	271.031	237.928	142.340	1397 706	1012.646	−12.301
4400	39.932	271.947	238.691	146.325	1399.689	1003.668	−11.915
4500	40.094	272.846	239.440	150.326	1401.673	994.644	−11.546
4600	40.258	273.729	240.176	154.344	1403.659	985.577	−11.192
4700	40.425	274.597	240.899	158.378	1405.647	976.467	−10.852
4800	40.595	275 449	241.610	162.429	1407.637	967.315	−10.527
4900	40.767	276.288	242.309	166.497	1409.630	958.121	−10.214
5000	40 942	277.114	242.997	170.583	1411.626	948.887	−9.913
5100	41.120	277.926	243.674	174.686	1413.625	939.612	−9.624
5200	41.299	278.726	244.340	178.807	1415.628	930.298	−9.345
5300	41.482	279.515	244.997	182.946	1417.635	920.946	−9.076
5400	41.666	280.292	245.643	187.103	1419.646	911.555	−8.818
5500	41.853	281.058	246.280	191.279	1421.662	902.127	−8.568
5600	42.042	281.814	246.908	195.474	1423 682	892.663	−8.326
5700	42.233	282.560	247.527	199.688	1425.706	883.163	−8.093
5800	42.425	283.296	248.137	203 920	1427.736	873.627	−7.868
5900	42.619	284 023	248 739	208 173	1429.771	864 055	−7.650
6000	42.815	284.741	249.333	212.444	1431.811	854 450	−7.439

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

$S°(298.15\ K) = [172.469 \pm 0.8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -137\ 43 \pm 3.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298\ 15\ K) = -143.59 \pm 3.8\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = [3770]\ cm^{-1}$ $\omega_e x_e = [74.7]\ cm^{-1}$ $\sigma = 1$
$B_e = [19.2]\ cm^{-1}$ $\alpha_e = [0.65]\ cm^{-1}$ $r_e = [0\ 9628]$ Å

Enthalpy of Formation

Branscomb[1] has obtained an electron affinity of OH of 1 83 ± 0.04 eV (42 2 ± 0.9 kcal mol^{-1}) from the photodetachment spectrum of OH^- The vibrational state was identified as the ground state since no other absorption sequence could be detected by a thorough search. Kay and Page[2] have also determined the electron affinity by the magnetron method and report 49.1 at 1820 K, which reduces to 40 ± 2.7 $kcal \cdot mol^{-1}$ at 0 K. They also disclaim prior papers, Page[3] and Page and Sugden,[4] which supported higher values. Feugier and Queraud[5] have reported an electron affinity at 2250 K of 2.13 eV (49.1 $kcal \cdot mol^{-1}$) which reduces to 37.7 kcal mol^{-1} at 0 K. We adopt the value reported by Branscomb[1] which yields $\Delta_f H°(OH^-, g)$ 0 K = −32.85 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Branscomb[1] deduced from his photodetachment spectra that ω_e, B_e and r_e are very close to the values for OH(g). Our adopted values are from the calculations of Cade[6] corrected for the mean deviations in OH and HF The values of $\omega_e x_e$ and α_e were estimated by comparison with OH(g) and other related hydrides. The ground state configuration was assumed to be that of HF(g) with which OH^- is isoelectronic.

References

[1]L. M. Branscomb, Phys. Rev 148, 11 (1966).
[2]J. Kay and F. M. Page, Trans. Faraday Soc. 62, 3081 (1966).
[3]F. M. Page, Discussions Faraday Soc. 19, 87 (1955).
[4]F. M. Page and T. M. Sugden, Trans. Faraday Soc. 53, 1092 (1957).
[5]A. Feugier and A. Queraud, Elec. MHD, Proc. Symp. 4, 2129 (1968).
[6]P. E. Cade, unpublished calculations, quoted in reference 1.

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

	J·K⁻¹mol⁻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	−8.606	−137 429		
100	29.127	140.647	198.369	−5.772			
200	29.130	160.836	175.134	−2.860			
250	29.135	167.336	172.948	−1.403			
298.15	29.141	172.469	172.469	0.	−143.595	−138.698	24.299
300	29.141	172.649	172.469	0.054	−143.633	−138.668	24.144
350	29.148	177.141	172.824	1.511	−144.678	−137.758	20.559
400	29.157	181.034	173.612	2.969	−145.736	−136.697	17.851
450	29.170	184.469	174.631	4.427	−146.806	−135.503	15.729
500	29.194	187.543	175.772	5.886	−147.888	−134.189	14.019
600	29.289	192.873	178.191	8.809	−150.087	−131.244	11.426
700	29 471	197.401	180.620	11.747	−152.325	−127.927	9.546
800	29.749	201.353	182.970	14.707	−154.588	−124.287	8.115
900	30 108	204.877	185.211	17.699	−156.864	−120.363	6.986
1000	30.525	208.070	187.340	20.730	−159 145	−116.185	6.069
1100	30.975	211.001	189.360	23.805	−161.422	−111.779	5.308
1200	31.439	213 716	191.278	26.926	−163.694	−107.165	4.665
1300	31.900	216.250	193.102	30.093	−165.957	−102.363	4.113
1400	32.347	218.631	194.841	33.305	−168.212	−97.386	3.634
1500	32.773	220.877	196.503	36.562	−170.459	−92.249	3.212
1600	33.176	223.005	198.093	39.859	−172.700	−86.962	2.839
1700	33.553	225.028	199.619	43.196	−174.934	−81.535	2.505
1800	33.904	226.956	201.084	46.569	−177.165	−75.976	2.205
1900	34.230	228.798	202.495	49.976	−179.392	−70.294	1.933
2000	34.532	230.561	203.855	53.414	−181.619	−64.494	1.684
2100	34.812	232.253	205.167	56.881	−183.846	−58.583	1.457
2200	35 072	233.879	206.435	60.376	−186.074	−52.566	1.248
2300	35.312	235.443	207.663	63.895	−188.304	−46.448	1.055
2400	35.536	236.951	208.852	67.438	−190.537	−40.232	0.876
2500	35.744	238.406	210.005	71.002	−192.774	−33.924	0.709
2600	35.938	239.811	211.124	74.586	−195.015	−27.525	0.553
2700	36.119	241.171	212.212	78.189	−197.261	−21.041	0.407
2800	36.288	242.488	213.270	81.809	−199.513	−14 473	0.270
2900	36.447	243.764	214.300	85.446	−201.771	−7.825	0.141
3000	36.596	245.002	215.303	89.098	−204.034	−1.098	0.019
3100	36.737	246.204	216.280	92.765	−206.304	5.704	−0.096
3200	36.870	247.373	217.234	96.446	−208.580	12.579	−0.205
3300	36.996	248.509	218.164	100.139	−210.862	19.525	−0.309
3400	37.115	249.616	219.073	103.844	−213.151	26.541	−0.408
3500	37.228	250.693	219.961	107.562	−215.447	33.624	−0.502
3600	37.336	251.743	220.830	111.290	−217.750	40.773	−0.592
3700	37.439	252.768	221.679	115.029	−220.059	47.986	−0.677
3800	37.538	253.768	222.510	118.778	−222.375	55.262	−0.760
3900	37.632	254.744	223.324	122.536	−224.698	62.599	−0.838
4000	37.723	255.698	224.122	126.304	−227.027	69.995	−0.914
4100	37.810	256.630	224.903	130.081	−229.364	77.449	−0.987
4200	37.894	257.542	225.670	133.866	−231.708	84.961	−1.057
4300	37.975	258.435	226.421	137.659	−234.058	92.528	−1.124
4400	38.053	259.309	227.159	141.461	−236.416	100.150	−1.189
4500	38.129	260.165	227.883	145.270	−238.781	107.826	−1.252
4600	38.203	261.004	228.594	149.086	−241.153	115.554	−1.312
4700	38.274	261.826	229.292	152.910	−243.533	123.335	−1.371
4800	38.344	262.633	229.978	156.741	−245.920	131.166	−1.427
4900	38.411	263.424	230.653	160.579	−248.315	139.047	−1.482
5000	38.477	264.201	231.316	164.423	−250.717	146.977	−1.535
5100	38.541	264.963	231.968	168.274	−253.127	154.954	−1.587
5200	38.604	265.712	232.610	172.132	−255.545	162.979	−1.637
5300	38.666	266.448	233.242	175.995	−257.970	171.051	−1.686
5400	38.726	267.172	233.863	179.865	−260.405	179.168	−1.733
5500	38.785	267.883	234.475	183.740	−262.847	187.331	−1.779
5600	38.843	268.582	235.078	187.622	−265.297	195.539	−1.824
5700	38.900	269.270	235.672	191.509	−267.756	203.789	−1.868
5800	38.955	269.947	236.257	195.402	−270.224	212.084	−1.910
5900	39.010	270.613	236.834	199.300	−272.700	220.420	−1.951
6000	39.064	271.270	237.402	203.204	−275.186	228.799	−1.992

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

$S°(298.15\ K) = [246.511 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -201.08 \pm 20.9\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -205.52 \pm 20.9\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights ϵ_i, cm^{-1}	g_i
0	[2]
[14700]	[2]
[15100]	[2]
[16000]	[2]

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[498](1)
[438](2)
[3650](1)

Point Group: [$C_{\infty v}$] $\sigma = 1$
Bond Distances: Sr–O = [2.10] Å O–H = [0.96] Å
Bond Angle: Sr–O–H = [180]°
Rotational Constant: B_0 = [0.251104] cm^{-1}

Enthalpy of Formation

The adopted enthalpy of formation is based on assessment of $D_0°$ values derived from flame spectra of CaOH, SrOH, and BaOH. Cotton and Jenkins[1] found both the alkaline earth monohydroxides and dihydroxides to be present in significant amounts in fuel–rich hydrogen–oxygen–nitrogen flames. They determined equilibrium constants for the reactions $M(g) + H_2O(g) = MOH(g) + H(g)$ and $M(g) + 2\ H_2O(g) = M(OH)_2(g) + 2\ H(g)$ and derived $D_0°$ values. For $D_0°$(Sr–OH), Cotton and Jenkins[1] gave 103 ± 5 kcal·mol^{-1}. Ryabova and Gurvich[2] considered SrOH to be the dominant compound and reported $D_0°$ = 95 ± 8 kcal·mol^{-1}. Sugden and Schofield[3] interpreted $Sr(OH)_2$ as dominant. Cotton and Jenkins[1] have recalculated the work of Ryabova and Gurvich[2] and of Sugden and Schofield[3] considering both SrOH and $Sr(OH)_2$ to be present and have obtained the recalculated $D_0°$(Sr–OH) values of 96 and 101 kcal·mol^{-1}, respectively. Gurvich *et al.*[4] made further measurements, interpreted SrOH as dominant, and reported $D_0°$(Sr–OH) = 93 ± 3 kcal·mol^{-1}. Kalff and Alkemade[5] chose flame conditions to minimize the dihydroxide formation and determined a 3rd law analysis of the experimental equilibrium constants tabulated by Cotton and Jenkins[1] using current JANAF auxiliary data[7] leads to $D_0°$(Sr–OH) = 103.7 kcal·mol^{-1} which is 0.7 kcal·mol^{-1} higher than the 103 kcal·mol^{-1} given by Cotton and Jenkins.[1] Applying the correction to the value of Ryabova and Gurvich[2] and Sugden and Schofield[3] as recalculated by Cotton and Jenkins[1] gives $D_0°$(Sr–OH) = 96.7 and 101.7 kcal·mol^{-1}, respectively.

Because the corrected dissociation energy of Ryabova and Gurvich was near the adopted value for $Ba(OH)_2(g)$,[7] their corrected value was adopted for $Sr(OH)_2(g)$.[7] While their corrected value for BaOH(g)[7] is not as close to the adopted value as in the dihydroxide case, it is nevertheless the nearest one, and therefore $D_0°$(Sr–OH) = 96.7 kcal·mol^{-1} is adopted.

The ratio of the dissociation energies of the alkaline earth monohalides to those of the corresponding dihalides range from 0.40 to 0.51 with the ratio for the strontium fluorides being 0.49.[7] The similarity between the halides and hydroxides has been established.[8–11] The ratio of the adopted values for the dissociation energies of SrOH(g) and $Sr(OH)_2$ is 0.49 where $D_0°$ of the dihydroxide is defined by the reaction $Sr(OH)_2(g) = Sr(g) + 2\ OH(g)$ and is 198.6 kcal·mol^{-1}.[7]

$\Delta_f H°$(SrOH, g, 0 K) = −48.11 ± 5 kcal·mol^{-1} is calculated from the adopted dissociation energy.

Heat Capacity and Entropy

The analogy between gaseous monohydroxides and monohalides, particularly the monofluorides, has been recognized.[8–11] The molecular configuration is assumed to be linear in accordance with the prediction of Walsh[12] and the evidence that the gaseous alkali metal hydroxide are linear.[13–15] The ground state is assumed to be $^2\Sigma^+$ by analogy with SrF and SrCl.[7] The electronic levels are estimated from the band spectra observed by James and Sugden,[16] Lagerqvist and Huldt,[17] Charton and Gaydon,[18] Zhitkevich *et al.*,[19] and Van der Hurk *et al.*,[20] and the comparison with SrF and SrCl.[7]

The Sr–O bond distance is estimated to be slightly larger, 0.02 Å, than the Sr–F distance[7] after noting the close similarity in the bond distance of the alkali metal fluorides and hydroxides. The O–H bond distance is that in water.[7]

The Sr–O stretching frequency, 498 cm^{-1}, is estimated to be the same as the Sr–F stretching frequency.[7, 11] The O–H stretching frequency, 3650 cm^{-1}, is estimated from the alkali hydroxide series. The bending frequency, 438 cm^{-1}, is estimated by assuming that the ratio of the bending force constant to the stretching force constant is 0.022, which is the average ratio found in the alkali metal monohydroxides by Acquista and Abramowitz.[11, 15]

The entropy in the present table is lower by 0.06 cal·K^{-1} mol^{-1} at 298.15 K and 0.10 cal·K^{-1}·mol^{-1} at 1000 K than that proposed by Jackson;[11] the data relevant to the calculation are nearly the same.

Continued on page 1358

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	−10.707	−201.082	−201.082	INFINITE
100	30.646	205.253	282.997	−7.774	−202.600	−206.619	107.927
200	39.954	229.305	250.551	−4.249	−204.366	−209.895	54.819
250	43.517	238.626	247.255	−2.157	−205.004	−211.206	44.129
298.15	45.958	246.511	246.511	0.	−205.518	−212.347	37.202
300	46.036	246.796	246.512	0.085	−205.536	−212.389	36.980
350	47.812	254.034	247.080	2.434	−206.003	−213.494	31.862
400	49.088	260.506	248.361	4.858	−206.431	−214.534	28.015
450	50.028	266.345	250.040	7.337	−206.842	−215.523	25.017
500	50.744	271.654	251.940	9.857	−207.251	−216.465	22.614
600	51.775	281.003	256.026	14.986	−208.096	−218.230	18.999
700	52.534	289.043	260.182	20.203	−209.009	−219.848	16.405
800	53.182	296.101	264.239	25.490	−210.007	−221.329	14.451
900	53.787	302.401	268.136	30.838	−211.722	−222.608	12.920
1000	54.371	308.098	271.852	36.246	−212.581	−223.772	11.689
1100	54.936	313.307	275.387	41.712	−221.325	−224.484	10.660
1200	55.477	318.110	278.750	47.233	−223.064	−224.694	9.781
1300	55.990	322.571	281.951	52.806	−224.789	−224.760	9.031
1400	56.470	326.738	285.003	58.430	−226.501	−224.694	8.383
1500	56.916	330.650	287.917	64.099	−228.202	−224.505	7.818
1600	57.329	334.336	290.704	69.812	−229.895	−224.203	7.319
1700	57.710	337.824	293.374	75.564	−368.496	−222.616	6.840
1800	58.062	341.132	295.936	81.353	−368.318	−214.040	6.211
1900	58.389	344.280	298.398	87.176	−368.143	−205.474	5.649
2000	58.694	347.283	300.768	93.030	−367.974	−196.917	5.143
2100	58.982	350.154	303.052	98.914	−367.817	−188.368	4.685
2200	59.256	352.904	305.256	104.826	−367.677	−179.826	4.270
2300	59.520	355.544	307.385	110.765	−367.560	−171.290	3.890
2400	59.777	358.083	309.445	116.730	−367.471	−162.759	3.542
2500	60.031	360.528	311.440	122.720	−367.418	−154.231	3.222
2600	60.283	362.887	313.374	128.736	−367.409	−145.703	2.927
2700	60.537	365.167	315.250	134.777	−367.452	−137.175	2.654
2800	60.793	367.373	317.072	140.843	−367.556	−128.645	2.400
2900	61.053	369.511	318.844	146.935	−367.728	−120.110	2.163
3000	61.319	371.585	320.567	153.054	−367.979	−111.567	1.943
3100	61.590	373.600	322.246	159.199	−368.317	−103.014	1.736
3200	61.867	375.560	323.881	165.372	−368.750	−94.450	1.542
3300	62.149	377.468	325.477	171.573	−369.288	−85.870	1.359
3400	62.438	379.328	327.033	177.802	−369.938	−77.272	1.187
3500	62.731	381.142	328.553	184.060	−370.707	−68.654	1.025
3600	63.029	382.913	330.039	190.348	−371.602	−60.011	0.871
3700	63.330	384.644	331.491	196.666	−372.629	−51.342	0.725
3800	63.634	386.337	332.912	203.014	−373.792	−42.643	0.586
3900	63.940	387.994	334.304	209.393	−375.094	−33.912	0.454
4000	64.247	389.617	335.666	215.803	−376.539	−25.146	0.328
4100	64.553	391.207	337.002	222.243	−378.127	−16.341	0.208
4200	64.858	392.766	338.311	228.713	−379.856	−7.497	0.093
4300	65.161	394.296	339.595	235.214	−381.729	1.391	−0.017
4400	65.461	395.797	340.855	241.745	−383.744	10.323	−0.123
4500	65.756	397.272	342.093	248.306	−385.896	19.303	−0.224
4600	66.046	398.720	343.308	254.896	−388.117	28.327	−0.322
4700	66.330	400.144	344.502	261.515	−390.513	37.406	−0.416
4800	66.608	401.543	345.676	268.162	−393.029	46.537	−0.506
4900	66.878	402.919	346.830	274.837	−395.659	55.722	−0.594
5000	67.140	404.273	347.966	281.537	−398.390	64.961	−0.679
5100	67.393	405.605	349.083	288.264	−401.201	74.254	−0.761
5200	67.637	406.916	350.182	295.016	−404.123	83.604	−0.840
5300	67.871	408.207	351.265	301.791	−407.129	93.013	−0.917
5400	68.096	409.478	352.331	308.590	−410.210	102.478	−0.991
5500	68.311	410.729	353.382	315.410	−413.360	112.001	−1.064
5600	68.515	411.962	354.417	322.251	−416.571	121.582	−1.134
5700	68.708	413.176	355.437	329.113	−419.835	131.221	−1.203
5800	68.891	414.373	356.443	335.993	−423.145	140.918	−1.269
5900	69.063	415.552	357.435	342.891	−426.285	150.647	−1.334
6000	69.225	416.714	358.413	349.805	−429.638	160.454	−1.397

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

Strontium Hydroxide, Ion ($SrOH^+$) — IDEAL GAS — M_r = 104.626791

$S°(298.15\ K) = [241\ 049 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 318.99 \pm 62.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 320.80 \pm 62.8\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[490](1)
[430](2)
[3650](1)

Ground State Quantum Weight: [1]
Point Group: [$C_{\infty v}$]
Bond Distances: Sr–O = [2.1] Å O–H = [0.96] Å
Bond Angle: Sr–O–H = [180]°
Rotational Constant: B_o = [0.251111] cm^{-1}

$\sigma = 1$

Enthalpy of Formation

The ionization potential of SrOH(g) was deduced by Kelly an Padley[1] to be 5.55 ± 0.1 eV. Using a rotating single probe, these authors quantitatively examined the total positive ion concentrations produced from Sr aqueous salt solutions in fuel rich, premixed $H_2 + O_2 + N_2$ flames. Using current JANAF auxiliary data,[2] we recalculate the ionization potential to be 5.75 eV.

Jensen[3] determined $\Delta_f H°(0\ K) = 25 \pm 8\ kcal \cdot mol^{-1}$ for $Sr(g) + OH(g) = SrOH^+(g) + e^-$ in atmospheric pressure $H_2 + O_2 + N_2$ flames using the microwave cavity resonance method. This value was calculated assuming a bent molecule for $SrOH^+$, the value is not significantly changed, within the uncertainty, by the change in the configuration. Using auxiliary data[2], we derive an ionization potential of 5.28 eV, which is in fair agreement with the value derived from the data of Kelly and Padly.[1]

We adopt IP = 5 39 eV (124.30 $kcal \cdot mol^{-1}$) which is an average of the above two studies.[1,3] This leads to $\Delta_f H°(0\ K) = 76.19\ kcal \cdot mol^{-1}$ and $\Delta_f H°(298.15\ K) = 76.67\ kcal \cdot mol^{-1}$ for $SrOH^+(g)$. We assign an uncertainty of ±15 kcal mol^{-1}.

In comparison, the ionization potential of SrF(g) is 5.03 eV[2] while that of Sr(g) is 5.692 eV.[4] Note that the average of these two values is very close to our adopted ionization potential.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the gaseous alkali metal hydroxides are linear[2,5-7] In addition, Walsh[8] had predicted that BAH molecules (H = hydrogen atom) with ten or less valence electrons ($SrOH^+$ has eight valence electrons) will be linear in their ground state. The molecule $SrOH^+$ is isoelectronic with RbOH.

The bond dissociation energy for $SrOH^+$ (103.7 $kcal \cdot mol^{-1}$),[2,4] for the process $SrOH^+(g) = Sr^+(g) + OH(g)$ is fairly close to that for SrOH (96.7 $kcal \cdot mol^{-1}$).[2] This suggests that the bonding in these two molecules may be quite similar Thus bond distances are assumed to be the same as those adopted for SrOH(g).[2] The vibrational frequencies are assumed to be similar to those adopted for SrOH(g).[2] The ground state quantum weight is assumed to be the same as that of KOH (g).[2]

References

[1]R. Kelly and P. J. Padley, Trans. Faraday Soc. 67, 1384 (1971).
[2]JANAF Thermochemical Tables: e^-, 3–31–65, $H_2(g)$ and $H_2O(g)$, 3–31–61; Sr(g), 12–31–70; OH(g), 12–31–70; H(g), 6–30–74, SrOH(g) and $Sr(OH)_2(g)$, 12–31–75.
[3]D. E. Jensen, Combustion and Flame 12, 261 (1968).
[4]C E. Moore, U. S. Nat. Bur Stand. Circ. 467, Vol. II, (1958).
[5]N. Acquista, S Abramowitz, and D. R Lide, J. Chem Phys. 49, 780 (1968).
[6]R. L Kuczkowski and D. R. Lide, J. Chem. Phys. 44, 3131 (1966).
[7]N Acquista and S. Abramowitz, U. S Nat Bur Stand. Report 9905, (1968).
[8]A. D. Walsh, J. Chem. Soc 1953, 2288 (1953).

Strontium Hydroxide, Ion ($SrOH^+$) — $H_1O_1Sr_1^+(g)$

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻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	−9.760	318.986		
100	30.774	199.518	277.769	−7.825			
200	40.248	223.738	245.112	−4.275			
250	43.779	233.120	241.797	−2.169			
298.15	46.180	241.049	241.049	0.	320.800	309.345	−54.196
300	46.256	241.335	241.050	0.085	320.820	309.274	−53.849
350	47.994	248.603	241.620	2.444	321.403	307.304	−45.863
400	49.238	255.098	242.906	4.877	322.023	305.248	−39.861
450	50.154	260.953	244.591	7.363	322.658	303.113	−35.184
500	50.850	266.275	246.498	9.888	323.294	300.907	−31.436
600	51.852	275.640	250.595	15.027	324.537	296.312	−25.796
700	52.592	283.691	254.762	20.250	325.709	291.514	−21.753
800	53.228	290.756	258.828	25.542	326.795	286.553	−18.710
900	53.824	297.060	262.732	30.895	327.162	281.535	−16.340
1000	54.401	302.760	266.454	36.306	328.386	276.399	−14.438
1100	54.961	307.972	269.995	41.774	321.722	271.506	−12.893
1200	55.498	312.777	273.363	47.297	322.064	266.926	−11.619
1300	56.007	317.240	276.568	52.873	322.420	262.317	−10.540
1400	56.484	321.408	279.624	58.498	322.788	257.680	−9.614
1500	56.927	325.320	282.541	64.169	323.167	253.016	−8.811
1600	57.335	329.008	285.331	69.882	323.554	248.327	−8.107
1700	57.710	332.495	288.004	75.635	187.031	244.793	−7.522
1800	58.052	335.803	290.568	81.423	189.288	248.126	−7.200
1900	58.364	338.951	293.033	87.244	191.540	251.333	−6.910
2000	58.648	341.952	295.404	93.095	193.783	254.422	−6.645
2100	58.907	344.819	297.690	98.973	196.013	257.399	−6.402
2200	59.143	347.565	299.895	104.876	198.222	260.271	−6.180
2300	59.358	350.199	302.025	110.801	200.405	263.042	−5.974
2400	59.554	352.730	304.085	116.747	202.553	265.719	−5.783
2500	59.734	355.164	306.080	122.711	204.658	268.307	−5.606
2600	59.897	357.511	308.013	128.693	206.712	270.812	−5.441
2700	60.047	359.774	309.889	134.690	208.704	273.240	−5.286
2800	60.185	361.960	311.710	140.702	210.625	275.595	−5.141
2900	60.311	364.074	313.479	146.727	212.463	277.882	−5.005
3000	60.428	366.121	315.200	152.764	214.210	280.108	−4.877
3100	60.535	368.104	316.875	158.812	215.853	282.278	−4.756
3200	60.634	370.028	318.506	164.870	217.384	284.395	−4.642
3300	60.725	371.895	320.095	170.938	218.792	286.467	−4.534
3400	60.810	373.709	321.646	177.015	220.069	288.499	−4.432
3500	60.888	375.473	323.159	183.100	221.204	290 494	−4.335
3600	60.961	377.189	324.636	189.193	222.192	292.460	−4.243
3700	61.029	378.860	326.079	195.292	223.026	294.399	−4.156
3800	61.092	380.489	327.489	201.398	223.699	296.320	−4.073
3900	61.151	382.076	328.869	207.510	224.209	298.224	−3.994
4000	61.205	383.625	330.218	213.628	224.551	300.116	−3.919
4100	61.257	385.137	331.539	219.751	224.725	302.003	−3.848
4200	61.305	386.614	332.833	225.879	224.732	303.887	−3.779
4300	61.350	388.057	334.101	232.012	224.569	305.774	−3.714
4400	61.392	389 468	335.343	238.149	224.239	307.666	−3.652
4500	61.432	390.848	336.561	244.291	223.746	309.567	−3.593
4600	61.470	392.199	337.756	250.436	223.159	311.475	−3.537
4700	61.505	393.521	338.929	256.584	222.371	313 404	−3.483
4800	61.538	394.816	340.080	262.737	221 439	315.350	−3.432
4900	61.570	396.086	341.210	268.892	220.369	317.318	−3.383
5000	61.599	397.330	342.320	275.050	219.174	319.308	−3.336
5100	61.627	398.550	343.410	281.212	217.876	321.321	−3.291
5200	61.654	399.747	344.482	287.376	216.445	323.363	−3.248
5300	61.679	400.921	345.536	293.542	214.909	325 434	−3.207
5400	61.703	402.074	346.572	299.712	213.277	327.534	−3.168
5500	61.725	403.207	347.592	305.883	211.557	329.666	−3.131
5600	61 747	404.319	348.595	312.057	209.757	331.830	−3.095
5700	61.767	405.412	349.582	318.232	207.886	334.026	−3.061
5800	61.787	406.487	350.554	324.410	205.952	336.256	−3.028
5900	61.805	407.543	351.511	330.590	204.172	338.495	−2.997
6000	61 823	408.582	352.454	336.771	202.164	340 789	−2.967

PREVIOUS June 1976 (1 atm) CURRENT June 1976 (1 bar)

Strontium Hydroxide, Ion ($SrOH^+$) — $H_1O_1Sr_1^+(g)$

$S°(298.15\ K) = 229.106 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 5.01 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 2.09 \pm 8.4\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$\tilde{X}[^2A'']$	0	2
$[^2A']$	7029.764	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
3410(1)
1390(1)
1095(1)

Point Group: C_1 $\sigma = 1$
Bond Distances: H–O = 0.977 Å O–O = 1.335 Å
Bond Angle: H–O–O = 104.1°
Product of the Moments of Inertia: $I_A I_B I_C = 0.9128 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

Wagman[1] and Cohen and Westburg[2] have reviewed the data which leads to the enthalpy of formation for HO_2(g). We adopt the value suggested by Wagman,[1] $\Delta_f H°(HO_2, g, 298.15\ K) = 0.5 \pm 2.0\ kcal \cdot mol^{-1}$ Gurvich *et al.*[3] have also critically reviewed many of the same sources and have adopted the same value for the enthaply of formation. The analysis by Wagman[1] follows.

Kochubei and Moin[4] made a kinetic determination of the enthaply of formation of the HO_2 radical by studying the bimolecular radical formation reactions (forward only) $HX(g) + O_2(g) = HO_2(g) + X(g)$, where X = Cl, Br, and I The basic rate data are not given for this study. However, Wagman corrected their reported results by a small amount due to the improperly used term designated as $\bar{T}d\Delta H/dT$). In the recalculation, the reported E_r–E_r values were used as the $\Delta_r H°$ at the stated mean temperature. Hence the $\Delta_f H°(298.15\ K)$ for HO_2(g) from this study is about 0.7 $kcal \cdot mol^{-1}$.

Calculations for $\Delta_f H°(HO_2, g)$ were also made using the reaction $H_3^+(g) + O_2(g) = HO_2^+(g) + H_2$ (g). For this reaction, Fennelly, *et al.*[5] obtained $\Delta_r H°(0\ K) = -0.05 + 0.07\ kcal \cdot mol^{-1}$. Kim *et al.*,[6] from rate constants for the above, obtain $\Delta_r G°(298.15\ K) = -0.41\ kcal \cdot mol^{-1}$. Estimating $\Delta S°(298.15\ K)$ to be $+0.40\ cal \cdot K^{-1} \cdot mol^{-1}$, and hence $\Delta_r H°(298.15\ K) = -0.3 \pm 0.10\ kcal \cdot mol^{-1}$. The best value is $\Delta_r H°(298.15\ K) = -0.2 \pm 0.2\ kcal \cdot mol^{-1}$ Quantum mechanical calculations of the energy of H_3^+ have been made by a number of people.[7,8] Using the results of Duben and Lowe[8] and ionization potential of HO_2 from Foner and Hudson,[9] Wagman obtained $\Delta_f H°(HO_2, g) = 1.1\ kcal \cdot mol^{-1}$. This yields $\Delta_f H°(HO_2, g, 298\ 15\ K) = 0.4\ kcal \cdot mol^{-1}$.

An additional calculation can be obtained from the ionization and appearance potentials for HO_2 from H_2O_2 Recent measurements by photoionization at NBS yield $\Delta_r H° = 348.7 \pm 0.2\ kcal \cdot mol^{-1}$ for $H_2O_2(g)$, $H_2O_2 + e^- = HO_{2+}(g) + H^+ + 2\,e^-$. Combining with the ionization potential of HO_2(g) leads to $\Delta_r H°$ for $H_2O_2(g) = HO_2(g) + H(g)$ and $\Delta_f H°(HO_2, g, 298.15\ K) = 0.6\ kcal \cdot mol^{-1}$.

In these last two calculations, the principal uncertainty lies in the value for the ionization potential of HO_2 reported by Foner and Hudson.[9] However the general consistency of the various paths indicates that a reasonable value for $\Delta_f H°(HO_2, g, 298.15\ K)$ is $0.5 \pm 2.0\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The vibrational frequencies adopted are those determined by Paukert and Johnston[11] from infrared absorption measurements on gas phase HO_2. Matrix studies of HO_2 yielded similar results.[12-14] The bond lengths and bond angles are taken from the microwave spectroscopic study of Beers and Howard.[15] Other measurements are in agreement with these values.[11, 14, 16, 17]

The energy separation between the ground and lowest excited electronic state was determined by Freedman and Jones.[18] Their measurements also yield $I_A I_B I_C$ to be $1.090 \times 10^{-117}\ g^3\ cm^6$ and $\nu_3 = 983\ cm^{-1}$ for the $^2A'$ state. This indicates that the structure of this excited state is quite similar to the ground state; thus, for convenience in calculating the entropy and heat capacity, the vibrational frequencies and moments of inertia of the excited state are taken to be the same as the ground state. For the ground electronic state, the principal moments of inertia are: $I_A = 0.1375 \times 10^{-39}$, $I_B = 2.5088 \times 10^{-39}$ and $I_C = 2.6463 \times 10^{-39}\ g \cdot cm^2$.

References

[1]D. D. Wagman, U. S. Nat. Bur. Stand., personal communication to Dr. Norman Cohen, (March 21, 1978).
[2]N. Cohen and K. Westburg, Aerospace Corporation, personal communication to Dr. Joseph Masi, (February 22, 1978).
[3]L. V. Gurvich *et al.*, "Thermodynamic Properties of Individual Substances, Vol. I, Books 1 and 2," Nauka, Moscow, USSR, (1978).
[4]V. F. Kochubie and J. B. Moin, Dokl. Akad. Nauk SSSR **219**, 141 (1974).
[5]P. F Fennelly, R. S. Hensworth, H I. Schiff, and D. K Bohme, J Chem. Phys. 59, 6405 (1973).
[6]J. K. Kim, L. P. Theard, and W T. Huntress, Chem. Phys. Letters 32, 610 (1975).

Continued on page 1358

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
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−10.003	5.006	5.006	INFINITE
100	33.258	192.430	259.201	−6.677	3.928	7.052	−3.683
200	33.491	215.515	232.243	−3.346	3.001	10.536	−2.752
250	34.044	223.040	229.676	−1.659	2.532	12.475	−2.606
298.15	34.905	229.106	229.106	0.	2.092	14.430	−2.528
300	34.943	229.322	229.107	0.065	2.076	14.506	−2.526
350	36.072	234.791	229.536	1.839	1.649	16.612	−2.479
400	37.296	239.688	230.504	3.673	1.260	18.777	−2.452
450	38.519	244.151	231.776	5.569	0.908	20.988	−2.436
500	39.687	248.271	233.222	7.524	0.591	23.236	−2.427
600	41.781	255.697	236.363	11.601	0.043	27.819	−2.422
700	43.558	262.275	239.603	15.870	−0.411	32.485	−2.424
800	45.084	268.193	242.813	20.304	−0.790	37.211	−2.430
900	46.418	273.582	245.937	24.880	−1.107	41.981	−2.436
1000	47.604	278.535	248.952	29.583	−1.368	46.783	−2.444
1100	48.672	283.123	251.853	34.397	−1.582	51.609	−2.451
1200	49.643	287.400	254.639	39.314	−1.754	56.452	−2.457
1300	50.535	291.410	257.315	44.323	−1.887	61.308	−2.463
1400	51.360	295.185	259.886	49.419	−1.988	66.173	−2.469
1500	52.128	298.755	262.360	54.593	−2.058	71.045	−2.474
1600	52.845	302.143	264.741	59.842	−2.102	75.920	−2.479
1700	53.518	305.367	267.037	65.161	−2.122	80.797	−2.483
1800	54.149	308.444	269.252	70.545	−2.121	85.674	−2.486
1900	54.742	311.388	271.393	75.989	−2.102	90.551	−2.489
2000	55.299	314.210	273.464	81.492	−2.067	95.427	−2.492
2100	55.820	316.921	275.469	87.048	−2.019	100.301	−2.495
2200	56.308	319.529	277.413	92.655	−1.960	105.172	−2.497
2300	56.763	322.042	279.299	98.309	−1 893	110 040	−2.499
2400	57.186	324.467	281.131	104.006	−1.818	114 905	−2.501
2500	57.578	326.809	282.911	109.745	−1.740	119.767	−2.502
2600	57.940	329 075	284.644	115.521	−1.659	124.625	−2.504
2700	58.274	331.268	286.330	121.332	−1.577	129 481	−2.505
2800	58.580	333.393	287.973	127.175	−1 497	134.334	−2.506
2900	58.860	335.453	289.575	133.047	−1.419	139.183	−2.507
3000	59.115	337.453	291.138	138.946	−1.346	144.030	−2.508
3100	59.347	339.395	292.663	144.869	−1.278	148.876	−2.509
3200	59.557	341.283	294.153	150.814	−1.218	153.718	−2.509
3300	59 745	343.118	295.609	156.780	−1.165	158.558	−2.510
3400	59.915	344.904	297.033	162.763	−1.122	163.398	−2.510
3500	60.066	346.643	298.426	168.762	−1.089	168.236	−2.511
3600	60.200	348.337	299.789	174.775	−1.067	173.074	−2.511
3700	60.318	349.989	301.123	180.801	−1.058	177.910	−2.512
3800	60.423	351.599	302.431	186.839	−1.061	182.748	−2.512
3900	60.513	353 169	303.711	192.886	−1.078	187.586	−2.512
4000	60.592	354 702	304.967	198.941	−1.109	192.423	−2.513
4100	60.659	356.199	306.199	205.004	−1.156	197.262	−2.513
4200	60.716	357.662	307.406	211.072	−1.217	202.102	−2.514
4300	60 764	359.091	308.592	217.146	−1.296	206.945	−2.514
4400	60.803	360.488	309.756	223.225	−1.391	211.788	−2.514
4500	60 834	361.855	310.898	229.307	−1.504	216.634	−2.515
4600	60.858	363.193	312.021	235.391	−1.634	221.482	−2.515
4700	60.876	364.502	313.123	241.478	−1.784	226.335	−2.515
4800	60.888	365.783	314.207	247.566	−1.952	231.190	−2.516
4900	60.895	367 039	315.272	253.656	−2.141	236.050	−2.516
5000	60.897	368.269	316.320	259.745	−2.350	240.913	−2.517
5100	60 894	369.475	317.351	265.835	−2.580	245 780	−2.517
5200	60 888	370.658	318.364	271.924	−2.831	250.652	−2.518
5300	60.879	371.817	319.362	278.012	−3.105	255.530	−2.518
5400	60.866	372.955	320.344	284.100	−3.402	260.412	−2.519
5500	60.851	374.072	321.311	290.185	−3.722	265.300	−2.520
5600	60.834	375.168	322.263	296.270	−4.067	270.195	−2.520
5700	60.814	376.245	323.200	302.352	−4.437	275.096	−2.521
5800	60 792	377.302	324.124	308.432	−4.832	280.004	−2.522
5900	60 769	378.341	325.034	314.511	−5.254	284.917	−2.522
6000	60 745	379.362	325.931	320.586	−5.702	289.839	−2.523

PREVIOUS September 1978 (1 atm) CURRENT September 1978 (1 bar)

$S°(298.15\ K) = 196.344\ J\cdot K^{-1}\ mol^{-1}$

$\Delta_f H°(0\ K) = 234.6 \pm 33.5\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 233.6 \pm 33.5\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^3\Sigma^-$	0	3
	[7650]	2
	[15150]	1
	29560	6
	[38110]	2
	[57490]	1

$\omega_e = 2380\ cm^{-1}$ $\omega_e x_e = [55]\ cm^{-1}$ $\sigma = 1$
$B_e = 8.412\ cm^{-1}$ $\alpha_e = [0.28]\ cm^{-1}$ $r_e = 1.43$ Å

Enthalpy of Formation

Jordan[1] estimated the dissociation energy of PH(g) as 70 44 kcal·mol^{-1} using a semiempirical theoretical method. The corresponding value for the enthalpy of formation $\Delta_f H°(298.15\ K)$ is 60.6 ± 8 kcal·mol^{-1}.

Heat Capacity and Entropy

Jordan[1] predicted five electronic levels ($X^3\Sigma$, $A^1\Delta$, $B^1\Sigma$, $D^1\Pi$, $E^1\Sigma$) based on the reported value[2] of 29560 cm^{-1} for the $C^3\Pi$ level (this level is designated $A^3\Pi$ by Herzberg.[2] Several qualitative spectroscopic investigations of PH(g) have been reported and are in general accord with the predictions of Jordan.[1] Ishaq and Pearse[3] reported the values of the rotational constant B_e and the fundamental vibrational frequency ω_e. The value of α_e is calculated from the Morse potential function. The bond distance is calculated from B_e. The value of the anharmonic vibrational term $\omega_e x_e$ is estimated from the relation $\omega_e x_e = \omega_e^2/(4D° + 2\omega_e)$.

References

[1]P. Jordan, J. Chem. Phys. **41**, 1442 (1964).
[2]G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, (1950).
[3]M. Ishaq and R. W B. Pearse, Proc. Roy. Soc. (London) **A173**, 265 (1939), and R. W. B. Pearse, ibid, **A129**, 328 (1930).

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	.000	.000	INFINITE	−8.650	234.555	234.555	INFINITE
100	29.117	164.523	222.248	−5.773	235.045	225.398	−117.736
200	29.130	184.709	199.010	−2.860	234.347	215.772	−56.354
250	29.140	191.210	196.824	−1.404	234.014	211.165	−44.120
298.15	29.162	196.344	196.344	.000	233.611	206.799	−36.230
300	29.163	196.525	196.345	.054	233.594	206.633	−35.978
350	29.217	201.024	196.700	1.513	232.393	202.248	−30.184
400	29.321	204.931	197.490	2.977	231.812	197.981	−25.854
450	29.485	208.394	198.513	4.446	231.235	193.787	−22.494
500	29.709	211.511	199.659	5.926	230.667	189.657	−19.813
600	30.302	216.978	202.102	8.925	229.569	181.559	−15.806
700	31.008	221.701	204.572	11.990	228.533	173.640	−12.957
800	31.742	225.889	206.980	15.128	227.561	165.865	−10.830
900	32.452	229.669	209.294	18.338	226 652	158.208	−9.182
1000	33.111	233.123	211.507	21.616	225.796	150.650	−7.869
1100	33.713	236.308	213.619	24.958	224.985	143.174	−6 799
1200	34.260	239.265	215 634	28.357	160.641	136.850	−5.957
1300	34.759	242.027	217.559	31.808	160.674	134.866	−5.419
1400	35.218	244.620	219.400	35.308	160.728	132.879	−4.958
1500	35.645	247.065	221.164	38.851	160.801	130.887	−4.558
1600	36.046	249.378	222.856	42.436	160.890	128.890	−4.208
1700	36.424	251.575	224.481	46.059	160.993	126.887	−3.899
1800	36.785	253.667	226.045	49.720	161.110	124 878	−3.624
1900	37.131	255.665	227.552	53.416	161.241	122 861	−3.378
2000	37 463	257.578	229.005	57.146	161.385	120.838	−3.156
2100	37.783	259.414	230.410	60.908	161.541	118.807	−2.955
2200	38.090	261.179	231.769	64.702	161.710	116.768	−2.772
2300	38.387	262.878	233.085	68.526	161.891	114.721	−2.605
2400	38.672	264.518	234.360	72.379	162.084	112.666	−2.452
2500	38.947	266.103	235.599	76.260	162.289	110.603	−2.311
2600	39.212	267.635	236.801	80 168	162.506	108.531	−2.180
2700	39.466	269 120	237.971	84.102	162.733	106.451	−2.059
2800	39.709	270.560	239.109	88.061	162.972	104.362	−1.947
2900	39.943	271.957	240.218	92.043	163.220	102.264	−1.842
3000	40.167	273.315	241.299	96.049	163.479	100 158	−1.744
3100	40.382	274.636	242.353	100.077	163.746	98.043	−1.652
3200	40.588	275.921	243.382	104.125	164.022	95.919	−1.566
3300	40.785	277.173	244.387	108.194	164.306	93.786	−1.485
3400	40.973	278.393	245.369	112.282	164.598	91.645	−1.408
3500	41 154	279.584	246.330	116.388	164.896	89 495	−1.336
3600	41.328	280.746	247.270	120.512	165.201	87.336	−1.267
3700	41.494	281.880	248.190	124.654	165.511	85.169	−1.202
3800	41.654	282.989	249.091	128.811	165.827	82.994	−1.141
3900	41.808	284.073	249.974	132.984	166.148	80.810	−1.082
4000	41.956	285.133	250.840	137.172	166.473	78.617	−1.027
4100	42.098	286.171	251.689	141.375	166.802	76.417	−.974
4200	42.237	287.187	252.522	145.592	167.134	74.208	−.923
4300	42.370	288.183	253.340	149.822	167.470	71.992	−.875
4400	42.500	289.158	254.143	154.066	167.809	69.768	−.828
4500	42.627	290.115	254.932	158.322	168.151	67.535	−.784
4600	42.750	291.053	255.707	162.591	168.495	65.296	−.741
4700	42.870	291.974	256.469	166.872	168.842	63.049	−.701
4800	42.988	292.877	257.218	171.165	169.191	60.794	−.662
4900	43.104	293.765	257.955	175.470	169.543	58.532	−.624
5000	43.218	294.637	258.680	179.786	169.897	56.263	−.588
5100	43.331	295.494	259.393	184.113	170.254	53.987	−.553
5200	43.442	296.336	260.096	188.452	170.613	51 704	−.519
5300	43.552	297.165	260.787	192.802	170.976	49.413	−.487
5400	43.661	297.980	261.468	197.162	171.342	47.116	−.456
5500	43.770	298.782	262.140	201.534	171.711	44.812	−.426
5600	43.878	299.572	262.801	205.916	172.085	42.502	−.396
5700	43.985	300.349	263.453	210.309	172.462	40.185	−.368
5800	44.092	301.115	264.096	214.713	172.844	37.861	−.341
5900	44.199	301.870	264.730	219.128	173.232	35.530	−.315
6000	44.307	302.614	265.355	223.553	173.625	33.193	−.289

PREVIOUS· June 1967 (1 atm) CURRENT June 1967 (1 bar)

$S°(298.15\ K) = 220.756\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 238.62 \pm 19.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 236.19 \pm 19.2\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi_{1/2}$	0	2
$^2\Pi_{3/2}$	[8000]	2

$\omega_e = 1564.1\ cm^{-1}$ $\omega_e x_e = 29.75\ cm^{-1}$ $\sigma = 1$
$B_e = 4.971\ cm^{-1}$ $\alpha_e = 0.144\ cm^{-1}$ $r_e = 1.8388$ Å

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from the dissociation energy of PbH(g) reported by Gaydon.[1]

Heat Capacity and Entropy

Ground state configuration and spectroscopic data were obtained from Herzberg.[2] Electronic levels and multiplicity were estimated by comparison with those for PbF(g).

References

[1]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, (1953).
[2]G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York (1950).

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	−8.678	238.620	238.620	INFINITE
100	29.121	188.877	246.747	−5.787	238.246	228.077	−119.135
200	29.160	209.070	223.438	−2.874	237.288	218.270	−57.006
250	29.261	215.585	221.240	−1.414	236.744	213.577	−44 624
298.15	29.476	220.756	220.756	0.	236.187	209.165	−36.645
300	29.487	220.938	220.756	0.055	236.165	208.998	−36.390
350	29.847	225.509	221.116	1.537	235.570	204.517	−30.522
400	30.311	229.524	221.921	3.041	234.970	200.121	−26.133
450	30.836	233.124	222.969	4.569	234.371	195.801	−22.728
500	31.384	236.401	224.151	6.125	233.778	191.548	−20.011
600	32.448	242.218	226.690	9.317	232.617	183.211	−15.950
700	33.390	247.293	229.278	12.610	226.619	175.865	−13.123
800	34.184	251.805	231.817	15.990	225.506	168.692	−11.014
900	34.846	255.871	234.267	19.443	224.486	161.652	−9.382
1000	35.400	259.571	236.616	22.956	223.542	154.722	−8.082
1100	35.872	262.968	238.859	26.520	222.662	147.883	−7.022
1200	36.285	266.107	241.001	30.128	221.837	141.122	−6.143
1300	36.656	269.027	243.045	33.776	221.054	134.427	−5.401
1400	36.999	271.756	245.000	37.459	220.292	127.792	−4.768
1500	37.326	274.320	246.870	41.175	219.540	121.212	−4.221
1600	37.644	276.739	248.662	44.924	218.791	114.681	−3.744
1700	37.957	279.031	250.381	48.704	218.038	108.197	−3.324
1800	38.267	281.209	252.034	52.515	217.281	101.757	−2.953
1900	38.577	283.286	253.625	56.357	216.517	95.360	−2.622
2000	38.886	285.273	255.158	60.230	215 745	89.003	−2.325
2100	39.194	287.178	256.637	64.134	37.745	89.801	−2.234
2200	39.499	289.008	258.067	68.069	37.347	92.288	−2.191
2300	39.800	290.770	259.451	72.034	36.876	94.796	−2.153
2400	40.096	292.471	260.792	76.029	36.328	97.326	−2.118
2500	40.386	294.113	262.092	80.053	35.704	99.880	−2.087
2600	40.667	295.703	263.354	84.106	35.005	102.461	−2.058
2700	40.940	297.243	264.581	88.186	34.232	105.069	−2.033
2800	41.203	298.736	265.774	92.293	33.388	107.708	−2.009
2900	41.456	300.187	266.936	96.426	32.478	110.378	−1.988
3000	41.698	301.596	268.068	100.584	31.507	113.081	−1.969
3100	41.929	302.967	269.172	104.766	30.479	115.817	−1.952
3200	42.149	304.302	270.249	108.970	29.401	118.587	−1.936
3300	42.357	305.602	271.301	113.195	28.279	121.391	−1.921
3400	42.554	306.870	272.328	117.441	27.118	124.230	−1.909
3500	42.739	308.106	273.333	121.705	25.925	127.104	−1.897
3600	42.914	309.312	274.316	125.988	24.705	130.012	−1.886
3700	43.079	310.490	275.277	130.288	23.465	132.954	−1.877
3800	43.233	311.641	276.219	134.604	22.209	135.930	−1.868
3900	43.378	312.766	277.142	138.934	20.942	138.939	−1.861
4000	43.513	313.866	278.046	143.279	19.670	141.981	−1.854
4100	43.640	314.942	278.933	147.637	18.395	145.054	−1.848
4200	43.759	315.995	279.803	152.007	17.121	148 159	−1.843
4300	43.870	317.026	280.657	156.388	15.852	151.294	−1.838
4400	43.973	318.036	281.495	160.780	14.591	154.458	−1.834
4500	44.070	319.025	282.318	165.183	13.340	157.651	−1.830
4600	44.161	319.995	283.127	169.594	12.100	160.872	−1.827
4700	44.246	320.945	283.921	174.014	10.875	164.119	−1.824
4800	44.325	321.878	284.702	178.443	9.664	167.393	−1.822
4900	44.400	322.793	285.470	182.879	8.470	170.691	−1.820
5000	44.470	323.690	286.226	187.323	7.293	174.014	−1.818
5100	44.536	324.572	286.969	191.773	6.133	177.359	−1.817
5200	44.598	325.437	287.700	196.230	4.991	180.728	−1.815
5300	44.657	326.287	288.420	200.693	3.867	184.118	−1.815
5400	44.712	327.122	289.129	205.161	2.762	187.530	−1.814
5500	44.765	327.943	289.828	209.635	1.675	190.961	−1.814
5600	44 815	328.750	290.516	214.114	0.606	194.413	−1.813
5700	44.863	329.544	291.193	218.598	−0.445	197.883	−1.813
5800	44.909	330.325	291.861	223.087	−1.480	201.371	−1.814
5900	44.953	331.093	292.520	227.580	−2.496	204.877	−1.814
6000	44.995	331.849	293.169	232.077	−3.496	208.400	−1 814

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

Mercapto (SH) **IDEAL GAS** $M_r = 33.06794$ **Mercapto (HS)** $H_1S_1(g)$

$S°(298.15\ K) = 195\ 628 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$(*)

$\Delta_f H°(0\ K) = 136.49 \pm 5.0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 139.33 \pm 5.0\ kJ \cdot mol^{-1}$

	Electronic States and Molecular Constants ($\sigma = 1$)						
State	ϵ_e, cm^{-1}	g_e	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	β_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Pi_i$	0	2	2689.6	45.5	9.601	0.285	1.345
	377.01	2					
$A^2\Sigma^+$	30663	2	1979.8	97.65	8.521	0.464	1.423
$B^2\Sigma$	59622	2	2670.6	56.8	8.785	0.259	1.428
$C^2\Delta$	[63900]	4					
$D^2\Delta$	71195	4					
$E^2\Sigma$	71318	2					
$F^2\Delta$	76708	4	[2689.6]	[45.5]	[9.601]	[0.285]	
$G^2\Delta$	79343	4					
$H^2\Delta$	80848	4					

Enthalpy of Formation

The previous JANAF[1] selection for $\Delta_f H°$(HS, g, 298.15 K) was Mackle's[2] estimate of 34.6 ± 4 kcal·mol^{-1} which he derived from the average of three independent determinations. Of these, the uncertainty can be reduced in the determination involving the calculation of $\Delta H_f°$(HS, g, 298.15 K) from $\Delta_f H°(H_2S, g, 298.15\ K)$, the ionization potential of HS(g), and the appearance potential of $HS^+(g)$ from $H_2S(g)$. A summary of previous work on the ionization potential is given below. From the spectroscopic and photoionization work we arrive at a value of $\Delta_f H°(0\ K)$ for the reaction $H_2S(g) = HS(g) + H(g)$ of 89.02 ± 1.5 kcal·mol^{-1}. Using the appropriate thermal functions for each of the species (see tables for $H_2S(g)$, HS(g), and H(g)[1]) and the selected enthalpies of formation of $H_2S(g)$ of −4.90 ± 2 kcal·mol^{-1} (see $H_2S(g)$ table[1]) and H(g) of 52.103 ± 0.001 kcal·mol^{-1},[8] one obtains 33.3 ± 1.2 kcal·mol^{-1} for $\Delta_f H°$(HS, g, 298.15 K) versus Mackle's[2] values of 33.7 ± 3 kcal·mol^{-1} for this determination. The new value is preferred because it is based on photoionization rather than electron impact studies.

Source	Method	Potential(eV)
$HS(g) \rightarrow HS^+(g) + e^-(g)$:		
Morrow[3]	Rydberg Extrapolation	10.40 ± 0.03
Palmer and Loosing[4]	Electron Impact	10.5 ± 0.1
$H_2S(g) \rightarrow HS^+(g) + H(g) + e^-(g)$		
Dibeler and Liston[5]	Photoionization	14.27 ± 0.04†
Dibeler and Rosenstock[6]	Electron Impact	14.43 ± 0.1
Palmer and Lossing[4]	Electron Impact	14.43 ± 0.1
Neuert and Clasen[7]	Electron Impact	15.2 ± 0.5

†The uncertainty given by the authors was doubled because the threshold value was not corrected to absolute zero.

Heat Capacity and Entropy*

Calculations were made using the vibrational and rotational constants for the respective electronic levels from Rosen.[12] Comparison of the results of the more exact treatment of Haar *et al.*[13] with those given in the previous JANAF[1] calculations (both used the same molecular constants for the ground state) suggests errors in our calculations are negligible above 400 K. Below this, they can be appreciable. In particular, it is recommended that 0.045 kcal·mol^{-1}, 0.012 cal·K^{-1}·mol^{-1} and −0.028 cal·K^{-1}·mol^{-1} be added to our values of $H°(0\ K)-H°(298.5\ K)$, $S°(298.15\ K)$, and $C_p°(298.15\ K)$. These errors result from dealing with the ground state ($X^2\Pi_i$) as two separate electronic states separated by 377.01 cm^{-1}.

The thermodynamic functions are calculated using first-order anharmonic corrections to Q_v' and Q_r' in the partition function $Q = Q_t \Sigma Q_v' Q_r' g_e \exp(-c_2\epsilon_e/T)$. The National Bureau of Standards prepared this table[9] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[9] we recalculate the table in terms of 1973 fundamental constants,[10] 1975 atomic weights[11] and current JANAF reference states for the elements.

References

[1]JANAF Thermochemical Tables, 2nd ed., NSRDS–NBS 37, (1971).
[2]H. Mackle, Tetrahedron 19, 1159 (1963).
[3]B. A. Morrow, Can. J. Phys. 44, 2447 (1966).
[4]T. F. Palmer and F. P. Lossing, J. Am. Chem. Soc. 84, 4661 (1962).

Continued on page 1359

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	−9.273	136.493	136.493	INFINITE
90	30.185	160.686	224.496	−6.381	137.541	127.135	−66.409
200	32.697	182.575	198.614	−3.208	138.547	116.337	−30.384
250	32.734	189.885	196.164	−1.570	138.977	110.733	−23.136
298.15	32.447	195.628	195.628	0.	139.327	105.260	−18.441
300	32.434	195.829	195.629	0.060	139.340	105.049	−18.291
350	32.052	200.800	196.022	1.672	139.644	99.309	−14.821
400	31.707	205.057	196.892	3.266	138.794	93.573	−12.219
450	31.446	208.775	198.010	4.844	138.679	87.922	−10.206
500	31.283	212.079	199.255	6.412	138.515	82.293	−8.597
600	31.228	217.773	201.881	9.535	138.381	71.064	−6.187
700	31.452	222.601	204.505	12.667	138.370	59.846	−4.466
800	31.844	226.825	207.036	15.831	138.452	48.624	−3.175
900	32.318	230.602	209.448	19.039	112.044	37.927	−2.201
1000	32.814	234.033	211.738	22.295	112.871	29.648	−1.549
1100	33.301	237.184	213.910	25.601	113.722	21.284	−1.011
1200	33.761	240.101	215.972	28.955	114.592	12.843	−0.559
1300	34.185	242.820	217.934	32.352	115.478	4.328	−0.174
1400	34.571	245.368	219.804	35.790	116.376	−4.256	0.159
1500	34.922	247.765	221.589	39.265	117.280	−12.904	0.449
1600	35.239	250.030	223.296	42.774	118.188	−21.613	0.706
1700	35.526	252.175	224.932	46.312	119.099	−30.378	0.933
1800	35.786	254.213	226.503	49.878	120.009	−39.197	1.137
1900	36.021	256.154	228.013	53.468	120.919	−48.067	1.321
2000	36.236	258.007	229.467	57.081	121.826	−56.984	1.488
2100	36.432	259.780	230.868	60.715	122.731	−65.947	1.640
2200	36.611	261.479	232.221	64.367	123.632	−74.953	1.780
2300	36.777	263.110	233.529	68.037	124.530	−83.999	1.908
2400	36.930	264.679	234.794	71.722	125.425	−93.085	2.026
2500	37.072	266.189	236.020	75.422	126.316	−102.208	2.136
2600	37.205	267.646	237.209	79.136	127.203	−111.366	2.237
2700	37.329	269.052	238.362	82.863	128.086	−120.559	2.332
2800	37.445	270.412	239.483	86.602	128.967	−129.784	2.421
2900	37.555	271.728	240.572	90.352	129.843	−139.041	2.504
3000	37.659	273.003	241.632	94.113	130.716	−148.327	2.583
3100	37.758	274.239	242.664	97.883	131.585	−157.643	2.656
3200	37.852	275.439	243.669	101.664	132.451	−166.987	2.726
3300	37.942	276.606	244.650	105.454	133.313	−176.358	2.792
3400	38.028	277.740	245.607	109.252	134.171	−185.755	2.854
3500	38.112	278.843	246.540	113.059	135.025	−195.177	2.913
3600	38.192	279.918	247.453	116.874	135.876	−204.623	2.969
3700	38.270	280.965	248.344	120.698	136.722	−214.093	3.022
3800	38.346	281.987	249.216	124.528	137.565	−223.586	3.073
3900	38.420	282.984	250.069	128.367	138.403	−233.101	3.122
4000	38.492	283.958	250.905	132.212	139.237	−242.637	3.169
4100	38.564	284.909	251.722	136.065	140.066	−252.194	3.213
4200	38.634	285.839	252.524	139.925	140.890	−261.771	3.256
4300	38.703	286.749	253.309	143.792	141.710	−271.368	3.296
4400	38.772	287.640	254.079	147.666	142.526	−280.984	3.336
4500	38.841	288.512	254.835	151.546	143.336	−290.619	3.373
4600	38.909	289.366	255.576	155.434	144.142	−300.271	3.410
4700	38.977	290.204	256.304	159.328	144.943	−309.941	3.445
4800	39.045	291.025	257.019	163.229	145.740	−319.627	3.478
4900	39.114	291.831	257.721	167.137	146.533	−329.331	3.511
5000	39.183	292.622	258.411	171.052	147.321	−339.050	3.542
5100	39.253	293.398	259.090	174.974	148.106	−348.786	3.572
5200	39.323	294.161	259.757	178.902	148.886	−358.536	3.602
5300	39.394	294.911	260.413	182.838	149.664	−368.302	3.630
5400	39.466	295.648	261.059	186.781	150.438	−378.082	3.657
5500	39.539	296.373	261.694	190.732	151.210	−387.877	3.684
5600	39.614	297.086	262.320	194.689	151.980	−397.685	3.709
5700	39.689	297.788	262.936	198.654	152.748	−407.507	3.734
5800	39.766	298.478	263.543	202.627	153.516	−417.343	3.759
5900	39.844	299.159	264.141	206.608	154.283	−427.192	3.782
6000	39.924	299.829	264.730	210.596	155.050	−437.054	3.805

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

$S°(298.15\ K) = 198.040 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 374.89 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 376.66 \pm 8.4\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i	Ref
A $^2\Pi$	0	2	1
	142.83	2	1
$^4\Sigma^-$	[21510]	4	2
A $^2\Delta$	24193.04	4	1
$^2\Sigma^-$	[24730]	2	2
C $^2\Sigma^+$	31899.8	2	3
B $^2\Sigma^+$	31909.7	2	3
D $^2\Delta$	48510.11	4	1
E $^2\Sigma^+$	52399.19	2	1

$\omega_e = 2041.80\ cm^{-1}$ $\omega_e x_e = 35.51\ cm^{-1}$ $\sigma = 1$
$B_e = 7.4996\ cm^{-1}$ $\alpha_e = 0.2190\ cm^{-1}$ $r_e = 1.5201$ Å

Enthalpy of Formation

Verma[4] has derived an upper limit for the dissociation energy of 24680 cm^{-1} (70.6 kcal mol^{-1}) from predissociation in the B $^2\Sigma^+$ state. Hildenbrand[5] has applied an ionic–covalent correction to the linear Birge–Sponer extrapolation and obtained $D_0° = 70$ kcal·mol^{-1} Rao and Lakshman[6] have estimated the ground state dissociation energy of 24040 cm^{-1} (68 7 kcal·mol^{-1}) from an evaluation of the potential energy curves and Franck–Condon factors. This last number, $D_0° = 68.7$ kcal·mol^{-1}, is adopted and may be compared with the average per–bond atomization energy of $SiH_4(g)$ of 75.7 kcal mol^{-1}. The $D_0°/\Delta_{at}H°(0\ K)$ ratio is 0.227 For SiF/SiF the ratio is 0 230, for $SiCl/SiCl_4$ it is 0.233 and for SiI/SiI_4 it is 0.245.[7] The adopted $D_0°$ and JANAF auxiliary data[7] lead to $\Delta_f H°(0\ K) = 89\ 6$ kcal·mol^{-1} The allowed error of ±2 kcal·mol^{-1} includes the upper limit value of $D_0°$.

Heat Capacity and Entropy

The observed and estimated electronic levels are taken from Herzberg *et al.*,[1] Jordan,[2] and Bollmark *et al.*[3] as indicated Wirsam's[8] ab initio self–consistent–field and configuration–interaction calculations predicted the electronic level for the $^4\Sigma^-$ state at 6430 and 8275 cm^{-1} respectively. Substitution of 6430 cm^{-1} for the adopted Jordan estimate of 21510 cm^{-1} increases the derived entropy starting near 700 K; at 6000 K, the entropy is 0.85 cal·K^{-1}·mol^{-1} higher.

The rotational and vibrational constants are those selected by Rosen.[9] The ground state is treated as two distinct levels because of the splitting of the ground state as expressed by the spin coupling constant ($A = 142\ 83$ cm^{-1}) This approximation gives slightly biased results at lower temperatures which are allowed for in the ±0.05 cal K^{-1}·mol^{-1} error assigned to $S°(298.15\ K)$.

References

[1]G. Herzberg, A. Lagerqvist, and B. J McKenzie, Can. J. Phys. 47, 1891 (1969).
[2]P. C. Jordan, J Chem. Phys. 44, 3400 (1966).
[3]P. Bollmark, L. Klynning, and P. Pages, Phys. Scr. 3, 219 (1971).
[4]R. D. Verma, Can. J. Phys. 43, 2136 (1965).
[5]D. L. Hildenbrand, Douglas Advanced Research Laboratories, personal communication, (December 30, 1969).
[6]T. V. Ramakrishna Rao and S. V. J. Lakshman, Physica (Utrecht) 56, 322 (1971).
[7]JANAF Thermochemical Tables· Si(g), 3–31–67; H(g), 6–30–74, SiF(g), SiCl(g), SII(g), 12–31–76; $SiF_4(g)$, $SiI_4(g)$, 6–30–76, SiCl4(g), 12–31–70.
[8]B Wirsam, Chem. Phys. Lett. 10, 180 (1971).
[9]B Rosen, Ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, (1970).

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	−9.227	374.886	374.886	INFINITE
100	32.654	163.854	225.373	−6.152	376.196	365.230	−190.776
200	30.840	185.896	200.810	−2.983	376.839	353.934	−92.438
250	30.349	192.720	198.537	−1.454	376.819	348.206	−72.754
298.15	30.088	198.040	198.040	0.	376.662	342.708	−60.041
300	30.082	198.226	198.041	0.056	376.654	342.497	−59.634
350	29 989	202.855	198.407	1.557	376.395	336.824	−50.268
400	30.043	206.861	199.219	3.057	376.080	331.192	−43.249
450	30.216	210.409	200.269	4.563	375.732	325.602	−37.795
500	30.480	213.605	201.445	6.080	375.364	320.051	−33.436
600	31.174	219.221	203.952	9.162	374.605	309.060	−26.906
700	31.950	224.085	206.488	12.318	373.844	298.196	−22.252
800	32.707	228.401	208.963	15.551	373.092	287 440	−18.768
900	33.400	232.294	211.342	18.857	372.349	276.778	−16.064
1000	34.013	235.846	213.618	22.228	371.608	266.199	−13.905
1100	34.549	239.113	215.789	25 657	370.861	255.694	−12.142
1200	35.015	242.140	217.860	29.136	370.102	245.258	−10.676
1300	35.420	244.959	219.838	32.658	369.323	234.886	−9.438
1400	35.774	247.597	221.727	36.218	368.519	224.574	−8.379
1500	36.084	250.076	223.535	39.811	367.684	214.321	−7.463
1600	36.359	252.414	225.268	43 434	366.815	204.125	−6.664
1700	36.603	254.626	226.930	47.082	315.731	194.432	−5 974
1800	36.822	256.724	228.528	50.753	315.016	187.317	−5.436
1900	37.020	258.720	230.065	54.446	314.303	180.242	−4.955
2000	37.201	260.624	231.545	58.157	313.589	173.205	−4.524
2100	37.366	262.443	232.974	61.885	312.875	166.203	−4.134
2200	37.519	264.185	234.353	65.630	312.161	159.235	−3 781
2300	37.661	265.856	235.687	69.389	311.445	152.300	−3 459
2400	37.794	267.461	236.977	73.162	310.727	145.396	−3 164
2500	37.920	269.007	238.228	76.947	310.008	138.522	−2.894
2600	38.040	270 496	239.441	80.745	309.288	131.677	−2.645
2700	38.156	271.934	240.618	84.555	308.566	124.860	−2.416
2800	38.268	273.324	241.761	88.376	307.843	118.069	−2.203
2900	38.377	274.669	242.873	92.209	307.119	111.304	−2.005
3000	38.485	275.972	243.954	96.052	306.394	104.564	−1.821
3100	38.592	277.235	245.008	99 906	305.668	97.848	−1.649
3200	38.699	278.462	246.034	103 770	304.942	91.156	−1.488
3300	38.806	279.655	247.035	107.645	304.216	84.487	−1.337
3400	38.916	280.815	248.011	111.531	303.490	77.839	−1.196
3500	39.027	281.944	248.965	115.429	302.765	71.213	−1.063
3600	39.142	283.045	249.896	119.337	−82.110	75.068	−1.089
3700	39.259	284.119	250.807	123.257	−82.418	79.438	−1.121
3800	39.380	285.168	251.697	127.189	−82.726	83.817	−1.152
3900	39.505	286.193	252.569	131.133	−83.032	88.204	−1.181
4000	39.635	287.194	253.422	135.090	−83.336	92.598	−1.209
4100	39.769	288 175	254.258	139.060	−83.637	97.000	−1.236
4200	39.908	289.135	255.077	143.044	−83.934	101.410	−1.261
4300	40.053	290.075	255.880	147.042	−84.226	105.826	−1.286
4400	40.202	290.998	256.667	151.055	−84.512	110.249	−1.309
4500	40.357	291.903	257.440	155.083	−84.792	114.679	−1.331
4600	40.518	292.792	258.199	159.126	−85.064	119.114	−1.353
4700	40.683	293.665	258.944	163.186	−85.328	123.556	−1.373
4800	40.854	294.523	259.677	167.263	−85.583	128.003	−1.393
4900	41.030	295.367	260.397	171.357	−85.829	132.455	−1.412
5000	41.212	296.198	261.104	175.469	−86.064	136.913	−1.430
5100	41.398	297.016	261.800	179.600	−86.288	141.374	−1 448
5200	41.589	297.822	262.485	183.749	−86.499	145.840	−1.465
5300	41.785	298.616	263.160	187.918	−86.699	150.310	−1.481
5400	41.985	299.399	263.824	192.106	−86.885	154.784	−1.497
5500	42.189	300.171	264.477	196.315	−87.056	159.261	−1.513
5600	42.397	300.933	265.122	200.544	−87.213	163.741	−1.527
5700	42.608	301 685	265.757	204.794	−87.355	168.223	−1.542
5800	42.823	302.428	266.382	209.066	−87.482	172.709	−1.555
5900	43.041	303.162	267.000	213.359	−87.592	177.195	−1.569
6000	43.262	303.887	267.608	217.674	−87.686	181.684	−1.582

PREVIOUS December 1976 (1 atm) CURRENT· December 1976 (1 bar)

Silylydyne, Ion (SiH^+) — IDEAL GAS — M_r = 29.09289 — Silylidyne, Ion (SiH^+) — $H_1Si_1^+(g)$

$S°(298.15\ K) = 186.789 \pm 0.004\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1140.27 \pm 11.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298\ 15\ K) = 1147.67 \pm 11.3\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
$A^1\Pi$	25025.2	2

$\omega_e = 2157.1\ cm^{-1}$ $\omega_e x_e = 34.21\ cm^{-1}$ $\sigma = 1$
$B_e = 7.6603\ cm^{-1}$ $\alpha_e = 0.2096\ cm^{-1}$ $r_e = 1.499$ Å

Enthalpy of Formation

According to Douglas and Lutz[1] the A state must have an extremely shallow potential curve since the observed first vibrational quantum is only $\Delta_{1/2}G' = 390.2\ cm^{-1}$. Since no other levels were observed they estimated ω_e' and $\omega_e x_e'$ for the A state from $\Delta_{1/2}G'$, α_e' and B_e'. From the estimated ω_e' and $\omega_e x_e'$ they obtained a dissociation limit of 1180 cm^{-1}. Thus, the dissociation limit of the A state is likely to lie between 390 and 1180 cm^{-1}, on this basis Douglas and Lutz select 780 ± 600 cm^{-1}. Since SiH^+ can correlate with normal products $Si^+(^2P)$ and $H(^2S)$ in both the X and A states these are assumed to be the products. Thus, the dissociation energy of the ground state to these 294.626 ± 1.0 $kcal \cdot mol^{-1}$[12] we obtain $\Delta_f H°(SiH^+, g) = 272.5 \pm 2.7\ kcal \cdot mol^{-1}$, which is adopted. This gives an ionization potential of 182.9 $kcal \cdot mol^{-1}$ (7.93 eV) with the JANAF value for SiH.[2]

Heat Capacity and Entropy

The electronic levels and vibrational and rotational constants are all from Douglas and Lutz.[1]

References

[1]A. E. Douglas and B. L. Lutz, Can. J. Phys. 48, 247 (1970).
[2]JANAF Thermochemical Tables; H(g) 9-30-65; Si(g) 3-31-67, SiH(g) 12-31-69; $Si^+(g)$ 12-31-71.

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
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−8.654	1140.271		
100	29.118	154.962	212.699	−5.774			
200	29.133	175.150	189.456	−2.861			
250	29 148	181.652	187.269	−1.404			
298.15	29.184	186.789	186.789	0.	1147.671	1110.818	−194.611
300	29.186	186.969	186.789	0.054	1147.700	1110.589	−193.371
350	29.273	191.474	187.145	1.515	1148.441	1104.344	−164.814
400	29.427	195.392	187.936	2.982	1149.132	1097.997	−143.384
450	29.652	198.870	188.961	4 459	1149.794	1091.565	−126.706
500	29.941	202.009	190.112	5.949	1150.438	1085.060	−113.355
600	30.651	207.529	192.567	8.977	1151.705	1071.866	−93.314
700	31.436	212.312	195.053	12.081	1152.971	1058.459	−78 983
800	32.208	216.561	197.481	15.264	1154.247	1044.871	−68.223
900	32.922	220.396	199.817	18.521	1155.533	1031.122	−59.845
1000	33.560	223.899	202.053	21.846	1156.823	1017.229	−53.135
1100	34 121	227.124	204.187	25.230	1158 111	1003.207	−47.638
1200	34 611	230.114	206.225	28 668	1159.389	989.068	−43.053
1300	35.039	232.902	208.171	32.151	1160.650	974.824	−39.169
1400	35.413	235.513	210.032	35.674	1161.887	960.483	−35.836
1500	35.741	237.967	211.813	39.232	1163.095	946.054	−32.945
1600	36.031	240.284	213.521	42.820	1164.271	931.546	−30.412
1700	36.288	242.476	215.160	46.437	1115.234	917.413	−28.189
1800	36.518	244.557	216.736	50.077	1116.567	905.738	−26.284
1900	36.725	246.537	218.253	53.739	1117.902	893.989	−24.577
2000	36.912	248.425	219.714	57.421	1119.238	882.169	−23.040
2100	37.083	250.230	221.125	61.121	1120.574	870.283	−21.647
2200	37.240	251.959	222.487	64.838	1121.910	858.333	−20.379
2300	37.385	253.618	223.805	68.569	1123.245	846.322	−19.221
2400	37.520	255.212	225.081	72.314	1124.579	834.254	−18.157
2500	37.646	256.746	226.317	76.073	1125.911	822.130	−17.177
2600	37.764	258.225	227.516	79.843	1127.242	809.952	−16.272
2700	37.876	259.652	228.680	83.625	1128.571	797.723	−15.433
2800	37.983	261.032	229.811	87.418	1129.898	785.445	−14.653
2900	38.085	262.366	230.910	91.222	1131.223	773.120	−13.925
3000	38.184	263.659	231.981	95.035	1132.547	760.749	−13.246
3100	38.280	264.913	233.023	98.859	1133.870	748.334	−12.609
3200	38.374	266.130	234.038	102.691	1135.190	735.876	−12.012
3300	38.467	267.312	235.029	106.533	1136.510	723.377	−11.450
3400	38.558	268.461	235.995	110.385	1137.828	710.838	−10.921
3500	38.649	269.581	236.939	114.245	1139.145	698.261	−10.421
3600	38.740	270.671	237.861	118.114	756.309	696.106	−10.100
3700	38.832	271.733	238.762	121.993	758.038	694.410	−9.803
3800	38.925	272.770	239.644	125.881	759.765	692.667	−9.521
3900	39.019	273.782	240.506	129.778	761.491	690.879	−9.253
4000	39.115	274.771	241.350	133.685	763.215	689.046	−8.998
4100	39.213	275.739	242.177	137.601	764.939	687.171	−8.755
4200	39.314	276.685	242.988	141.528	766.663	685.253	−8.522
4300	39.416	277.611	243.782	145.464	768.389	683.295	−8.300
4400	39.522	278.518	244.561	149.411	770.115	681.296	−8.088
4500	39.630	279.408	245.326	153.369	771.844	679.258	−7.885
4600	39.741	280.280	246.076	157.337	773.575	677.181	−7.690
4700	39.855	281.136	246.813	161.317	775.309	675.067	−7.503
4800	39.973	281.976	247.537	165.308	777.047	672.916	−7.323
4900	40.093	282.802	248.248	169.311	778.789	670.728	−7.150
5000	40.216	283.613	248.947	173.327	780.536	668.505	−6.984
5100	40.343	284.410	249.635	177.355	782.288	666.247	−6.824
5200	40.472	285.195	250.311	181.396	784.047	663.955	−6.670
5300	40.605	285.967	250.977	185.449	785.811	661.629	−6.521
5400	40.740	286.727	251.632	189.517	787.583	659.269	−6.377
5500	40.879	287.476	252.277	193.598	789.362	656.876	−6.238
5600	41.019	288.214	252.912	197.692	791 149	654.451	−6.104
5700	41.163	288.941	253.538	201.802	792.944	651.994	−5.975
5800	41.308	289.659	254.154	205.925	794.748	649.506	−5.849
5900	41 456	290.366	254.762	210.063	796.561	646.986	−5.728
6000	41 606	291.064	255.361	214.216	798.385	644.435	−5.610

PREVIOUS: December 1971 (1 atm) CURRENT December 1971 (1 bar)

Silylidyne, Ion (SiH^+) $H_1Si_1^+(g)$

Zirconium Hydride (ZrH) IDEAL GAS M_r = 92.22794 Zirconium Hydride (ZrH) H_1Zr_1(g)

$S°(298.15\ K)$ = [216.158] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [517.346] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [516.306] $kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
[$^2\Pi$]	0	[4]

ω_e = [1400] cm^{-1} $\omega_e x_e$ = [19] cm^{-1} σ = 1
B_e = [5.1] cm^{-1} α_e = [0.09] cm^{-1} r_e = [1.821] Å

Enthalpy of Formation

$\Delta_f H°(0\ K)$ was estimated as 123.7 $kcal·mol^{-1}$ by Gordon.[1] $\Delta_f H°(298.15\ K)$ is then calculated.

Heat Capacity and Entropy

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

Reference

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

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	−8.690	517.346	517.346	INFINITE
100	29.126	184.229	242.222	−5.799	517.851	505.870	−264.240
200	29.195	204.430	218.853	−2.885	517.226	494.091	−129.043
250	29.368	210.961	216.645	−1.421	516.775	488.359	−102.037
298.15	29.687	216.158	216.158	0.	516.306	482.928	−84.607
300	29.702	216.342	216.159	0.055	516.287	482.721	−84.049
350	30.178	220.955	216.522	1.551	515.788	477.166	−71.213
400	30.741	225.021	217.335	3.074	515.294	471.682	−61.595
450	31.338	228.676	218.396	4.626	514.811	466.260	−54.122
500	31.930	232.008	219.593	6.208	514.342	460.891	−48.149
600	33.015	237.928	222.168	9.457	513.435	450.286	−39.201
700	33.923	243.088	224.795	12.805	512.548	439.832	−32.821
800	34.661	247.668	227.374	16.236	511.652	429.505	−28.044
900	35.258	251.786	229.861	19.732	510.714	419.292	−24.335
1000	35.743	255.527	232.244	23.283	509.707	409.187	−21.374
1100	36.143	258.953	234.518	26.878	508.611	399.187	−18.956
1200	36.478	262.113	236.688	30.510	503.702	389.513	−16.955
1300	36.762	265.044	238.758	34.172	502.935	380.029	−15.270
1400	37.007	267.778	240.734	37.861	502.131	370.604	−13.827
1500	37.221	270.338	242.623	41.573	501.276	361.239	−12.579
1600	37.411	272.747	244.431	45.304	500.355	351.933	−11.489
1700	37.581	275.020	246.164	49.054	499.357	342.686	−10.529
1800	37.735	277.172	247.828	52.820	498.270	333.501	−9.678
1900	37.876	279.216	249.426	56.601	497.084	324.379	−8.918
2000	38.006	281.162	250.965	60.395	495.786	315.323	−8.235
2100	38.127	283.020	252.448	64.202	494.367	306.334	−7.620
2200	38.242	284.796	253.878	68.020	471.493	298.161	−7.079
2300	38.350	286.498	255.259	71.850	469.383	290.330	−6.594
2400	38.452	288.133	256.595	75.690	467.268	282.590	−6.150
2500	38.551	289.704	257.888	79.540	465.149	274.939	−5.745
2600	38.645	291.218	259.141	83.400	463.026	267.373	−5.372
2700	38.736	292.678	260.357	87.269	460.899	259.888	−5.028
2800	38.824	294.089	261.536	91.147	458.769	252.482	−4.710
2900	38.910	295.453	262.682	95.034	456.634	245.152	−4.416
3000	38.993	296.773	263.797	98.929	454.497	237.896	−4.142
3100	39.075	298.053	264.881	102.832	452.356	230.711	−3.887
3200	39.155	299.295	265.938	106.744	450.213	223.596	−3.650
3300	39.233	300.501	266.967	110.663	448.067	216.547	−3.428
3400	39.310	301.673	267.970	114.590	445.918	209.564	−3.220
3500	39.386	302.814	268.950	118.525	443.766	202.643	−3.024
3600	39.461	303.925	269.906	122.467	441.612	195.785	−2.841
3700	39.535	305.007	270.840	126.417	439.455	188.986	−2.668
3800	39.608	306.062	271.753	130.374	437.296	182.245	−2.505
3900	39.680	307.092	272.646	134.339	435.135	175.561	−2.351
4000	39.752	308.097	273.520	138.310	432.972	168.933	−2.206
4100	39.823	309.080	274.375	142.289	430.806	162.359	−2.068
4200	39.893	310.040	275.213	146.275	428.638	155.838	−1.938
4300	39.963	310.980	276.034	150.268	426.468	149.368	−1.814
4400	40.032	311.899	276.839	154.267	424.296	142.949	−1.697
4500	40.101	312.800	277.628	158.274	422.122	136.579	−1.585
4600	40.170	313.682	278.402	162.288	419.947	130.258	−1.479
4700	40.238	314.546	279.162	166.308	417.770	123.984	−1.378
4800	40.306	315.394	279.908	170.335	−145.346	129.373	−1.408
4900	40.373	316.226	280.641	174.369	−147.177	135.115	−1.440
5000	40.441	317.042	281.360	178.410	−149.027	140.895	−1.472
5100	40.508	317.844	282.068	182.457	−150.893	146.712	−1.503
5200	40.574	318.631	282.764	186.511	−152.774	152.566	−1.533
5300	40.641	319.405	283.448	190.572	−154.668	158.456	−1.562
5400	40.707	320.165	284.121	194.640	−156.574	164.382	−1.590
5500	40.773	320.912	284.783	198.714	−158.489	170.343	−1.618
5600	40.839	321.648	285.434	202.794	−160.413	176.339	−1.645
5700	40.905	322.371	286.076	206.882	−162.343	182.370	−1.671
5800	40.971	323.083	286.708	210.975	−164.278	188.434	−1.697
5900	41.036	323 784	287.331	215.076	−166.216	194.532	−1.722
6000	41 102	324.474	287.944	219.183	−168.156	200.663	−1.747

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

Hydrogen (H_2) REFERENCE STATE – IDEAL GAS M_r = 2.01588 Hydrogen (H_2) H_2(ref)

0 to 6000 K Ideal Gas

D_0° = 432.071 ± 0.012 kJ mol^{-1} $\Delta_f H^\circ$(0 K) = 0 kJ·mol^{-1}

S°(298.15 K) = 130.680 ± 0.033 J·K^{-1}·mol^{-1} $\Delta_f H^\circ$(298.15 K) = 0 kJ·mol^{-1}

Vibrational and Rotational Levels (cm^{-1})
Direct Summation of Electronic Ground State

$E = G - G_0 + F = G - G_0 + BZ - DZ^2 + HZ^3 - LZ^4 + \ldots \sim - G - G_0 + BZ - DZ^2 + H^2Z^3/(H+LZ)$,
where $Z = J(J+1)$, $Y = v + 1/2$, and we omit subscript v on G, F, B, D, H, and L

$G = 4403.566Y - 123.8573Y^2 + 1.87269Y^3 - 0.173514Y^4 + 9.93128 \times 10^{-3}Y^5 - 4.38015 \times 10^{-4}Y^6$

$B = 60.8904 - 3.16997Y + 0.155932Y^2 - 4.60094 \times 10^{-2}Y^3 + 8.72205 \times 10^{-3}Y^4$
$-9.59207 \times 10^{-4}Y^5 + 5.31722 \times 10^{-5}Y^6 - 1.21393 \times 10^{-6}Y^7$

$D = 4.6573 \times 10^{-2} - 1.5085 \times 10^{-3}Y - 2.7385 \times 10^{-4}Y^2 + 1.0242 \times 10^{-4}Y^3 - 1.172 \times 10^{-5}Y^4 + 4.684 \times 10^{-7}Y^5$

$H = 5.224 \times 10^{-5} - 7.240 \times 10^{-6}Y + 9.619 \times 10^{-7}Y^2 - 4.838 \times 10^{-8}Y^3$

$L = 6.70 \times 10^{-8} - 1.426 \times 10^{-8}Y + 1.388 \times 10^{-9}Y^2$

$v_{max} = 14$, $J_{max} = 38 - 32v/v_{max}$

Normalized rotational statistical weights = 1/4 (even J) and 3/4 (odd J)

Ground State Configuration: $^1\Sigma_g^+$ r_e = 0.7414 Å

Enthalpy of Formation

Zero by definition. Refer to the monatomic hydrogen gas table for a discussion of the dissociation energy.

Heat Capacity and Entropy

These are calculated by direct summation over vibration–rotation energy levels of the electronic ground state. We performed the direct summation with an extended version of a program written by W. H. Evans and provided through cooperation of D. D. Wagman, both of the U. S. National Bureau of Standards. Contributions of excited states (T_0 >90000 cm^{-1}) are negligible at 6000 K. Polynomials G, B, D, and H are our fits of data from Stoicheff,[1] Herzberg and Howe[2] and Rank *et al.*[3,4] We estimate polynomial L such that our approximation[5,6] for the infinite series F yields high-J rotational levels in reasonable agreement with the theoretical values of Waech and Bernstein.[7] Maximum deviations in our F values are about ±400 cm^{-1}, these occur near $1 \le v \le 4$ and $29 \le J \le 36$ which is far into the extrapolated region of F. Only about one-third of the vibration–rotation levels have been observed spectroscopically and the theoretical calculations[7,6] provide the best available extrapolation to high values of J. Accuracy of the thermodynamic functions near 6000 K depends on this extrapolation and on the rotational cutoff procedure. We assume a linear approximation[5] for the limiting values (J_{max}) of rotational quantum number. Values in the J_{max} equation are estimated from theoretical calculations.[7,6] We omit the nuclear-spin contribution (R ln 4) to entroy and Gibbs energy function.

We adopt ortho–para "equilibrium" H_2 as the reference state at all temperatures. The previous JANAF reference state[8] referred to "normal" H_2 (75% ortho and 25% para). Our new reference state has signficiant changes in C_p°, S° and $H^\circ(T)-H^\circ(298.15\ K)$ at 100 K and slight changes at 200 K. Use of "equilibrium" H_2 as a reference state was proposed on the NBS H_2 table[9] which discusses three alternatives. Preferred alternatives are either "equilibrium" H_2 or "normal" H_2. "Normal" H_2 is the form always encountered except in low-temperature generation or catalytic ortho–para equilibrium. Use of "normal" H_2 involves a possible complication, depending on the choice of zero energy for ortho-H_2. If we chose the lowest allowed level (v=0, J=1 instead of v=0, J=0), then H°(298.15 K)–H°(0 K) would be 0.254 kcal·mol^{-1} less for "normal" than for "equilibrium" H_2. This would change the difference between $\Delta_f H^\circ$(0 K) and $\Delta_f H^\circ$(298.15 K) for all species involving hydrogen.[8,10] No such change would occur if we chose the lowest level (v=0, J=0) as the energy zero for ortho-H_2. "Equilibrium" H_2 is the form which parallels most substances, i.e., those maintaining equilibrium among all rotational levels.[9]

JANAF values and uncertainties at 298.15 K are the same as those selected by CODATA.[10] Previous thermochemical tables based on direct-summation calculations of Woolley *et al.*[6] include that of Gurvich *et al.*[11] and that of NBS–JANAF.[9,8] Differences of the new JANAF values from the NBS table are greatest near 5300 K, reaching maximum of 0.005 cal·K^{-1}·mol^{-1} in S° and 0.018 kcal·mol^{-1} in $H^\circ(T)-H^\circ(298.15\ K)$. Differences from Gurvich *et al.* at 6000 K are 0.006 cal·K^{-1} mol^{-1} in S° and 0.030 kcal·mol^{-1} in $H^\circ(T)-H^\circ(298.15\ K)$. Errors larger than these differences arise from uncertainty in extrapolation of the rotational levels.

References

[1] B. P. Stoicheff, Can. J. Phys. 35, 730 (1957).
[2] G. Herzberg and L. L. Howe, J. Phys. 37, 636 (1959).
[3] J. V. Foltz, D. H. Rank, and T. A. Wiggins, J. Mol. Spectrosc. 21, 203 (1966).
[4] U. Fink, T. A. Wiggins and D. H. Rank, J. Mol. Spectrosc. 18, 384 (1965).
[5] G. A. Khachkuruzov, Opt. Spectrosc. 30, 455 (1971).
[6] H. W. Woolley, R. B. Scott, and F. G. Brickwedde, J. Res. Natl. Bur. Stand. 41, 379 (1948).
[7] T. G. Waech and R. B. Bernstein, J. Chem. Phys. 46, 4905 (1967).
[8] H. Prophet and D. R. Stull, ed., JANAF Thermochemical Tables, 2 ed., NSRDS–NBS 37, (1971).
[9] S. Abramowitz *et al.*, U. S. Natl. Bur. Stand. Rept. 10904, 239, (July 1972).
[10] J. D. Cox, chairman, ICSU–CODATA Task Group on Key Values for Thermodynamics, J. Chem. Thermodyn. 4, 331 (1972); 8, 603 (1976).
[11] L. V. Gurvich, G. A. Khachkuruzov *et al.*, "Thermodynamic Properties of Individual Substances," 2nd ed., Vol. II, Nauka, Moscow, (1962).

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})	$-[G^\circ-H^\circ(T_r)]/T$ (J·K^{-1}mol^{-1})	$H^\circ-H^\circ(T_r)$ (kJ·mol^{-1})	$\Delta_f H^\circ$ (kJ·mol^{-1})	$\Delta_f G^\circ$ (kJ·mol^{-1})	log K_f
0	0	0	INFINITE	−8.467	0	0.	0.
100	28.154	100.727	155.408	−5.468	0	0.	0.
200	27.447	119.412	133.284	−2.774	0.	0.	0.
250	28.344	125.640	131.152	−1.378	0	0	0.
298.15	28.836	130.680	130.680	0.	0	0.	0.
300	28.849	130.858	130.680	0.053	0	0.	0.
350	29.081	135.325	131.032	1.502	0	0.	0.
400	29.181	139.216	131.817	2.959	0	0.	0.
450	29.229	142.656	132.834	4.420	0.	0	0.
500	29.260	145.737	133.973	5.882	0	0	0.
600	29.327	151.077	136.392	8.811	0.	0	0.
700	29.441	155.606	138.822	11.749	0.	0	0
800	29.624	159.548	141.171	14.702	0.	0.	0.
900	29.881	163.051	143.411	17.676	0.	0	0
1000	30.205	166.216	145.536	20.680	0.	0	0.
1100	30.581	169.112	147.549	23.719	0.	0	0.
1200	30.992	171.790	149.459	26.797	0.	0	0
1300	31.423	174.288	151.274	29.918	0.	0.	0.
1400	31.861	176.633	153.003	33.082	0.	0	0
1500	32.298	178.846	154.652	36.290	0.	0.	0.
1600	32.725	180.944	156.231	39.541	0.	0.	0.
1700	33.139	182.940	157.743	42.835	0.	0.	0.
1800	33.537	184.846	159.197	46.169	0.	0.	0.
1900	33.917	186.669	160.595	49.541	0.	0.	0.
2000	34.280	188.418	161.943	52.951	0.	0.	0.
2100	34.624	190.099	163.244	56.397	0.	0.	0.
2200	34.952	191.718	164.501	59.876	0.	0.	0.
2300	35.263	193.278	165.719	63.387	0	0.	0.
2400	35.559	194.785	166.899	66.928	0.	0.	0.
2500	35.842	196.243	168.044	70.498	0.	0.	0.
2600	36.111	197.654	169.155	74.096	0	0	0.
2700	36.370	199.021	170.236	77.720	0	0.	0.
2800	36.618	200.349	171.288	81.369	0	0	0.
2900	36.856	201.638	172.313	85.043	0.	0	0.
3000	37.087	202.891	173.311	88.740	0.	0.	0
3100	37.311	204.111	174.285	92.460	0.	0	0
3200	37.528	205.299	175.236	96.202	0.	0	0.
3300	37.740	206.457	176.164	99.966	0.	0.	0.
3400	37.946	207.587	177.072	103.750	0.	0.	0.
3500	38.149	208.690	177.960	107.555	0.	0.	0.
3600	38.348	209.767	178.828	111.380	0.	0.	0.
3700	38.544	210.821	179.679	115.224	0.	0.	0.
3800	38.738	211.851	180.512	119.089	0.	0.	0.
3900	38.928	212.860	181.328	122.972	0.	0.	0.
4000	39.116	213.848	182.129	126.874	0.	0.	0.
4100	39.301	214.816	182.915	130.795	0.	0.	0.
4200	39.484	215.765	183.686	134.734	0.	0.	0.
4300	39.665	216.696	184.442	138.692	0.	0	0.
4400	39.842	217.610	185.186	142.667	0	0.	0.
4500	40.017	218.508	185.916	146.660	0	0	0.
4600	40.188	219.389	186.635	150.670	0.	0	0.
4700	40.355	220.255	187.341	154.698	0.	0.	0
4800	40.518	221.106	188.035	158.741	0.	0	0
4900	40.676	221.943	188.719	162.801	0.	0.	0.
5000	40.829	222.767	189.392	166.876	0.	0.	0.
5100	40.976	223.577	190.054	170.967	0.	0.	0.
5200	41.117	224.374	190.706	175.071	0	0.	0.
5300	41.252	225.158	191.349	179.190	0.	0.	0.
5400	41.379	225.931	191.982	183.322	0.	0.	0.
5500	41.498	226.691	192.606	187.465	0.	0.	0.
5600	41.609	227.440	193.222	191.621	0.	0.	0.
5700	41.712	228.177	193.829	195.787	0.	0.	0.
5800	41.806	228.903	194.427	199.963	0.	0	0.
5900	41.890	229.619	195.017	204.148	0.	0.	0.
6000	41.965	230.323	195.600	208.341	0.	0.	0.

PREVIOUS: March 1961 (1 atm) CURRENT: March 1977 (1 bar)

D_0° = 255.760 ± 0.004 kJ·mol^{-1}
S°(298.15 K) = 142.370 ± 0.04 J·K^{-1}·mol^{-1}

$\Delta_f H^\circ$(0 K) = 1488.358 ± 0.004 kJ·mol^{-1}
$\Delta_f H^\circ$(298.15 K) = [1494.671] kJ·mol^{-1}

Vibrational and Rotational Levels (cm^{-1})
Direct Summation of Electronic Ground State

$E = G - G_0 + F = G - G_0 + BZ - DZ^2 + HZ^3 - LZ^4 + \ldots \approx G - G_0 + BZ - DZ^2 + H^2Z^3/(H+LZ)$,
where $Z = N(N+1)$, $Y = v + 1/2$, and we omit subscript v on G, F, B, D, H, and L
$G = 2323.23\ Y = 67.39\ Y^2 + 0.93\ Y^3 - 0.029\ Y^4$
$B = 29.946 - 1.594\ Y + 0.032\ Y^2 - 0.013\ Y^3$
$D = 0.01991 - 0.00087\ Y + 0.00003\ Y^2$; $H = 1.75 \times 10^{-5} - 6 \times 10^{-7}\ Y$; and $L = 1.6 \times 10^{-8}$
$v_{max} = 18$ and $N_{max} = 41.33v/v_{max}$
Normalized rotational statistical weights = 1/4 (even N) or 3/4 (odd N)

Ground State Configuration: $^2\Sigma_g^+$ r_e = 1.057 Å[1,13]

Enthalpy of Formation

The adopted value for the enthalpy of formation of H_2^+(g), $\Delta_f H^\circ$(0 K) = 355.727 ± 0.001 kcal·mol^{-1}, is based on the ionization potential of H_2(g) determined by Herzberg and Jungen.[1] These authors studied in high resolution absorption two Rydberg series of ortho– and para–hydrogen which converge to the $X^2\Sigma_g^+$ ground state of H_2^+(g). This ionization potential, IP = 124417.2 ± 0.4 cm^{-1} is recommended by Rosenstock[2] as the definitive value. The IP or $\Delta_f H^\circ$(0 K) value is converted to a $\Delta_f H^\circ$(298.15 K) value for H_2^+(g) by including JANAF[3] enthalpy differences, H°(0 K)–H°(298.15 K), for H_2^+(g), H_2(ref) and e^-(ref). $\Delta_f H^\circ$(298.15 K) should not be interpreted as a room–temperature ionization threshold due to inclusion of these enthalpies and to threshold effects noted by Rosenstock *et al.*[4]

Rosenstock *et al.*[4] had earlier recommened IP = 16.4256 eV (124418 4 cm^{-1}) based on the spectroscopic studies of Takezawa[5] and Herzberg.[6] In both studies the results were derived from extended Rydberg series The more recent work of Herzberg and Jungen[1] provides a more accurate experimental value for the ionization potential due to the recognition of a pressure shift which was felt to be negligible in the earlier study.[6] The theroetical value, IP = 124417.3 cm^{-1}, is in excellent agreement (0.1 cm^{-1}) with our adopted value. This theoretical value, as discussed by Herzberg and Jungen,[1] is essentially the value of Hunter and Pritchard[7] with the relativistic and Lamb shift corrections of Jeziorski and Kolos[8] and the nonadiabatic correction of Bunker.[9]

Heat Capacity and Entropy

Thermodynamic functions for ortho–para "equilibrim" H_2^+ are calculated, as they were for H_2,[3] by direct summation over energy levels of the electronic ground state. We use 1973 fundamental constants[10] in an extended version of a computer program written by W. H. Evans and provided by D D Wagman of the U. S. National Bureau of Standards. Excited electronic states are neglected because they are either repulsive or too high lying[11] to contribute significantly. The electronic statistical weight is taken equal to the multiplicity since we neglect rotational splitting. Assumption of negligible splitting is common practice in theoretical calculation of H_2^+ energy levels[11–13] and it is justified thermodynamically by the small splitting constant.[14]

Coefficients of the energy–level polynomials are those derived from theoretical levels by Beckel *et al.*[13] New calculations[15] yield slightly different levels. The polynomials are confirmed by vibrational (v<3) and rotational (N<4) levels obtained from Rydberg spectra.[1] The value of L was derived[13] from a fit of theoretical levels with v = 0 to 14. Our adopted v_{max}, derived from the G polynomial, is one unit too low.[13,11] Limiting rotaitonal quantum numbers N_{max} are an approximation of values from theoretical calculations.[11 13] The resulting energy–level equations are very approximate near N_{max}, but they do closely reproduce thermodynamic functions[12,11] calculated directly from energy levels. More accurate equations do not signficantly improve the thermodynamic functions up to 6000 K.

We adopt functions closely reproducing those of Iorish and Yungman.[12] The effect of slightly different fundamental constants[12] is barely detectable. Our Gibbs–energy function deviates by less than 0.001 cal·K^{-1}·mol^{-1} at all temperatures. C_p°, S° and H° begin to deviate near 2000 K; differences range from +0.005 to −0.012 cal·K^{-1}·mol^{-1} in C_p°, ±0.001 cal·K^{-1}·mol^{-1} in S° and ±5 cal·K^{-1}·mol^{-1} in H°. C_p° of Patch and McBride[11] is slightly lower at 4000 to 6000 K but well within the probable uncertainty. Due to the high thermal energy (−20% of D_0° at 6000 K), C_p° depends on the number of levels included in the summation. We follow the published references[11 12] which include contributions from quasibound levels lying above D_0°. At 6000 K these levels contribute 0.42 cal·K^{-1}·mol^{-1} to C_p° and 0.05 cal·K^{-1}·mol^{-1} to the Gibbs–energy function.

References

[1]G. Herzberg and Ch. Jungen, J Mol. Spectrosc. 41, 425 (1972).
[2]H. M. Rosenstock, U. S. Nat. Bur. Stand., personal communication, (November 29, 1977).
[3]JANAF Thermochemical Tables: H_2(ref), e^-(ref), 3–31–77.
[4]H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T Herron, J. Phys Chem. Ref. Data 6, Supp. 1 (1977).
[5]S. Takezawa, J. Chem. Phys. 52, 5793 (1970).
[6]G. Herzberg, Phys. Rev. Lett. 23, 1081 (1969).

Continued on page 1359

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}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.583	1488.358	1488.358	INFINITE
90	27.510	110.873	168.264	−5.739	1490.282	1489.440	−778.004
200	29.175	130.698	145.046	−2.870	1492.536	1487.743	−388.559
298.15	29.288	142.370	142.370	0.	1494.671	1484.931	−260.154
300	29.292	142.551	142.371	0 054	1494.711	1484.870	−258.539
400	29.525	151.004	143.522	2.993	1496.822	1481.272	−193.434
500	30.016	157.641	145.705	5.968	1498.953	1477.139	−154.316
600	30.719	163.173	148.167	9.003	1501.138	1472.571	−128.199
700	31.529	167.968	150 661	12.115	1503.391	1467.633	−109.516
800	32.357	172.233	153.095	15.310	1505.711	1462.367	−95.483
900	33.152	176.090	155.439	18.586	1508.091	1456.807	−84.551
1000	33.887	179.622	157.684	21.938	1510.518	1450.979	−75.791
1100	34.559	182.884	159.828	25.361	1512.981	1444 906	−68.613
1200	35.168	185.917	161.877	28.848	1515.468	1438.608	−62.621
1300	35 720	188.754	163.837	32.393	1517.971	1432.102	−57.543
1400	36.226	191.420	165.713	35.990	1520.483	1425.402	−53.182
1500	36.691	193.935	167.511	39.636	1522.999	1418.523	−49.397
1600	37.123	196.317	169.238	43.327	1525.518	1411.476	−46.080
1700	37.530	198.580	170.898	47.060	1528.036	1404.271	−43 148
1800	37.918	200.737	172.496	50.833	1530.553	1396.918	−40.538
1900	38.291	202.797	174.037	54.643	1533.069	1389.426	−38.198
2000	38.654	204.770	175.525	58.491	1535.585	1381.800	−36.089
2100	39.011	206.665	176.963	62.374	1538 102	1374.049	−34.178
2200	39.365	208.488	178.355	66.293	1540.620	1366.178	−32.437
2300	39.716	210.245	179 703	70.247	1543.142	1358.193	−30.846
2400	40.065	211.943	181 011	74.236	1545.668	1350.097	−29.384
2500	40.413	213.585	182.282	78.260	1548.201	1341.896	−28.037
2600	40.757	215.177	183.516	82.318	1550.740	1333.594	−26.792
2700	41.096	216.722	184.718	86.411	1553.287	1325.194	−25.637
2800	41.427	218.222	185.888	90.537	1555.843	1316.699	−24.563
2900	41.746	219.682	187.028	94.696	1558.406	1308.113	−23.562
3000	42.050	221.102	188.140	98.886	1560.978	1299.439	−22.625
3100	42.335	222.486	189.226	103.105	1563.556	1290.678	−21.748
3200	42.599	223.834	190.286	107.352	1566.139	1281.834	−20.924
3300	42.836	225.148	191.323	111.624	1568.726	1272.910	−20.148
3400	43.045	226.430	192.337	115.919	1571.315	1263 907	−19 418
3500	43.222	227.681	193.329	120.232	1573.902	1254.828	−18.727
3600	43.366	228.901	194.300	124.562	1576.486	1245.675	−18.074
3700	43.475	230.090	195.251	128.904	1579.062	1236.450	−17.456
3800	43.547	231.251	196.183	133.256	1581.628	1227.156	−16.868
3900	43.583	232.382	197.097	137.612	1584.180	1217.795	−16.311
4000	43.582	233.486	197.993	141.971	1586.715	1208.368	−15.780
4100	43.545	234.562	198.872	146.328	1589.229	1198.878	−15.274
4200	43.473	235.610	199.734	150.679	1591.720	1189.327	−14.791
4300	43.367	236.632	200.581	155.021	1594.183	1179.717	−14.331
4400	43.229	237.627	201.411	159.351	1596.616	1170.050	−13.890
4500	43.060	238.597	202.227	163.666	1599.017	1160.328	−13.469
4600	42.862	239.541	203.028	167.962	1601.381	1150.554	−13.065
4700	42.639	240.461	203.815	172.237	1603.708	1140.728	−12.678
4800	42.391	241.356	204.587	176.489	1605.994	1130.853	−12.306
4900	42.122	242.227	205.347	180 715	1608.239	1120.931	−11.949
5000	41.834	243.075	206.093	184.913	1610.440	1110.964	−11.606
5100	41.528	243.901	206.826	189.081	1612.597	1100.952	−11.276
5200	41.208	244.704	207.547	193.218	1614.708	1090.900	−10.958
5300	40.875	245.486	208.255	197.322	1616.772	1080.807	−10.652
5400	40.532	246.247	208.952	201.393	1618.790	1070.675	−10.357
5500	40 179	246.987	209.637	205.428	1620.760	1060.506	−10.072
5600	39.820	247.708	210.310	209.428	1622.683	1050.303	−9.797
5700	39.456	248.410	210.972	213.392	1624.559	1040.065	−9.531
5800	39.087	249.093	211.624	217.319	1626.389	1029.795	−9.274
5900	38.717	249.758	212.265	221.209	1628.173	1019.493	−9.026
6000	38.346	250.405	212.895	225.063	1629.912	1009.161	−8.786

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

D_0° = 118.0 ± 42 kJ·mol^{-1}
S°(298.15 K) = 143.75 ± 0.4 J K^{-1}·mol^{-1}

$\Delta_f H^\circ$(0 K) = 241 4 ± 42 kJ·mol^{-1}
$\Delta_f H^\circ$(298.15 K) = [235.373] kJ·mol^{-1}

Electonic Levels and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2\Sigma_u^+$	0	2

ω_e = [1700] cm^{-1} $\omega_e x_e$ = [35] cm^{-1} σ = 2
B_e = [25.3] cm^{-1} α_e = [0.398] cm^{-1} r_e = [1.15] Å

Enthalpy of Formation

The heat of formation at 0 K for H_2^-(g) is based on the electron affinity value derived from a Rydberg–Klein–Rees configuration–interaction calculation.[1] This study by Sharpe[1] led to EA (H_2) = −2.5 eV Using auxiliary data,[2] we calculate $\Delta_f H^\circ$(0 K) kcal·mol^{-1} and $D_0^\circ(H_2^-)$ = 28.2 ± 10 kcal mol^{-1}; the latter value assumes dissociation into ground state H(g) and H^-(g) This adopted EA(H_2) value is suggested to be the more reliable value of eight studies considered by Rosenstock *et al.*[3]

In terms of molecular orbitals, the ground state for H_2^-(g) is the $(1s\sigma_g)^2(2p\sigma_u)\,2\Sigma_u^+$ state involving two bonding electrons and one antibonding electron.[4] We would expect, however, the ground state to be $(1s\sigma_g)^2(2s\sigma_u)$. As stated by Massey,[4] we should expect only a weakly–bound molecule as compared with H_2(g) for which the ground state has no electron in an antibonding orbital. Our calculated EA(H_2) value is consistent with this viewpoint. Further discussion of the H_2^-(g) ion may be found in Massey.[4]

$\Delta_f H^\circ$(0 K) is converted to $\Delta_f H^\circ$(298.15 K) by use of JANAF[2] enthalpies, H°(0 K)–H°(298 15 K), for H_2(g), H_2^-(g), and e^-(ref). $\Delta_f H^\circ$(298.15 K) should not be interpreted as a room temperature electron affinity due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3]

Heat Capacity and Entropy

The vibrational constants for H_2^-(g) are estimated to be the same as in the isoelectronic species He_2^+.[5] The internuclear distance is estimated to be ~8% larger than that for He_2^+(g). The same relationship appeared to exist for the (N_2^-, NO, O_2^+) isoelectronic series. B_e is calculated from r_e whereas α_e is calculated assuming a Morse function for the ground state.

The ground and excited electronic states are discussed in detail by Massey.[4] No excited state contributions are included in this calculation. By assuming the same force constant to exist for H_2^- as in He_2^+, we would calculate ω_e = 3384 cm^{-1}. This leads to an entropy at 298.15 K which is 0.06 cal K^{-1}·mol^{-1} smaller than our adopted value. The vibrational constants derived by Comer and Read[5] for some resonant state of H_2^- suggests ω_e values of 1500, 2300, and 2800 cm^{-1}. Thus, the ω_e value is very uncertain.

References

[1]T. E. Sharpe, Lockheed Report LMSC 5–10–69–9 (1969).
[2]JANAF Thermochemical Tables: H(g) 3–31–82, H^-(g) 3–31–82, H_2(g) 3–31–77, e^-(ref) 3–31–82.
[3]H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, J. Phys. Chem. Ref. Data 6, Supp. 1 (1977).
[4]H. S. W. Massey, "Negative Ions," 3rd ed., Cambridge University Press, Cambridge, (1976).
[5]B. Rosen, Ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, (1970).
[6]J. Comer and F. H. Read, J. Phys. B. 4, 368 (1971).

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°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−8.621	241.417		
100	29.209	111.749	169.836	−5.809			
200	29.285	132.014	146.437	−2.885			
250	29.378	138.557	144.231	−1.418			
298.15	29.556	143.746	143.746	0.	235.373	237.732	−41.650
300	29.564	143.928	143.746	0.055	235.335	237.747	−41.395
350	29.866	148.507	144.107	1.540	234.332	238.228	−35.554
400	30.271	152.520	144.913	3.043	233.339	238.852	−31.191
450	30.751	156.113	145.961	4.568	232.365	239.600	−27.812
500	31.272	159.380	147.142	6.119	231.414	240.455	−25.120
600	32.333	165.175	149.677	9.299	229.587	242.437	−21.106
700	33.320	170.235	152.260	12.583	227.854	244.717	−18.261
800	34.187	174.742	154.793	15.959	226.199	247.239	−16.143
900	34.932	178.813	157.240	19.416	224.602	249.966	−14.508
1000	35.568	182.527	159.585	22.942	223.046	252.868	−13.208
1100	36.114	185.944	161.828	26.527	221.513	255.924	−12.153
1200	36.586	189.107	163.971	30.162	219.992	259.119	−11.279
1300	36.999	192.052	166.019	33.842	218.472	262.442	−10.545
1400	37.365	194.807	167.978	37.560	216.948	265.881	−9.920
1500	37.692	197.397	169.854	41.314	215.414	269.430	−9.382
1600	37.988	199.839	171.653	45.098	213.869	273.081	−8.915
1700	38.259	202.150	173.379	48.910	212.309	276.830	−8.506
1800	38.509	204.344	175.039	52.749	210.735	280.670	−8.145
1900	38.742	206.432	176.637	56.612	209.147	284.599	−7.824
2000	38.961	208.425	178.177	60.497	207.543	288.611	−7.538
2100	39.168	210.331	179.663	64.403	205.926	292.705	−7.281
2200	39.365	212.158	181.099	68.330	204.295	296.875	−7.049
2300	39.553	213.912	182.487	72.276	202.652	301.120	−6.839
2400	39.735	215.599	183.832	76.241	200.996	305.437	−6.648
2500	39.910	217.225	185.136	80.223	199.330	309.822	−6.473
2600	40.079	218.793	186.400	84.222	197.653	314.275	−6.314
2700	40.244	220.309	187.628	88.239	195.966	318.793	−6.167
2800	40.406	221.776	188.822	92.271	194.271	323.373	−6.033
2900	40.563	223.196	189.983	96.320	192.567	328.014	−5.908
3000	40.718	224.574	191.113	100.384	190.855	332.713	−5.793
3100	40.869	225.912	192.214	104.463	189.136	337.470	−5.686
3200	41.019	227.212	193.287	108.557	187.410	342.283	−5.587
3300	41.166	228.476	194.335	112.667	185.677	347.149	−5.495
3400	41.311	229.707	195.357	116.791	183.938	352.068	−5.409
3500	41.455	230.907	196.356	120.929	182.193	357.039	−5.329
3600	41.597	232.077	197.332	125.082	180.442	362.059	−5.253
3700	41.738	233.218	198.286	129.248	178.686	367.128	−5.183
3800	41.878	234.333	199.220	133.429	176.924	372.245	−5.117
3900	42.016	235.423	200.135	137.624	175.157	377.408	−5.055
4000	42.154	236.488	201.030	141.832	173.384	382.616	−4.996
4100	42.291	237.531	201.908	146.055	171.607	387.869	−4.942
4200	42.426	238.552	202.768	150.291	169.825	393.166	−4.890
4300	42.562	239.551	203.612	154.540	168.038	398.504	−4.841
4400	42.696	240.531	204.440	158.803	166.247	403.885	−4.795
4500	42.830	241.492	205.253	163.079	164.452	409.306	−4.751
4600	42.963	242.435	206.051	167.369	162.653	414.767	−4.710
4700	43.096	243.361	206.835	171.672	160.850	420.267	−4.671
4800	43.228	244.269	207.605	175.988	159.044	425.806	−4.634
4900	43.360	245.162	208.363	180.317	157.235	431.382	−4.599
5000	43.491	246.039	209.107	184.660	155.423	436.995	−4.565
5100	43.622	246.902	209.840	189.015	153.610	442.644	−4.534
5200	43.753	247.750	210.561	193.384	151.795	448.329	−4.504
5300	43.883	248.585	211.270	197.766	149.980	454.049	−4.475
5400	44.013	249.406	211.969	202.161	148.165	459.804	−4.448
5500	44.143	250.215	212.657	206.569	146.350	465.591	−4.422
5600	44.272	251.012	213.335	210.989	144.537	471.412	−4.397
5700	44.401	251.796	214.003	215.423	142.726	477.265	−4.374
5800	44.530	252.570	214.661	219.870	140.918	483.150	−4.351
5900	44.659	253.332	215.310	224.329	139.114	489.066	−4.330
6000	44 788	254 084	215.950	228.801	137.314	495.013	−4.309

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

Diiodosilane (SiH_2I_2) IDEAL GAS M_r = 283.91038 Diiodosilane (SiH_2I_2) $H_2I_2Si_1(g)$

$S°(298.15\ K) = [326.797 \pm 3.3]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-28.11 \pm 20.9]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-38.07 \pm 20.9]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2205 (1)	[2230](1)
925 (1)	497 (1)
[350](1)	796 (1)
[90](1)	[410](1)
[650](1)	

Ground State Quantum Weight: [1] σ = [2]
Point Group: [C_{2v}]
Bond Distances: Si–H = [1.49] Å Si–I = [2.44] Å
Bond Angles: H–Si–H = [111]° I–Si–I = [110]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.067590 \times 10^{-112}]\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is estimated by linear interpolation between the values[1] of $SiI_4(g)$ and $SiH_4(g)$. There are no experimental $\Delta_f H°$ data for SiH_3I, SiH_2I_2 and $SiHI_3$. Data for the iodomethanes[2] have a surprising progression (SiH3I, g);[1] they are of doubtful use in predicting $\Delta_f H°$ of the iodosilanes. We conclude, as did Hunt and Sirtl,[3] that the available data justify only linear interpolation of $\Delta_f H°$.

Heat Capacity and Entropy

The molecular structure is estimated by comparison with SiH_3I, SiI_4 and the various bromo–, chloro– and flurosilanes.[1] The principal moments of inertia are: $I_A = 10.2009 \times 10^{-39}$, $I_B = 168.8775 \times 10^{-39}$ and $I_C = 178.0688 \times 10^{-39}\ g \cdot cm^2$.

Five vibrational frequencies are estimated by comparison with the dihalo–, monohalo– and trihalosilanes[1] plus $SiHBrI_2$ and $SiHClI_2$.[4] Frequencies ν_1, ν_2 and ν_8 were observed in gas–phase infrared spectra,[5] while ν_7 was observed in liquid–phase infrared spectra.[6]

We neglect excited states and assume the electronic ground state to be a singlet. We expect that contributions from excited states should be unimportant, as discussed on the tables for SiH_3Br and SiH_2Cl_2.[1]

References

[1]JANAF Thermochemical Tables: $H_3ISi(g)$, $HI_3Si(g)$, $BrH_3Si(g)$, $Br_2H_2Si(g)$, $Br_3HSi(g)$, $ClH_3Si(g)$, Cl2H2Si(g), $Cl_3HSi(g)$ 12–31–76, $FH_3Si(g)$, $F_2H_2Si(g)$, $F_3HSi(g)$, $I_4Si(g)$ 6–30–76
[2]S. A. Kudchadker and A. P. Kudchadker, J. Phys. Chem. Ref. Data 4, 457 (1975).
[3]L. P. Hunt and E. Sirtl, J. Electrochem. Soc. 120, 806 (1973).
[4]E. Hengge and F. Hoefler, Z. Naturforsch. A26, 768 (1971).
[5]H. J. Emeleus, A. G. MacDiarmid and A. G Maddock, J. Inorg. Nucl. Chem. 1, 194 (1955).
[6]E. A. V. Ebswroth, M. Onyszchuk and N. Sheppard, J. Chem. Soc. 1958, 1453 (1958).

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

	J·K⁻¹mol⁻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	−14.917	−28.108	−28.108	INFINITE
100	43.099	267.914	379.301	−11.139	−30.645	−40.881	21.354
200	56.780	301.906	332.682	−6.155	−34.466	−49.641	12.965
250	62.986	315.261	327.889	−3.157	−36.342	−53.217	11.119
298.15	67.980	326.797	326.797	0.	−38.074	−56.308	9.865
300	68.153	327.218	326.798	0.126	−38.140	−56.421	9.824
350	72.371	338.051	327.644	3.643	−39.919	−59.328	8.854
400	75.838	347.949	329.572	7.351	−57.581	−61.436	8.023
450	78.748	357.054	332.127	11.217	−60.332	−61.752	7.168
500	81.249	365.483	335.046	15.219	−103.110	−57.968	6.056
600	85.398	380.678	341.413	23.559	−103.829	−48.867	4.254
700	88.749	394.102	348.000	32.272	−104.269	−39.668	2.960
800	91.512	406.139	354.528	41.289	−104.492	−30.422	1.986
900	93.803	417.054	360.878	50.558	−104.550	−21.158	1.228
1000	95.709	427.039	367.002	60.037	−104.488	−11.895	0.621
1100	97.298	436.238	372.884	69.690	−104.345	−2.642	0.125
1200	98.628	444.763	378.523	79.488	−104.157	6.596	−0.287
1300	99.745	452.702	383.927	89.408	−103.954	15.817	−0 636
1400	100.689	460.130	389.108	99.431	−103.764	25.023	−0.934
1500	101.491	467.105	394.077	109.541	−103.614	34.217	−1.192
1600	102.176	473.677	398.849	119.725	−103.524	43.402	−1.417
1700	102.764	479.890	403.435	129.973	−153.690	53.031	−1.629
1800	103.273	485.778	407.847	140.276	−153.542	65.186	−1.892
1900	103.714	491.374	412.097	150.625	−153.455	77.335	−2.126
2000	104.100	496.704	416.196	161.017	−153.434	89.481	−2.337
2100	104.438	501.791	420.151	171.444	−153.480	101.628	−2.528
2200	104.736	506.657	423.974	181.903	−153.590	113.778	−2.701
2300	105.000	511.318	427.671	192.390	−153.758	125.935	−2.860
2400	105.235	515.792	431.250	202.902	−153.977	138.100	−3.006
2500	105.444	520.092	434.718	213.436	−154.237	150.275	−3.140
2600	105.632	524.232	438.082	223.990	−154.527	162.461	−3.264
2700	105.801	528.222	441.347	234.562	−154.835	174.659	−3.379
2800	105.953	532.072	444.519	245.150	−155.153	186.868	−3.486
2900	106.091	535.793	447.602	255.752	−155.468	199.089	−3.586
3000	106.216	539.391	450.602	266.367	−155.773	211.320	−3.679
3100	106.330	542.876	453.523	276.995	−156.059	223.561	−3.767
3200	106.433	546.253	456.368	287.633	−156.318	235.811	−3.849
3300	106.528	549.530	459.142	298.281	−156.546	248.069	−3.927
3400	106.616	552.712	461.847	308.938	−156.738	260.333	−4 000
3500	106.696	555.803	464.488	319.604	−156.889	272.602	−4.068
3600	106.770	558.810	467.066	330.277	−541.150	295.336	−4.285
3700	106.838	561.736	469.586	340.958	−540.800	318.567	−4 497
3800	106.901	564.586	472.048	351.645	−540.406	341.788	−4.698
3900	106.959	567.364	474.457	362.338	−539.967	364.998	−4.889
4000	107.014	570.073	476.814	373.036	−539.483	388.196	−5.069
4100	107.064	572.716	479.121	383.740	−538.954	411.381	−5.241
4200	107.111	575.296	481.380	394.449	−538.381	434.554	−5.404
4300	107.155	577.817	483.593	405.162	−537.764	457.711	−5.560
4400	107.196	580.281	485.763	415.880	−537.105	480.854	−5.708
4500	107.234	582.691	487.890	426.601	−536.404	503.982	−5.850
4600	107.270	585.048	489.977	437.327	−535.664	527.093	−5.985
4700	107.304	587.355	492.024	448.055	−534.885	550.189	−6.115
4800	107.336	589.615	494.034	458.787	−534.068	573.267	−6.238
4900	107.366	591.828	496.007	469.523	−533.216	596.328	−6.357
5000	107.394	593.997	497.945	480.261	−532.330	619.371	−6.471
5100	107.420	596.124	499.850	491.001	−531.411	642.396	−6.579
5200	107.445	598.211	501.721	501.745	−530.461	665.402	−6.684
5300	107.469	600.257	503.561	512.490	−529.480	688.390	−6.784
5400	107.491	602.266	505.370	523.238	−528.470	711.360	−6.881
5500	107.512	604.239	507.150	533.988	−527.431	734.309	−6.974
5600	107.533	606.176	508.901	544.741	−526.366	757.241	−7.063
5700	107.552	608.080	510.625	555.495	−525.275	780.153	−7.149
5800	107.570	609.951	512.321	566.251	−524.159	803.046	−7.232
5900	107.587	611.790	513.991	577.009	−523.019	825.918	−7.312
6000	107.603	613.598	515.636	587.768	−521.854	848.772	−7.389

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = [327\,996 \pm 8.4]\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -641.95 \pm 12.6\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -654.80 \pm 12.6\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}
[273](1)	[3700](1)
[150](1)	[3700](1)
[235](1)	[1250](1)
[150](1)	[1250](1)
[255](1)	[1250](1)
[258](1)	[1250](1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2h}
Bond Distances. K–O = [2.43] Å O–H = [0.96] Å
Bond Angles. K–O–K = [90]° K–O–H = [110]°
Product of the Moments of Inertia. $I_A I_B I_C = [3.758094] \times 10^{-113}\ g^3\cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(K_2(OH)_2, g, 298.15\ K)$ is calculated from the enthalpy of dimerization, $\Delta_{dim}H°(298.15\ K) = -45.3 \pm 3.0\ kcal\cdot mol^{-1}$, and the enthalpy of formation of the monomer, $\Delta_f H°(KOH, g, 298.15\ K) = -55.6 \pm 3.0\ kcal\cdot mol^{-1}$. Refer to the KOH(g) table for details.

Heat Capacity and Entropy

A key to the molecular structure of $K_2(OH)_2$(g) is provided by the work of Buchler *et al.*[1] which involves the electric deflection of molecular beams of $Cs_2(OH)_2$(g) and $Na_2(OH)_2$(g). Their results indicate that these dimers are nonpolar which implies a planar structure for at least the M_2O_2 part of the molecule. The three models proposed thus far for the dimeric alkali metal hydroxides each incorporate this planar configuration for the alkali and oxygen atoms. Bauer *et al.*[2] proposed a model consisting of a square planar configuration for the alkali and oxygen atoms with two hydrogen bonded bridges between the oxygens and hydrogens. Schoonmaker and Porter[3] adopted the square planar model for the M_2O_2 configuration but did not allow for hydrogen bonding. Berkowitz *et al.*[4] proposed a model for $Li_2(OH)_2$(g) which consisted of a trans configuration with hydrogens above and below the plane of a rhombus formed by the lighium and oxygen atoms, the O–Li–O bond angle being 100°. The adopted molecular structure for $K_2(OH)_2$(g) is similar to the model of Berkowitz *et al.*[4] but with the O–K–O bond angle equal to 90°. The K–O–H bond angle is assumed equal to 110°. The K–O bond distance is estimated as being 10% longer than that in KOH(g). The O–H bond distance is estimated to be the same as in H_2O(g). The principal moments of inertia are: $I_A = [17.5192] \times 10^{-39}$, $I_B = [38.5520] \times 10^{-39}$, and $I_C = [55.6426] \times 10^{-39}\ g\cdot cm^2$.

The first six vibrational frequencies are taken equal to those for dimeric K_2F_2(g) (See K_2F_2(g) table), and the remaining O–H stretching and bending modes are estimates taken from the work of Berkowitz *et al.*[4]

References

[1]A. Buchler, J. L. Stauffer, and W. Klemperer, J. Chem. Phys. 46, 605 (1967).
[2]S. H. Bauer, R. H. Diner, and R. F. Porter, J. Chem. Phys. 29, 991 (1958).
[3]R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
[4]J. Berkowitz, D. J. Meschi, and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).

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	−18.473	−641.954	−641.954	INFINITE
100	56.735	251.157	394.722	−14.357	−647.206	−637.798	333.151
200	73.990	296.990	335.219	−7.646	−651.289	−626.711	163.680
250	78.049	313.955	329.318	−3.841	−653.087	−620.357	129.616
298.15	81.444	327.996	327.996	0.	−654.796	−613.898	107.552
300	81.571	328.500	327.997	0.151	−654.862	−613.644	106.845
350	84.944	341.329	329.003	4.314	−661.407	−606.440	90.506
400	88.173	352.884	331.277	8.643	−663.204	−598.462	78.151
450	91.187	363.446	334.273	13.128	−664.824	−590.271	68.517
500	93.941	373.198	337.684	17.757	−666.286	−581.907	60.791
600	98.651	390.758	345.099	27.395	−668.816	−564.786	49.169
700	102.458	406.261	352.750	37.457	−670.938	−547.275	40.838
800	105.603	420.153	360.322	47.865	−672.774	−529.481	34.572
900	108.278	432.750	367.681	58.562	−674.422	−511.469	29.685
1000	110.604	444.281	374.773	69.509	−675.967	−493.279	25.766
1100	112.656	454.921	381.581	80.674	−835.387	−465.717	22.115
1200	114.482	464.803	388.110	92.033	−834.813	−432.135	18.810
1300	116.113	474.032	394.368	103.564	−834.143	−398.606	16.016
1400	117.572	482.692	400.371	115.249	−833.393	−365.130	13.623
1500	118.878	490.849	406.133	127.073	−832.578	−331.711	11.551
1600	120.048	498.559	411.671	139.020	−831.711	−298.348	9.740
1700	121.097	505.869	416.999	151.079	−830.802	−265.041	8.144
1800	122.039	512.818	422.131	163.236	−829.865	−231.788	6.726
1900	122.885	519.439	427.080	175.483	−828.908	−198.587	5.460
2000	123.647	525.762	431.857	187.810	−827.942	−165.437	4.321
2100	124.333	531.812	436.474	200.210	−826.976	−132.336	3.292
2200	124.953	537.610	440.940	212.675	−826.019	−99.280	2.357
2300	125.513	543.177	445.265	225.199	−825.080	−66.268	1.505
2400	126.021	548.530	449.457	237.776	−824.168	−33.296	0.725
2500	126.483	553.684	453.523	250.401	−823.291	−0.361	0.008
2600	126.903	558.653	457.472	263.071	−822.456	32.540	−0.654
2700	127.286	563.449	461.308	275.781	−821.673	65.409	−1.265
2800	127.635	568.085	465.040	288.527	−820.948	98.251	−1.833
2900	127.956	572.569	468.671	301.307	−820.290	131.067	−2.361
3000	128.250	576.912	472.207	314.117	−819.707	163.863	−2.853
3100	128.520	581.122	475.653	326.956	−819.208	196.640	−3.313
3200	128.768	585.206	479.013	339.820	−818.800	229.402	−3.745
3300	128.998	589.172	482.291	352.709	−818.474	262.152	−4.150
3400	129.210	593.027	485.491	365.619	−818.266	294.895	−4.531
3500	129.406	596.775	488.618	378.550	−818.170	327.633	−4.890
3600	129.588	600.423	491.673	391.500	−818.200	360.370	−5.229
3700	129.757	603.976	494.660	404.467	−818.365	393.110	−5.550
3800	129.914	607.438	497.583	417.451	−818.672	425.857	−5.854
3900	130.060	610.815	500.443	430.450	−819.132	458.614	−6.142
4000	130.197	614.109	503.244	443.463	−819.740	491.382	−6.417
4100	130.325	617.326	505.987	456.489	−820.522	524.169	−6.678
4200	130.444	620.468	508.676	469.527	−821.492	556.978	−6.927
4300	130.556	623.539	511.311	482.577	−822.653	589.812	−7.165
4400	130.660	626.541	513.896	495.638	−823.460	622.621	−7.391
4500	130.759	629.479	516.432	508.709	−824.895	655.501	−7.609
4600	130.851	632.354	518.921	521.790	−826.524	688.416	−7.817
4700	130.939	635.169	521.365	534.879	−828.312	721.365	−8.017
4800	131.021	637.926	523.764	547.977	−830.086	754.331	−8.209
4900	131.098	640.629	526.122	561.083	−832.272	787.362	−8.393
5000	131.171	643.278	528.439	574.197	−834.665	820.440	−8.571
5100	131.240	645.876	530.716	587.317	−837.267	853.568	−8.742
5200	131.305	648.425	532.955	600.445	−840.080	886.748	−8.907
5300	131.367	650.927	535.157	613.578	−843.106	919.985	−9.067
5400	131.426	653.383	537.324	626.718	−846.343	953.281	−9.221
5500	131.482	655.795	539.456	639.864	−849.793	986.638	−9.370
5600	131.535	658.165	541.555	653.014	−853.452	1020.061	−9.515
5700	131.585	660.493	543.621	666.170	−856.629	1053.455	−9.654
5800	131.632	662.782	545.656	679.331	−860.614	1087.001	−9.789
5900	131.678	665.033	547.660	692.497	−864.792	1120.614	−9.921
6000	131.721	667.246	549.635	705.667	−869.158	1154.302	−10.049

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

$S°(298.15\ K) = [269.794 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -699.39 \pm 33.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -711.28 \pm 33.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies (ν, cm^{-1}, all singly degenerate)

[400]	[400]	[500]	[500]	[450]	[350]	[3700]	[3700]	[1250]	[1250]	[1250]	[1250]

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: [C_{2h}]
Bond Distances. Li–O = [1.74] Å O–H = [0.97] Å
Bond Angles. Li–O–Li = [90]° Li–O–H = [110]°
Product of the Moments of Inertia: $I_A I_B I_C = [4\ 293246 \times 10^{-115}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The reaction between water vapor and condensed lithium oxide has been investigated as a function of temperature and water pressure by means of such techniques as mass spectrometry[1,2] and transpiration.[3] At low water pressures (<0.01 Torr) in the temperature range 780–900 K, Schoonmaker and Porter[1] observed only Li^+ and $LiOH^+$ ion species in the mass spectrum of the reaction products. The precursor of these two ions was assumed to be monomeric LiOH. Berkowitz *et al.*[2] in a more extensive mass spectrometric study of the $Li_2O(cr)$–$H_2O(g)$ equilibrium detected not only monomeric and dimeric LiOH in the vapor phase, but also trace amounts of trimer ($Li_3(OH)_3$) Their work covered the temperature range 1100–1400 K at water pressures of 0.04 and 0.16 Torr. Absolute equilibrium constants were determined for the dimerization reaction, 2 LiOH(g) = $Li_2(OH)_2$(g), by calibrating the mass spectrometer in units of pressure This was accomplished by measuring the water pressure externally and simultaneously monitoring the intensity of the H_2O^+ peak. In an attempt to investigate the same equilibrium at water pressures inaccessible to mass spectrometry, Berkowitz–Mattuck and Buchler[3] used the transpiration method. Their work covered water pressures of 4.58 and 19.5 Torr at 1095 and 1145 K. An analysis of these equilibrium data are summarized below

Source	Reaction[a]	Method	T/K	Data Points	$\Delta_r H°$(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}
Berkowitz, *et al.*[2]	A	Mass Spec.	1119–1352	9[b]	−57.2	−63.8 ± 1.4	−5.4 ± 2.8	−175.8 ± 4.0
Berkowitz–Mattock	B	Transp.	1095, 1145	2		12.7		−188.2 ± 4.0

[a]Reactions· A) 2 LiOH(g) = $Li_2(OH)_2$(g) B) H_2O(g) + Li_2O(cr) = $Li_2(OH)_2$(g)
[b]One point rejected due to failure of a statistical test.

It seems most likely that the equilibrium data of Berkowitz–Mattuck and Buchler[3] are in error, since no satisfactory compromise in the flow rates of the inert carrier gas could be found such that saturation was achieved while eliminating thermal diffusion effects. Under these conditions the simple equations relating partial pressures to the masses transported during the transpiration experiment are now longer valid. Furthermore, the authors assumed that under the conditions of their experiment only dimer LiOH would be formed. The work of Berkowitz *et al.*[2] clearly establishes the existence of a trimer at water pressures some 100 times lower than those employed by Berkowitz–Mattuck and Buchler.[3]

Trends in the dimerization energies for the higher alkali metal hydroxides, as well as for the dimeric alkali fluorides and chlorides, suggest that the enthalpy of dimerization for LiOH from the work of Berkowitz *et al.*[2] may be slightly high. Such a comparison results in $\Delta_f H°$(dimerization, 298.15 K) values in the range −(52–61) kcal·mol^{-1}. Further support for a lower value comes from the mass spectral work of Porter and Schoonmaker.[1] They investigated the reaction of H_2O(g) with a mixture of condensed Li_2O–Na_2O. From the reported ion current intensities for the various ions found in the reaction products we calculate, $\Delta_{dim}H°$(NaOH, g, 298.15 K) −$\Delta_{dim}H°$(LiOH, g, 298.15 K) = 5.3 kcal·mol^{-1}. This value yields $\Delta_{dim}H°(298.15\ K) = -56.0 \pm 5$ kcal·mol^{-1}for LiOH(g) when used in combination with the adopted value for NaOH(g).[4] A high enthalpy of dimerization from the mass spectral work of Berkowitz *et al.*[2] is easily reconciled in terms of nonequilibrium measurements Based upon these findings, we adopt $\Delta_{dim}H°(298.15\ K) = -58.0 \pm 5.0$ kcal mol for LiOH(g). Combining this result with the enthalpy of formation for LiOH(g),[4] that for the dimer is $\Delta_f H°(Li_2(OH)_2, g, 298.15\ K) = -170.0 \pm 8$ kcal·mol^{-1}

Heat Capacity and Entropy

The molecular structure of $Li_2(OH)_2$(g) is assumed identical to that adopted for the higher alkali metal hydroxide dimers. It consists of a planar configuration for the lithium and oxygen atoms with the O–Li–O bond angle equal to 90°. The hydrogen atoms are placed in a trans–configuration above and below the plane of the rhombus formed by the lithium and oxygen atoms. The Li–O–H bond angle is assumed equal to 110°. The Li–O bond distance is estimated as being 10% longer than in LiOH(g). The O–H bond distance is estimated to be the same as in H_2O(g). The principal moments of inertia are· $I_A = [3.7044 \times 10^{-39}]$, $I_B = [9.2519 \times 10^{-39}]$, and $I_C = [12.5268 \times 10^{-39}]\ g \cdot cm^2$.

The first six vibrational frequencies are estimated by comparison with calculated[5] and experimental[4,6] frequencies for Li_2F_2(g). In the estimation it is assumed that the bulkier OH group would tend to reduce the frequencies of $Li_2(OH)_2$(g) relative to those for Li_2F_2(g) The remaining OH stretching and bending frequencies are estimates from the work of Berkowitz *et al.*[2]

Continued on page 1359

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	−14.502	−699.387	−699.387	INFINITE
100	37.588	212.012	323.024	−11.101	−702.880	−695.209	363.140
200	57.261	244.155	275.895	−6.348	−707.415	−685 736	179.096
250	65.023	257.797	270.933	−3.284	−709.461	−680.076	142.094
298.15	71.223	269.794	269.794	0.	−711.280	−674.249	118 126
300	71.443	270.235	269.795	0.132	−711.347	−674.019	117.357
350	76.958	281.672	270.686	3.845	−713.085	−667.659	99.643
400	81.765	292.270	272.730	7.816	−714.741	−661.056	86.325
450	85.956	302.148	275.456	12.011	−716.370	−654.247	75.943
500	89.602	311.397	278.592	16.402	−724.002	−646.643	67.554
600	95.542	328.283	285.495	25.673	−726.787	−630.900	54.925
700	100 130	343.370	292 704	35.466	−729.036	−614 734	45.872
800	103.799	356.988	299.902	45.669	−730.916	−598.274	39.063
900	106.840	369.395	306.945	56.205	−732.542	−581.594	33.755
1000	109.432	380.789	313.767	67.022	−733.963	−564.744	29 499
1100	111.684	391.327	320.345	78.080	−735.215	−547.760	26.011
1200	113.662	401.131	326.674	89.349	−736.324	−530.668	23.099
1300	115 412	410.300	332.758	100.805	−737.317	−513.489	20.632
1400	116 966	418 911	338 607	112.425	−738.207	−496.238	18.515
1500	118.349	427 029	344.234	124.192	−739.004	−478 926	16.678
1600	119.583	434.707	349.650	136.090	−739.723	−461.564	15 069
1700	120.685	441.990	354.870	148.105	−1030.849	−429.806	13.206
1800	121.671	448.917	359.904	160.223	−1029.941	−394.477	11 447
1900	122 554	455.519	364.764	172.435	−1029.005	−359 199	9 875
2000	123.348	461.826	369.460	184.731	−1028.049	−323.971	8.461
2100	124.062	467 862	374 004	197 102	−1027 081	−288 791	7.183
2200	124 705	473.648	378.402	209.541	−1026.110	−253 656	6.023
2300	125.287	479.205	382.665	222.041	−1025.142	−218.567	4.964
2400	125 813	484.548	386.799	234.597	−1024.183	−183.519	3.994
2500	126.291	489.694	390.813	247.202	−1023.240	−148.511	3.103
2600	126.725	494.656	394.712	259.854	−1022.319	−113.540	2.281
2700	127 121	499.446	398.503	272.546	−1021 425	−78.604	1.521
2800	127 482	504.076	402.191	285.277	−1020.564	−43.700	0 815
2900	127.813	508.555	405 782	298.042	−1019.741	−8.827	0.159
3000	128.116	512.893	409.281	310.838	−1018.961	26.019	−0 453
3100	128.395	517.099	412.691	323.664	−1018.227	60.840	−1.025
3200	128.651	521.179	416.018	336.517	−1017.546	95.636	−1.561
3300	128.888	525.142	419.265	349.394	−1016.919	130.413	−2.064
3400	129.106	528.993	422.436	362.293	−1016.352	165.173	−2.538
3500	129.308	532.738	425.534	375.214	−1015.849	199.916	−2.984
3600	129.495	536.384	428.563	388 155	−1015.412	234 646	−3 405
3700	129.669	539.934	431.525	401.113	−1015.046	269 364	−3.803
3800	129.831	543.394	434.424	414.088	−1014.753	304.074	−4.180
3900	129.981	546.769	437.261	427.079	−1014.538	338.778	−4.537
4000	130.122	550.061	440.040	440.084	−1014.403	373.476	−4.877
4100	130.253	553.276	442.763	453.103	−1014.351	408.172	−5.200
4200	130.376	556.416	445.432	466.134	−1014.387	442.868	−5.508
4300	130.491	559.485	448.049	479.178	−1014.513	477.566	−5.801
4400	130.598	562.487	450.616	492.232	−1014.690	512.264	−6.081
4500	130 700	565.423	453.134	505.297	−1014.986	546.970	−6.349
4600	130.795	568.296	455.607	518.372	−1015.385	581.684	−6.605
4700	130.884	571.110	458.034	531.456	−1015.884	616.408	−6.851
4800	130.968	573.867	460.419	544.549	−1016.487	651.144	−7.086
4900	131.048	576.568	462.762	557.649	−1017.197	685.894	−7.312
5000	131 123	579.216	465.065	570.758	−1018.017	720.660	−7.529
5100	131.194	581.813	467.328	583.874	−1018.940	755.441	−7.737
5200	131.261	584.362	469.555	596.997	−1019.988	790.242	−7.938
5300	131.325	586.863	471.744	610.126	−1021.157	825.066	−8.132
5400	131.385	589.318	473.899	623.261	−1022.450	859.912	−8.318
5500	131 442	591.729	476.020	636.403	−1023.870	894.783	−8.498
5600	131.496	594.098	478.107	649.550	−1025.421	929.682	−8.672
5700	131.548	596.426	480.162	662.702	−1027.107	964.609	−8.840
5800	131.597	598 714	482.187	675.859	−1028.930	999.568	−9.002
5900	131.643	600.964	484.181	689.021	−1030.895	1034.557	−9.159
6000	131.688	603.177	486.146	702.188	−1033.005	1069.583	−9.312

PREVIOUS: June 1971 (1 atm) CURRENT June 1971 (1 bar)

$S°(298.15\ K) = 31.091 \pm 0.84\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -68.00 \pm 9.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -76.15 \pm 9.2\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of hydrolysis of MgH_2(cr) was measured by Sinke and Stull.[1] The value of $\Delta_f H°(298.15\ K)$ was calculated to be -19.1 ± 2 kcal·mol^{-1}. From the decomposition pressure measurements for MgH_2(cr) reported by Ellinger[2] and Stampfer *et al.*[3] the values of $\Delta_f H°(298.15\ K)$ for MgH_2(cr) were found to be -17.9 ± 1.0 and -17.7 kcal·mol^{-1}, respectively. The value used was the average of these three.

Heat Capacity and Entropy

The low temperature heat capacities (25–300 K) were measured by Sinke and Hildenbrand.[4] Above 300 K the $C_p°$ values were estimated by comparison with those for MgF_2(cr) $S°(298.15\ K)$ is obtained from Sinke and Hildenbrand[4] using $S°(25\ K) = 0.037$ cal·K^{-1}·mol^{-1} (extrap.).

Decomposition Data

$T_{dcm} = 560$ K is estimated from the value of $\Delta_f G°$ in the table.

References

[1]G. C. Sinke and D. R. Stull, The Dow Chemical Company, personal communication, (July 1956).
[2]F. H. Ellinger, *et al.*, J. Amer. Chem. Soc. 77, 2647 (1955).
[3]J. F. Stampfer, Jr., C. E. Holley, Jr. and J. F. Suttle, J. Amer. Chem Soc. 82, 3504 (1960).
[4]G. C. Sinke and D L. Hildenbrand, The Dow Chemical Company, personal communication, (February 1958).

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	−5.314	−67.997	−67.997	INFINITE
100	12.774	6.389	55.049	−4.866	−71.191	−60.806	31.762
200	25.284	19.372	33.974	−2.920	−73.946	−49.309	12.878
298.15	35.334	31.091	31.091	0.	−76.149	−36.716	6.432
300	35.510	31.310	31.092	0.066	−76.183	−36.471	6.350
400	43.304	42.620	32.581	4.015	−77.694	−22.989	3.002
500	49.999	53.029	35.644	8.693	−78.606	−9.195	0.961
600	55.229	62.621	39.352	13.962	−79.033	4.734	−0.412
700	59.538	71.468	43.316	19.706	−79.099	18.705	−1.396
800	63.095	79.659	47.353	25.844	−78.901	32.665	−2.133
900	65.898	87.259	51.370	32.300	−78.539	46.591	−2.704
1000	67.990	94.315	55.316	38.998	−86.701	61.184	−3.196
1100	69.486	100.867	59.163	45.874	−86.295	75.953	−3.607
1200	70.751	106.969	62.896	52.888	−85.790	90.682	−3.947
1300	71.761	112.673	66.508	60.015	−85.214	105.365	−4.234
1400	72.592	118.023	69.998	67.234	−212.000	123.169	−4.595
1500	73.204	123.052	73.369	74.525	−209.996	147.039	−5 120
1600	73.722	127.794	76.624	81.872	−207.978	170.776	−5.575
1700	74.088	132.274	79.767	89.262	−205.960	194.386	−5.973
1800	74.475	136.520	82.803	96.690	−203.945	217.878	−6.323
1900	74.883	140.557	85.737	104.158	−201.929	241.257	−6.633
2000	75.312	144.409	88.575	111.667	−199.908	264.531	−6.909

PREVIOUS June 1963 CURRENT: September 1963

$S°(298.15\ K) = 63.243\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -915.64 \pm 2.1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 924.66 \pm 2.1\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted value is an average of −221.10 and −220.86 kcal·mol^{-1} obtained from $\Delta_r H°(298.15\ K)$ = 9 08 and 8.84 kcal·mol^{-1} for the dehydration reaction $Mg(OH)_2(cr) = MgO(cr) + H_2O(l)$, using auxiliary data.[13, 14] The two values correspond to natually occurring brucite and to synthetic $Mg(OH)_2$ prepared from MgO by hydration at 177 °C under a steam pressure of about 9 atm. The enthalpies of reaction are derived from studies of Taylor and Wells[1] on the enthalpys of solution of various samples of $Mg(OH)_2$and MgO in aqueous HCl. These studies show that the enthalpy of dehydration is quite dependent on the nature of the MgO sample, e.g., values for synthetic $Mg(OH)_2$ vary monotonically from 9.79 to 8.84 kcal·mol^{-1} for MgO ignited at temperatures from 450 to 1425 °C, respectively. The authors ascribe this difference primarily to increase in particle size at the higher ignition temperatures. More recent work[15] suggests that the difference is caused by crystalline disorder rather than particle size alone. We have adopted the results at 1425 °C since they are reasonably consistent with the high temperature samples on which the JANAF enthalpy of formation for MgO is based. The uncertainty is estimated as ±0.5 kcal·mol^{-1}.

Shomate and Huffman[2] have confirmed the enthalpy of solution of MgO (ignited at 1000°C) within about 0.3 kcal·mol^{-1}. Their value may be combined with the enthalpy of solution for synthetic $Mg(OH)_2$, determined under similar conditions by Torgeson and Sahama[3] to obtain $\Delta_r H°$ = 8.85 kcal·mol^{-1} for the dehydration reaction. At the other extreme, the enthalpy of solution data of Giauque and Archibald[4] lead to $\Delta_r H°$ = 9.74 kcal·mol^{-1}; however, this value corresponds to MgO ignited at 350 °C. The MgO sample was microcrystalline and had significant excess $C_p°$ as suggested by Giauque and Archibald[4] and later confirmed by data of Barron *et al.*[5] Giauque and Archibald[4] intentionally used the microcrystalline form which would be similar to the product in their decomposition pressure measurements (190 and 212 °C). Thus, it is not surprising that 3rd law analysis of their decomposition pressures yields essentially the same enthalpy of formation as their solution data (see summary below). Decomposition data at higher pressures have been reported by Fyfe[6] Roy and Roy[7] Kennedy[8] Zhabrova and Kadenatsi[9] and Berg and Rassonskaya.[10] These data do not significantly affect the enthalpy of formation, however, because of uncertainties in the attainment of equilibrium and in reduction to standard state values.

Source	$Mg(OH)_2$ Sample	Temp. of MgO Formation, °C	Enthalpy of Dehydration $\Delta_r H°(298.15\ K)$, kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$
Taylor & Wells[1])	Brucite	1425	9.08	−221.10
	Synthetic	1425	8.84	−220.86
	Synthetic	1000	9.18	−221.20
	Synthetic	450	9.79	>−221.81
Torgeson[3] Shomate[2]	Synthetic	1000	8.85	−220.87
Giauque & Archibald[4]	Synthetic[a]	350	9.74	>−221.74
K_p data	Synthetic[a]	190, 212	20.10[b]	>−221.59

[a]Prepared by reaction of KOH with $MgCl_2$(aq) at 210 °C, rather than by hydration of MgO.
[b]For $Mg(OH)_2(cr) = MgO(cr) + H_2O(g)$ rather than $Mg(OH)_2(cr) = MgO(cr) + H_2O(l)$.

Heat Capacity and Entropy

The low temperature heat capacities are from the measurements (22–321 K) of Giauque and Archibald[4] who used a synthetic, macrocrystalline sample of magnesium dihydroxide prepared by reacting KOH with aqueous $MgCl_2$ at 210°C. The entropy is derived from the heat capacities starting with $S°(20\ K)$ = 0.027 cal·K^{-1}·mol^{-1} from a T^3 extrapolation. $S°(298.15\ K)$ = 15.11 cal·K^{-1}·mol^{-1} compares favorably with 15.09 cal·K^{-1}·mol^{-1} given by Giauque and Archibald.[4] The drop calorimeter enthalpy measurements (350–699 K) of King *et al.*[11] are used to derive heat capacities above 298.15 K. They used a ground sample of natural brucite, which analyzed 98.77% $Mg(OH)_2$. Their published data are corrected for impurities and to one atmosphere total pressure. The low and high temperature heat capacities were joined smoothly by mathematical curve fitting techniques. Heat capacities above 700 K are obtained by extrapolation.

The reference temperature for the enthalpy measurements (393–667 K) of Lashchenko and Kompanskii[12] is uncertain. Their values appear to be near those of King *et al.*[11] up to around 550 K, above 550 K their values average about 5% lower than those of King *et al.*[11]

Decomposition Data

T_{dcm} = 542.2 K is calculated as the temperature at which the fugacity of $H_2O(g)$ is 1 atm for the reaction $Mg(OH)_2(cr) = MgO(cr) + H_2O(g)$.

References

[1]K. Taylor and L. S. Wells, J. Res. Nat. Bur. Stand. 21, 133 (1938).
[2]C. H. Shomate and E. H. Huffman, J. Amer. Chem. Soc. 65, 1625 (1943).
[3]D. R. Torgeson and Th. G. Sahama, J. Amer. Chem. Soc. 70, 2156 (1948).
[4]W. F. Giauque and R. C. Archibald, J Amer. Chem. Soc. 59, 561 (1937).
[5]T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. (London) A250, 70 (1959).
[6]W. S. Fyfe, Amer. J. Sci. 256, 729 (1958).
[7]D. M. Roy and R. Roy, Amer. J. Sci. 255, 573 (1957).

Continued on page 1359

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	−13.127	−915.642	−915.642	INFINITE
100	21.618	9.770	116.934	−10.716	−919.778	−892.401	466.142
200	56.868	36.341	69.736	−6.679	−923.352	−863.412	225.500
298.15	77.249	63.242	63.242	0.	−924.664	−833.652	146.052
300	77.555	63.721	63.244	0.143	−924.675	−833.087	145.053
400	91.705	88.120	66.474	8.659	−924.591	−802.538	104.801
500	99.617	109.525	72.994	18.266	−923.632	−772.123	80.663
600	104.441	128.143	80.669	28.484	−922.270	−741.945	64.592
700	107.880	144.513	88.644	39.108	−920.710	−712.012	53.131
800	110.579	159.101	96.556	50.036	−919.060	−682.311	44.550
900	112.847	172.259	104.248	61.210	−917.385	−652.817	37.889
1000	114.851	184.254	111.658	72.597	−924.320	−622.798	32.532

PREVIOUS: March 1967 CURRENT: December 1975

Magnesium Hydroxide ($Mg(OH)_2$) IDEAL GAS M_r = 58.31968

$S°(298.15\ K) = [267.270 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -564.70 \pm 33.5\ kJ\ mol^{-1}$
$\Delta_f H°(298.15\ K) = -572.37 \pm 33.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[508](1)
[215](1)
[875](1)
[3650](2)
[492](4)

Ground State Quantum Weight. [1] $\sigma = 2$
Point Group: $[C_{2v}]$
Bond Distances· Mg–O = [1 79] Å O–H = [0.96] Å
Bond Angles· O–Mg–O = [158]° Mg–O–H = [180]°
Product of the Moments of Inertia. $I_A I_B I_C$ = [1.092990 × 10^{-115}] $g^3\ cm^6$

Enthalpy of Formation

Alexander, *et al.*[1] determined the temperature dependence of the equilibrium constant for the reaction $MgO(cr) + H_2O(g) = Mg(OH)_2(g)$ in the range of 1650 to 2020 K by measuring vapor densities using a transpiration technique. The data are presented graphically and are represented by a linear equation With auxiliary data,[2] analysis of the equation yields a 2nd law $\Delta_r H°(298\ 15\ K) = 67\ 1\ kcal \cdot mol^{-1}$ and a 3rd law $\Delta_r H°(298.15\ K) = 64.70\ kcal \cdot mol^{-1}$ with a drift of −1 3 cal $K^{-1} \cdot mol^{-1}$. From the 3rd law heat of reaction, the adopted $\Delta_f H°(298.15\ K) = -136.80\ kcal\ mol^{-1}$ is calculated. An uncertainty of ±8 0 kcal mol^{-1} is assigned to allow for the uncertainty shown in the vapor density measurements and for the uncertainty in the entropy.

The enthalpy of dissociation listed by Jackson[6] leads to $\Delta_f H°(Mg(OH)_2, g, 298.15\ K) = -140.74\ kcal \cdot mol^{-1}$. Another recent compilation[7] lists $\Delta_f H°(298.15\ K) = -134\ kcal \cdot mol^{-1}$.

Based on the adopted $\Delta_f H°(298\ 15\ K) = -136.80 \pm 8\ kcal \cdot mol^{-1}$, $\Delta_r H°(0\ K) = 188.6\ kcal \cdot mol^{-1}$ is calculated for the reaction $Mg(OH)_2(g) = Mg(g) + 2\ OH(g)$.

Heat Capacity and Entropy

The analogy between gaseous mono– and dihydroxides and gaseous mono– and dihalides, particularly the mono– and difluorides, has been recognized.[3-6] The O–Mg–O bond angle is assumed to be the same as the F–Mg–F bond angle;[2] the Mg–O–H bond is considered to be linear as in MgOH.[2] The Mg–O bond distance is estimated to be slightly larger, 0.02 Å, than the Mg–F distance in MgF_2[2] after noting the close similarity in the bond distance of the alkali metal fluorides and hydroxides The O–H bond distance is taken to be the same as in water.[2]

The vibrational frequencies are estimated to be the same as in MgF_2[2] (O–Mg–O symmetrical and asymmetrical stretch, and bend) and as in MgOH[2] (O–H stretch and Mg–O–H bend). The principal moments of inertia are: $I_A = 0.3029 \times 10^{-39}$, $I_B = 18\ 8449 \times 10^{-39}$, and $I_C = 19.1478 \times 10^{-39}\ g \cdot cm^2$.

Jackson[6] has used a different molecular configuration and different vibrational frequencies to estimate $S°(298.15\ K) = 63.829\ cal \cdot K^{-1} \cdot mol^{-1}$. We assign an uncertainty of ± 3.0 cal $K^{-1} \cdot mol^{-1}$ to the adopted entropy.

References

[1] C. A. Alexander, J. S Ogden, and A. Levy, J. Chem. Phys. 39, 3057 (1963).
[2] JANAF Thermochemical Tables: MgO(cr), 12–31–74, $H_2O(g)$, 3–31–61; $Mg(OH)_2(g)$, MgOH(g), 12–31–75, $MgF_2(g)$, 6–30–75.
[3] R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
[4] J. Berkowitz, D. J Meschi, and W. A Chupka, J. Chem. Phys. 33, 533 (1960).
[5] F. E. Stafford and J. Berkowitz, J. Chem. Phys. 40, 2963 (1964).
[6] D. D Jackson, Lawrence Livermore Laboratory, Univ. of Calif., Report UCRL–51137, (December 8, 1971).
[7] U. S. Nat. Bur. Stand. Tech. Note 270–6, (1971).

Magnesium Hydroxide ($Mg(OH)_2$) $H_2Mg_1O_2(g)$

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻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	−14 472	−564.695	−564.695	INFINITE
100	38.926	209.778	319.782	−11.000	−567.769	−560.393	292.719
200	56.563	242.056	273.257	−6.240	−570.621	−551.824	144.122
250	63.982	255.509	268.385	−3.219	−571.624	−547.003	114.290
298.15	69.476	267.270	267.270	0	−572.371	−542.190	94.989
300	69.659	267.700	267.271	0.129	−572.396	−542.003	94.371
350	73.933	278.775	268.136	3.724	−572.989	−536.888	80 126
400	77.165	288.868	270 106	7.505	−573 453	−531.698	69.433
450	79.646	298.106	272.711	11.428	−573.828	−526.455	61 109
500	81.588	306.602	275.681	15 460	−574.145	−521.174	54.447
600	84.438	321.746	282.128	23.771	−574.691	−510.528	44.445
700	86.510	334.924	288.749	32.322	−575.204	−499.793	37.295
800	88.203	346.589	295.264	41.060	−575.743	−488.984	31.927
900	89 704	357 066	301.559	49.957	−576.345	−478.104	27.748
1000	91.089	366.590	307.593	58.997	−585.627	−466.440	24.364
1100	92.385	375.333	313.359	68.172	−586.431	−454 482	21.582
1200	93.596	383 424	318.865	77.471	−587.190	−442.452	19.259
1300	94.723	390.961	324.124	86.888	−587.908	−430.362	17.292
1400	95.765	398 020	329.153	96.413	−716.000	−415.050	15 486
1500	96.722	404.660	333.968	106 038	−715.303	−393.578	13.706
1600	97.597	410.930	338.584	115.755	−714.584	−372 153	12.150
1700	98.395	416.871	343.016	125.555	−713.847	−350.773	10 778
1800	99.121	422.516	347 277	135 432	−713.099	−329.438	9.560
1900	99 781	427.894	351.379	145.377	−712.344	−308.144	8 471
2000	100.380	433.027	355.334	155.386	−711.587	−286.889	7 493
2100	100.925	437.938	359.152	165.451	−710.831	−265.673	6.608
2200	101 419	442.645	362.841	175.569	−710 080	−244 492	5.805
2300	101.869	447.163	366.409	185.734	−709.337	−223.346	5.072
2400	102.279	451.507	369.865	195.942	−708.604	−202.232	4.401
2500	102.653	455.690	373.215	206 188	−707.884	−181 148	3.785
2600	102 994	459.723	376.465	216.471	−707.179	−160.093	3.216
2700	103.307	463 616	379.621	226.786	−706.491	−139.064	2.690
2800	103.593	467.379	382.689	237 131	−705.822	−118.060	2.202
2900	103 856	471.018	385.672	247.504	−705 174	−97.081	1.749
3000	104 097	474.543	388.576	257.902	−704.549	−76.122	1.325
3100	104.319	477.960	391.405	268.323	−703.948	−55.184	0.930
3200	104.524	481.276	394.162	278.765	−703.374	−34.266	0.559
3300	104.714	484.495	396.850	289.227	−702.829	−13.365	0.212
3400	104.889	487.624	399.474	299.708	−702.314	7.520	−0.116
3500	105.052	490 667	402.037	310.205	−701.832	28.390	−0.424
3600	105.203	493.628	404.540	320 718	−701.385	49.247	−0.715
3700	105.343	496.512	406.987	331.245	−700.975	70.092	−0.990
3800	105.474	499.324	409.380	341.786	−700.605	90.928	−1.250
3900	105.595	502.065	411.721	352.339	−700.276	111 753	−1.497
4000	105.709	504.740	414.014	362.905	−699.992	132.570	−1.731
4100	105.815	507.351	416.258	373.481	−699.754	153 381	−1 954
4200	105.915	509.902	418.458	384.067	−699.566	174.187	−2.166
4300	106.008	512.396	420.613	394.664	−699.429	194.989	−2.369
4400	106.096	514.834	422.727	405.269	−699.347	215.788	−2.562
4500	106.178	517.219	424.801	415.883	−699.321	236.586	−2.746
4600	106.255	519.554	426.835	426.504	−699.354	257.384	−2.923
4700	106.328	521.839	428.832	437.134	−699 448	278.184	−3.092
4800	106.397	524.079	430.793	447.770	−699.606	298.986	−3.254
4900	106.461	526.273	432.720	458.413	−699.830	319.793	−3.409
5000	106.523	528 425	434.612	469.062	−700.122	340.604	−3.558
5100	106.581	530.535	436.473	479 717	−700.485	361.422	−3.702
5200	106.635	532 605	438.301	490.378	−700.919	382.247	−3.840
5300	106.687	534 637	440.100	501.044	−701.427	403.083	−3.973
5400	106.736	536 631	441.869	511.715	−702.012	423.928	−4.101
5500	106.783	538.590	443.610	522.391	−702.674	444.784	−4.224
5600	106.827	540.515	445.323	533.072	−703.416	465.654	−4.343
5700	106.869	542.406	447.010	543.757	−704.239	486.537	−4.459
5800	106.910	544.265	448.671	554.446	−705.145	507.437	−4.570
5900	106.948	546.093	450.306	565.139	−706.136	528.350	−4.678
6000	106.984	547.890	451.918	575.835	−707.212	549.283	−4.782

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

Magnesium Hydroxide ($Mg(OH)_2$) $H_2Mg_1O_2(g)$

$S°(298.15\ K) = [355.620 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -842.89 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -851.03 \pm 4.2\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[2000](1)	[100](1)	[830](1)
[1000](1)	[150](1)	[200](1)
[700](1)	[100](1)	[950](1)
[800](1)	[3600](1)	[200](1)
[250](1)	[600](1)	[250](1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: [C_{2v}]
Bond Distances: Mo–O = [1.83] Å O–H = [0.958] Å
Bond Angles: O–Mo–O = [109.5]° H–O–Mo = [104.5]°
HO–Mo–OH plane perpendicular to O–M–O plane
Product of the Moments of Inertia: $I_A I_B I_C$ = [1.536748 × 10^{-113}] $g^3\ cm^6$

Enthalpy of Formation

The enhanced volatility of metallic molybdenum and molybdenum trioxide in the presence of water vapor at high temperatures has been investigated by several workers[1,2,3] using transpiration techniques. Glemser and Haeseler[1] and Bulten[2] have shown that the major volatilization reaction of the oxide is:

A $MoO_3(cr) + H_2O(g) = MoO_2(OH_2)(g)$.

For the reaction of metallic molybdenum with water vapor, Belton and Jordan[3] reported the existence of $MoO_2(OH)_2(g)$ according to the equilibrium.

B. $Mo(cr) + 4H_2O(g) = MoO_2(OH)_2(g) + 3H_2(g)$.

2nd and 3rd law analyses of these equilibrium data are summarized below.

Source	Reaction	T/K	Data Points	$\Delta_r H°$(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}
Glemser and Haeseler[1]	A	873–963	Equation	36.2	31.9 ± 0.3	−4.2	−204.0 ± 0.5
Buiten[2]	A	673–773	Equation	30.0	32.2 ± 0.3	3.6	−203.7 ± 0.5
Belton and Jordan[3]	B	1473–1773	Equation	30.1	28.6 ± 0 1	−0.1	−202.6 ± 0.3

The adopted value, $\Delta_f H°(MoO_2(OH)_2, g) = -203.4 \pm 1.0$ kcal·mol^{-1}, is an average of these three results.

Heat Capacity and Entropy

The assumed tetrahedral structure for $MoO_2(OH)_2$ is from Jordan.[4] The O–H bond length and H–O–Mo bond angle are assumed to be the same as for $H_2O(g)$. The Mo–O bond length is from the compilation of Sutton[5] and assumed to be the same as for Ag_2MoO_4. Principal moments of inertia are: $I_A = 23.7897 \times 10^{-39}$, $I_B = 25.3843 \times 10^{-39}$, and $I_C = 25.4477 \times 10^{-39}$ g·cm^2

The vibrational frequencies are estimated by comparison with those for $H_2SO_4(g)$[6,7] and are adjusted to give $S°(MoO_2(OH)_2, g) = 137.4$ cal·K^{-1}·mol^{-1} at 1600 K. This entropy value is derived from a 2nd law analysis of the equilibrium data for reaction *B* reported by Belton and Jordan.[3]

References

[1] V. O. Glemser and R. V Haeseler, Z. anorg. allg. Chem. **316**, 168 (1962).
[2] J. Buiten, J. Catalysis **10**, 188 (1968).
[3] G. R. Belton and A. S. Jordan, J. Phys Chem. **69**, 2065 (1965).
[4] A. S. Jordan, Ph.D. Thesis, Univ. Penn., (1965).
[5] L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London (1958).
[6] P. A. Giguere and R. Savoie, J. Amer. Chem. Soc. **85**, 287 (1963).
[7] S M. Chackalachal and F. E. Stafford, J. Amer Chem. Soc. **88**, 723 (1966).

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	−22.282	−842.889	−842.889	INFINITE
100	68.112	262.488	437.713	−17.523	−847.429	−828.241	432.629
200	89.457	317.041	364.698	−9.531	−849.796	−808.032	211.036
250	97.403	337.873	357.298	−4.856	−850.551	−797.499	166.628
298.15	104.154	355.620	355.620	0.	−851.026	−787.234	137.920
300	104.395	356.265	355.622	0.193	−851.039	−786.838	137.001
350	110.374	372.819	356.916	5.566	−851.282	−776.115	115.829
400	115.405	387.896	359.860	11.214	−851.321	−765.372	99.947
450	119.623	401.740	363.755	17.093	−851.202	−754.635	87.596
500	123.177	414.532	368.201	23.166	−850.959	−743.917	77.716
600	128.789	437.512	377.882	35.778	−850.212	−722.574	62.906
700	133.009	457.696	387.871	48.877	−849.232	−701.376	52.337
800	136.310	475.681	397.744	62.350	−848.107	−680.329	44.421
900	138.977	491.895	407.319	76.118	−846.891	−659.429	38.272
1000	141.185	506.656	416.526	90.130	−845.620	−638.668	33.361
1100	143.043	520.202	425.344	104.344	−844.325	−618.035	29.348
1200	144.627	532.718	433.777	118 729	−843.034	−597.520	26.009
1300	145.988	544.349	441.840	133.262	−841.770	−577.112	23.189
1400	147.167	555.212	449.554	147.921	−840.552	−556.800	20.774
1500	148 192	565.401	456.941	162.690	−839.398	−536.573	18.685
1600	149 089	574.995	464.023	177.555	−838.326	−516.420	16.859
1700	149.876	584.057	470.820	192.504	−837.349	−496.331	15.250
1800	150.570	592.644	477.351	207.527	−836 483	−476.297	13.822
1900	151 184	600.802	483.636	222.615	−835 741	−456.308	12.545
2000	151.729	608.571	489.690	237 762	−835.136	−436.353	11.396
2100	152.214	615.985	495.529	252.959	−834.682	−416.426	10.358
2200	152.648	623.077	501.166	268.203	−834.389	−396.516	9 414
2300	153.037	629.871	506.615	283.487	−834.271	−376.617	8.553
2400	153.386	636.391	511.888	298.809	−834.340	−356.718	7 764
2500	153 701	642.659	516.994	314.163	−834.609	−336.812	7.037
2600	153.987	648.693	521.944	329.548	−835.100	−316.892	6.366
2700	154.245	654.510	526.747	344.960	−835.854	−296.947	5.745
2800	154.480	660.124	531 411	360.396	−836.934	−276.968	5.167
2900	154.694	665.548	535.943	375.855	−874.304	−256.896	4.627
3000	154.890	670.796	540.351	391.334	−874.242	−235.607	4.102
3100	155.069	675.878	544.642	406.833	−874.221	−214.319	3.611
3200	155.233	680.804	548.820	422.348	−874.241	−193.033	3.151
3300	155.384	685.583	552.892	437.879	−874.301	−171 745	2.718
3400	155.524	690.224	556.864	453.424	−874.401	−150.453	2.311
3500	155.652	694.734	560.739	468.983	−874.540	−129.159	1.928
3600	155.771	699.120	564.522	484.554	−874.718	−107.860	1.565
3700	155.882	703.390	568.218	500.137	−874.933	−86.556	1.222
3800	155.984	707.548	571.830	515.730	−875.187	−65.243	0.897
3900	156.079	711 601	575.362	531.334	−875.477	−43.925	0.588
4000	156.168	715.554	578.818	546.946	−875.803	−22.600	0.295
4100	156.250	719.411	582.200	562.567	−876.166	−1.265	0.016
4200	156.327	723.177	585.512	578.196	−876.564	20.078	−0.250
4300	156.399	726.857	588.756	593.832	−876.998	41.433	−0.503
4400	156.467	730 453	591.936	609.476	−877.468	62.796	−0.745
4500	156.530	733.970	595.053	625 125	−877.972	84.170	−0.977
4600	156.590	737.411	598.111	640.782	−878.513	105.557	−1.199
4700	156.646	740.779	601.111	656.443	−879.089	126.956	−1.411
4800	156 699	744.078	604.055	672.111	−879.701	148.368	−1.615
4900	156.748	747.309	606.945	687.783	−880.350	169.794	−1.810
5000	156.795	750 477	609.785	703 460	−1472.420	196.964	−2.058
5100	156.839	753.582	612.574	719.142	−1474.822	230.376	−2.360
5200	156.881	756.628	615.315	734.828	−1477.409	263.834	−2.650
5300	156.921	759.617	618.009	750.518	−1480.178	297.347	−2.931
5400	156.958	762.550	620.659	766.212	−1483.131	330.912	−3.201
5500	156.994	765.430	623.265	781.910	−1486.263	364.532	−3.462
5600	157.027	768.260	625.829	797.611	−1489.576	398.215	−3.714
5700	157.059	771.039	628.352	813.315	−1493.065	431.955	−3.958
5800	157.090	773.771	630.836	829.023	−1496.731	465.761	−4 195
5900	157.119	776 457	633.281	844.733	−1500.570	499.626	−4.423
6000	157.146	779.098	635 690	860.446	−1504.583	533.563	−4.645

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

$S°(298.15\ K) = 194.707\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 193.246 \pm 6.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 190.372 \pm 6.3\ kJ·mol^{-1}$

Electronic Levels (Quantum Weights) and Vibrational Frequencies (Degeneracies)

State	ϵ, cm^{-1}	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}
$\tilde{X}^2B_1$	0(2)	[3173](1)	1497.2(1)	3220 (1)
$\tilde{A}^2A_1(\pi)$	10249(2)	3325 (1)	633 (1)	[3220](1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: N–H = 1.024 Å
Bond Angle: H–N–H = 103°
Product of the Moments of Inertia: $I_A I_B I_C = 0.0085 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

Direct kinetic studies[1-5] onthe decomposition of hydrazine, $N_2H_4(g) = 2\ NH_2(g)$, give activation energies which suggest $\Delta_f H°(NH_2, 298.15\ K) \leq 40\ kcal·mol^{-1}$. [The kinetic rates are discribed by k_d for the the forward reaction and k_r for the reverse reaction]. The pre-exponential factor suggests $k_r \sim 10^7 - 10^8$ 1/(mol s). This is exceptionally slow for a radical combination reaction[6] and is at variance with the most recent direct measurements of $k_r = 10^{10.8}$ 1/(mol s) (300 K, 1500 mmHg)[7] and $k_r = 10^{9.4}$ 1/(mol s) (300 K, 10 mmHg).[8] A possible explanation for this discrepancy is that the hydrazine decomposition studies have been carried out in the energy dependent region.[9,10] This has been confirmed on the basis of RRKM calculations. With $\Delta_f H°(298.15\ K) = 40\ kcal·mol^{-1}$, it is not possible to simultaneously reproduce the measured forward (k_d) and backward (k_r) rates by orders of magnitude. With a value of $\Delta_f H°(298.15\ K) = 45.5\ kcal·mol^{-1}$, all of the rate data can be fitted to a factor of three. For higher values of $\Delta_f H°(298.15\ K)$, the discrepancy increases.

Data on the thermal decomposition of benzylamine from toluene–carrier studies[2,11] yield $\Delta_f H°(298.15\ K) = 36\ kcal·mol^{-1}$. This technique, however, has consistently yielded erroneous rate paramters.[12] Using their very low pressure pyrolysis technique, Golden *et al.*[13] find $\Delta_f H°(NH_2, 298.15\ K) = 47.2\ kcal·mol^{-1}$. This is in reasonable agreement with the recommended value.

Heat Capacity and Entropy

The bond distance and angle are from the electronic absorption spectrum as summarized by Herzberg.[14] The vibrational frequencies are obtained from Herzberg[14] and from matrix-isolation studies of Milligan and Jacox.[15]

The National Bureau of Standards prepared this table[16] by critical analysis of data existing in 1972. Using $S°$, $C_p°$ and $\Delta_f H°$ selected by NBS,[16] we recalculate the table in terms of current JANAF reference states for the elements.

References

[1]M. Szwarc, Proc. Roy. Soc. A198, 267 (1949).
[2]J. A. Kerr, R. C. Sekhar, and A. F. Trotman–Dickenson, J. Chem. Soc. 3217 (1963).
[3]E. T. McHale, B. E. Knox, and H. B. Palmer, "Tenth Symposium on Combustion (International)," p. 341, The Combustion Institute, Pittsburgh, Pa., (1965).
[4]K. W. Michel and H. Gg. Wagner, "Tenth Symposium on Combustion (International)," p. 353, The Combustion Institute, Pittsburgh, Pa., (1965).
[5]E. Meyer, H. A. Olscheusek, T. Troe, and H. Gg. Wagner, "Eleventh Symposium on Combustion (International)," p. 345, The Combustion Institute, Pittsburgh, Pa., (1967).
[6]S. W. Benson and H. E. O'Neal, NSRDS–NBS 21, p. 34, (1970).
[7]S. Gordon, W. Mulac, and P. Nangia, J. Phys. Chem. 75, 2087 (1971).
[8]J. D. Saltzman and E. J Bair, J. Chem. Phys. 41, 3564 (1964).
[9]M. Gilbert, Combustion and Flame 2, 137, 149 (1958).
[10]D. W. Setzer and W. C. Richardson, Can. J. Chem. 47, 2593 (1969).
[11]M. Szwarc, Proc. Roy. Soc. A198, 285 (1949).
[12]S. W. Benson, J. Chem. Education 42, 505 (1965).
[13]D. M. Golden, R. K. Solly, N. A. Gac, and S. W. Benson, J. Amer. Chem. Soc. 94, 363 (1972).
[14]G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, (1966).
[15]D. E. Milligan and M. E. Jacox, J. Chem. Phys. 43, 4487 (1965).
[16]S. Abramowitz *et al.*, U. S. Nat. Bur. Stand. Report 10904, 239, (July 1972).

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	−9.929	193.246	193.246	INFINITE
100	33.259	158.327	224.351	−6.602	192.122	194.352	−101.519
200	33.280	181.381	197.762	−3.276	191.299	196.904	−51.426
298.15	33.572	194.707	194.707	0.	190.372	199.846	−35.012
300	33.585	194.915	194.708	0.062	190.354	199.905	−34.807
400	34.395	204.680	196.034	3.458	189.386	203.236	−26.540
500	35.533	212.474	198.567	6.953	188.488	206.804	−21.605
600	36.838	219.066	201.448	10.571	187.685	210.545	−18.330
700	38.254	224.851	204.386	14.325	186.980	214.412	−16.000
800	39.715	230.054	207.274	18.224	186.371	218.373	−14.258
900	41.179	234.817	210.074	22.269	185.853	222.405	−12.908
1000	42.597	239.229	212.771	26.458	185.419	226.491	−11.831
1100	43.945	243.353	215.366	30.786	185.059	230.616	−10.951
1200	45.196	247.231	217.861	35.244	184.764	234.771	−10.219
1300	46.355	250.895	220.263	39.822	184.525	238.948	−9.601
1400	47.417	254.370	222.576	44.511	184.333	243.142	−9.072
1500	48.392	257.675	224.807	49.303	184.182	247.348	−8.613
1600	49.292	260.827	226.960	54.187	184.066	251.563	−8.213
1700	50.128	263.841	229.042	59.159	183.982	255.784	−7.859
1800	50.907	266.728	231.056	64.211	183.925	260.010	−7.545
1900	51.647	269.501	233.007	69.339	183.895	264.238	−7.264
2000	52.346	272.168	234.899	74.539	183.891	268.467	−7.012
2100	53.020	274.738	236.735	79.807	183.912	272.695	−6.783
2200	53.664	277.220	238.519	85.142	183.957	276.922	−6.575
2300	54.287	279.619	240.254	90.539	184.027	281.146	−6.385
2400	54.894	281.942	241.943	95.999	184.123	285.366	−6.211
2500	55.484	284.195	243.588	101.518	184.243	289.583	−6.050
2600	56.053	286.383	245.192	107.095	184.389	293.793	−5.902
2700	56.605	288.508	246.757	112.728	184.560	297.998	−5.765
2800	57.145	290.577	248.286	118.415	184.757	302.196	−5.638
2900	57.664	292.591	249.779	124.156	184.977	306.386	−5.519
3000	58.162	294.555	251.239	129.947	185.222	310.569	−5.407
3100	58.643	296.470	252.667	135.788	185.489	314.742	−5.303
3200	59.103	298.339	254.065	141.675	185.778	318.907	−5.206
3300	59.542	300.164	255.435	147.608	186.088	323.063	−5.114
3400	59.961	301.948	256.776	153.583	186.417	327.209	−5.027
3500	60.359	303.692	258.092	159.599	186.763	331.345	−4.945
3600	60.735	305.398	259.383	165.654	187.126	335.471	−4.868
3700	61.087	307.067	260.649	171.746	187.503	339.586	−4.794
3800	61.417	308.700	261.892	177.871	187.892	343.691	−4.724
3900	61.725	310.299	263.113	184.028	188.291	347.786	−4.658
4000	62.011	311.866	264.312	190.215	188.700	351.870	−4.595
4100	62.274	313.400	265.491	196.430	189.115	355.945	−4.535
4200	62.517	314.904	266.649	202.669	189.535	360.009	−4.477
4300	62.740	316.378	267.789	208.932	189.958	364.063	−4.422
4400	62.944	317.822	268.909	215.217	190.383	368.107	−4.370
4500	63.128	319.239	270.012	221.521	190.807	372.141	−4.320
4600	63.291	320.628	271.098	227.842	191.230	376.166	−4.271
4700	63.438	321.991	272.166	234.178	191.650	380.182	−4.225
4800	63.568	323.328	273.218	240.529	192.066	384.189	−4.181
4900	63.684	324.640	274.254	246.891	192.476	388.187	−4.138
5000	63.785	325.928	275.275	253.265	192.879	392.177	−4.097
5100	63.871	327.192	276.280	259.648	193.275	396.159	−4.057
5200	63.944	328.433	277.271	266.039	193.663	400.133	−4.019
5300	64.003	329.651	278.248	272.436	194.042	404.100	−3.983
5400	64.052	330.848	279.211	278.839	194.412	408.060	−3.947
5500	64.091	332.024	280.161	285.246	194.772	412.013	−3.913
5600	64.116	333.179	281.097	291.657	195.122	415.960	−3.880
5700	64.134	334.314	282.021	298.069	195.462	419.901	−3.848
5800	64.143	335.429	282.932	304.483	195.791	423.835	−3.817
5900	64.144	336.526	283.831	310.898	196.110	427.764	−3.787
6000	64.137	337.604	284.718	317.312	196.419	431.688	−3.758

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

$S°(298.15\ K) = [218.603]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 220.00 \pm 20.9\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 212.97 \pm 10.9\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[3095](1)	[3205](1)
[1406](1)	[1495](1)
[1360](1)	[910](1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: N–H = [1.014] Å; N–N = [1.23] Å
Bond Angle: H–N–N = [100]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.3981 \times 10^{-117}]\ g^3\cdot cm^6$

Enthalpy of Formation

The standard enthalpy of formation, $\Delta_f H°(N_2H_2, g, 298.15\ K) = 50.9\ kcal\cdot mol^{-1}$, was calculated from the appearance and ionization potentials of di-imide reported by Foner and Hudson[1] using the JANAF $\Delta_f H°(N_2H_4, g, 0\ K) = 26.1\ kcal\cdot mol^{-1}$ in calculation. For example:

	$\Delta_r H°(0K)$
$N_2H_4(g) \rightarrow N_2H_2^+ + H_2(g) + e$	$11.0 \pm 0.2\ cal\cdot K^{-1}\cdot mol^{-1}$
$N_2H_2(g) \rightarrow N_2H_2^+ + e$	$9.85 \pm 0.1\ cal\cdot K^{-1}\cdot mol^{-1}$
$N_2H_4(g) \rightarrow N_2H_2(g) + H_2$	$1.15 \pm 0.2\ cal\cdot K^{-1}\cdot mol^{-1}$
	$26.5 \pm 5\ kcal\cdot mol^{-1}$

From the above enthalpy of formation and that for NH(g) in the JANAF Tables 12–31–65, one can calculate a N–N bond energy of $109.4 \pm 5\ kcal\cdot mol^{-1}$ at 0 K. This is in agreement with the N–N bond in molecules such as N_2F_2.

Heat Capacity and Entropy

The bond distances and angle were obtained from a quantum-mechanical calculation by Wheland and Chen.[2] The principal moments of inertia are: $I_A = [0.3114] \times 10^{-39}$, $I_B = [1.9689] \times 10^{-39}$ and $I_C = [2.2803] \times 10^{-39}\ g\cdot cm^2$.

Since there are 12 valency electrons in N_2H_2, Walsh[3] has predicted a bent ground state, existing in either a cis or a trans configuration for diimide. Blau and Hochheimer[4] have measured the infrared spectrum of diimide which was frozen in a cold trap as one of the decomposition products of N_2H_4. The spectrum of the solid N_2H_2 at liquid nitrogen temperature agrees with the predicted non-linear planar structure, and the molecule N_2H_2 appears mainly in cis form. They have also assigned six fundamental vibrational frequencies for cis H_2H_4(s) which have been adopted here for gaseous cis N_2H_2. Blau and Hochheimer also observed two gas phase bands (1277–1314 and 3050–3190 cm^{-1}). Rosengren and Pimentel[5] have observed these bands in matrix isolation studies. They assigned ν_1 or $\nu_4 = 3074\ cm^{-1}$ and $\nu_3 = 1279\ cm^{-1}$ which are in satisfactory agreement with the selected frequencies.

References

[1]S. N. Foner and R. L. Hudson, J. Chem. Phys. 29, 442 (1958).
[2]W. Wheland and P. S. K. Chen, J. Chem. Phys. 24, 67 (1956).
[3]A. D. Walsh, J. Chem. Soc. 2288 (1953).
[4]E. J. Blau and B. F. Hochheimer, J. Chem. Phys. 41, 1174 (1964).
[5]K. Rosengren and G. C. Pimentel, J. Chem. Phys. 43, 507 (1965).

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

	J·K⁻¹mol⁻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	−10.107	219.996	219.996	INFINITE
100	33.261	181.498	249.315	−6.782	217.420	225.324	−117.697
200	33.870	204.651	221.843	−3.438	215.159	234.108	−61.143
250	34.966	212.315	219.195	−1.720	214.026	238.977	−49.932
298.15	36.554	218.603	218.603	0.	212.966	243.880	−42.727
300	36.624	218.829	218.604	0.068	212.926	244.071	−42.497
350	38.678	224.625	219.057	1.949	211.901	249.345	−37.213
400	40.937	229.936	220.089	3.939	210.974	254.758	−33.268
450	43.247	234.891	221.461	6.044	210.153	260.282	−30.213
500	45.508	239.565	223.040	8.263	209.436	265.891	−27.777
600	49.713	248.242	226.529	13.028	208.288	277.296	−24.141
700	53.426	256.190	230.206	18.189	207.469	288.866	−21.555
800	56.683	263.541	233.919	23.698	206.916	300.535	−19.623
900	59.540	270.386	237.595	29.512	206.579	312.259	−18.123
1000	62.049	276.792	241.198	35.594	206.417	324.012	−16.925
1100	64.250	282.812	244.710	41.912	206.398	335.773	−15.945
1200	66.179	288.487	248.124	48.435	206.495	347.531	−15.128
1300	67.871	293.852	251.437	55.140	206.685	359.277	−14.436
1400	69.353	298.937	254.650	62.002	206.950	371.005	−13.842
1500	70.655	303.767	257.765	69.004	207.275	382.712	−13.327
1600	71.799	308.365	260.785	76.128	207.649	394.396	−12.876
1700	72.807	312.748	263.713	83.359	208.061	406.055	−12.477
1800	73.697	316.936	266.555	90.686	208.504	417.689	−12.121
1900	74.486	320.942	269.313	98.095	208.972	429.298	−11.802
2000	75.186	324.781	271.991	105.580	209.457	440.882	−11.515
2100	75.809	328.464	274.593	113.130	209.957	452.441	−11.254
2200	76.366	332.004	277.122	120.739	210.468	463.976	−11.016
2300	76.865	335.410	279.583	128.401	210.986	475.487	−10.799
2400	77.313	338.691	281.978	136.111	211.508	486.976	−10.599
2500	77.718	341.855	284.310	143.863	212.034	498.443	−10.414
2600	78.083	344.911	286.583	151.653	212.560	509.889	−10.244
2700	78.413	347.864	288.798	159.478	213.085	521.315	−10.085
2800	78.714	350.721	290.959	167.335	213.608	532.721	−9.938
2900	78.987	353.488	293.067	175.220	214.127	544.109	−9.800
3000	79.237	356.170	295.126	183.131	214.642	555.479	−9.672
3100	79.466	358.772	297.138	191.067	215.151	566.832	−9.551
3200	79.675	361.298	299.103	199.024	215.653	578.168	−9.438
3300	79.868	363.753	301.025	207.001	216.149	589.489	−9.331
3400	80.045	366.140	302.906	214.997	216.636	600.795	−9.230
3500	80.209	368.463	304.746	223.010	217.114	612.087	−9.135
3600	80.360	370.724	306.547	231.038	217.583	623.365	−9.045
3700	80.500	372.928	308.312	239.081	218.041	634.631	−8.959
3800	80.630	375.077	310.040	247.138	218.490	645.884	−8.878
3900	80.751	377.173	311.735	255.207	218.927	657.125	−8.801
4000	80.863	379.219	313.397	263.288	219.352	668.356	−8.728
4100	80.968	381.217	315.026	271.379	219.766	679.576	−8.658
4200	81.066	383.169	316.626	279.481	220.168	690.786	−8.591
4300	81.157	385.077	318.196	287.592	220.557	701.986	−8.527
4400	81.243	386.944	319.737	295.712	220.933	713.178	−8.466
4500	81.323	388.771	321.251	303.841	221.296	724.361	−8.408
4600	81.399	390.559	322.738	311.977	221.646	735.536	−8.352
4700	81.470	392.310	324.200	320.120	221.984	746.704	−8.299
4800	81.536	394.026	325.637	328.271	222.308	757.865	−8.247
4900	81.599	395.708	327.050	336.427	222.619	769.019	−8.198
5000	81.658	397.357	328.439	344.590	222.917	780.168	−8.150
5100	81.714	398.975	329.807	352.759	223.202	791.309	−8.105
5200	81.767	400.562	331.152	360.933	223.475	802.446	−8.061
5300	81.817	402.120	332.476	369.112	223.736	813.578	−8.018
5400	81.865	403.650	333.780	377.296	223.986	824.705	−7.977
5500	81.909	405.153	335.064	385.485	224.224	835.826	−7.938
5600	81.952	406.629	336.329	393.678	224.452	846.945	−7.900
5700	81.992	408.080	337.575	401.875	224.670	858.059	−7.863
5800	82.031	409.506	338.803	410.077	224.878	869.169	−7.828
5900	82.067	410.909	340.013	418.282	225.076	880.275	−7.793
6000	82.102	412.288	341.207	426.490	225.267	891.379	−7.760

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

Sodium Hydroxide ($(NaOH)_2$) IDEAL GAS M_r = 79.99422 Sodium Hydroxide ($(NaOH)_2$) $H_2Na_2O_2(g)$

$S°(298.15\ K) = [307\ 396 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -594.77 \pm 25.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -607\ 52 \pm 25.1\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}
[350](1)	[3700](1)
[209](1)	[3700](1)
[270](1)	[1250](1)
[201](1)	[1250](1)
[294](1)	[1250](1)
[313](1)	[1250](1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2h}
Bond Distances: Na–O = [2.17] Å O–H = [0.96] Å
Bond Angles Na–O–Na = [90]° Na–O–H = [110]°
Product of the Moments of Inertia: $I_A I_B I_C = [8.159128 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Mass spectrometric studies of the vapors in equilibrium with NaOH(l)[1,2] and mixed NaOH–KOH condensed phases,[3,4] along with a study of the vapor composition by a molecular beam velocity analysis technique,[5] have established the importance of monomeric and dimeric species in the temperature range 573–1050 K. Absolute partial pressures for the monomer and dimer calculated from peak intensity data by Porter and Schoonmaker[3] are analyzed by the 3rd law method with JANAF Gibbs energy functions[6] to give a enthalpy of dimerization of −50.0 $cal \cdot mol^{-1}$ at 298.15 K. Schoonmaker and Porter[4] also calculated differences in the Gibbs energies of dimerization for several alkali metal hydroxide pairs from peak intensity data on mixed systems. A 3rd law analysis of the Gibbs energy data for the NaOH–KOH system leads to a difference in their enthalpies of dimerization of −6.0 $kcal \cdot mol^{-1}$ at 298 15 K. Based upon the adopted value for KOH(g), $\Delta_{dim}H°(= -45.3\ kcal \cdot mol^{-16}$, we derive $\Delta_{dim}H°(= -51.3\ kcal \cdot mol^{-1}$ for NaOH(g) For the reaction 2 NaOH(g) = $Na_2(OH)_2$(g), we adopt a mean of these two results, $\Delta_{dim}H°(298.15\ K) = -50.7 \pm 3.0\ kcal \cdot mol^{-1}$. Combining this result with the adopted enthalpy of formation for NaOH(g),[6] that for the dimer is $\Delta_f H°(Na_2(OH)_2, g, 298.15\ K) = -145.2 \pm 6.0\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

A key to the molecular structure of $Na_2(OH)_2$(g) is provided by the work of Buchler *et al.*[7] which involves the electric deflection of molecular beams of $Cs_2(OH)_2$(g) and $Na_2(OH)_2$(g). Their results indicate that these dimers are nonpolar which implies a planar structure for at least the M_2O_2 part of the molecule. The three models proposed thus far for the dimeric alkali metal hydroxides each incorporate this planar configuration for the alkali and oxygen atoms. Bauer *et al.*[8] proposed a model consisting of a square planar configuration for the alkali and oxygen atoms with two hydrogen bonded bridges between the oxygens and hydrogens. Schoonmaker and Porter[4] adopted the square planar model for the M_2O_2 configuration but did not allow for hydrogen bonding. Berkowitz *et al.*[9] proposed a model for $Li_2(OH)_2$(g) which consisted of a trans–configuration with hydrogens above and below the plane of a rhombus formed by the lithium and oxygen atoms, the O–Li–O bond angle being 100°. The adopted molecular structure for $Na_2(OH)_2$(g) is similar to the model of Berkowitz *et al.*[9] but with the O–Na–O bond angle equal to 90°. The Na–O–H bond angle is assumed equal to 110°. The Na–O bond distance is estimated as being 12% longer than that in NaOH(g). The O–H bond distance is estimated to be the same as in H_2O(g). The principal moments of inertia are: $I_A = [14.0843] \times 10^{-39}$, $I_B = [18.1898] \times 10^{-39}$, and $I_C = [31.8478] \times 10^{-39}\ g\ cm^2$.

The first six vibrational frequencies are estimated by comparison with those for other alkali metal fluorides and hydroxides The remaining O–H stretching and bending modes are estimates taken from the work of Berkowitz *et al.*[9]

References

[1]R. F. Porter and R. C. Schoonmaker, J. Chem. Phys. 28, 168 (1958).
[2]R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 28, 454 (1958).
[3]R. F. Porter and R. C. Schoonmaker, J. Phys. Chem. 62, 486 (1958).
[4]R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
[5]V. S. Rao and R. C. Schoonmaker, J. Chem. Phys. 33, 1718 (1960).
[6]JANAF Thermochemical Tables: NaOH(g) and $Na_2(OH)_2$(g), 12–31–70; KOH(g), 12–31–70.
[7]A. Buchler, J L. Stauffer, and W. Klemperer, J. Chem. Phys. 46, 605 (1967).
[8]S. H. Bauer, R H. Diner, and R. F. Porter, J. Chem. Phys. 29, 991 (1958).
[9]J. Berkowitz, D J. Meschi, and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).

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

T/K	$C_p°$ ($J \cdot K^{-1} mol^{-1}$)	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ ($kJ \cdot mol^{-1}$)	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0	0.	INFINITE	−17.301	−594.774	−594 774	INFINITE
100	49.910	235.707	370.856	−13.515	−599.571	−590.975	308.694
200	70 007	277.594	314.373	−7.356	−603.928	−580.589	151.634
250	75.172	293.797	308.679	−3.720	−605.796	−574.535	120.043
298.15	79.284	307.396	307.396	0.	−607.517	−568.358	99.574
300	79.433	307.887	307.398	0.147	−607.582	−568.115	98.918
350	83.306	320.426	308.379	4.217	−609.343	−561.398	83.784
400	86.884	331.787	310.606	8.473	−616.377	−554.016	72.347
450	90 149	342.212	313.546	12.900	−618.052	−546.119	63.392
500	93.089	351.866	316.901	17.482	−619.551	−538.044	56.209
600	98.048	369.293	324.213	27.048	−622.106	−521.494	45.400
700	102.010	384.716	331.775	37.058	−624.193	−504.554	37.650
800	105.258	398.556	339.273	47.427	−625.932	−487.341	31.820
900	108.004	411.117	346.568	58.093	−627.420	−469.926	27.274
1000	110.381	422.622	353.606	69.015	−628.738	−452.355	23.629
1100	112.472	433.242	360.369	80.160	−629.958	−434.656	20.640
1200	114.327	443.110	366.858	91.502	−824.665	−411.970	17.933
1300	115.980	452.327	373.082	103.019	−824.009	−377.604	15.172
1400	117 457	460.977	379.055	114.692	−823.270	−343.293	12.808
1500	118.778	469.127	384.790	126.505	−822.464	−309.037	10.762
1600	119 960	476.831	390.304	138.443	−821.602	−274.836	8.972
1700	121.020	484.136	395.611	150.493	−820.694	−240.691	7.396
1800	121.970	491.081	400.723	162.643	−819.752	−206.600	5.995
1900	122.823	497.699	405.655	174.884	−818.783	−172.562	4.744
2000	123.590	504.019	410.416	187.205	−817.794	−138.576	3.619
2100	124.282	510.066	415.018	199.599	−816.793	−104 640	2.603
2200	124.906	515.862	419.471	212.059	−815.785	−70.751	1.680
2300	125.471	521 427	423.784	224.578	−814.776	−36.909	0.838
2400	125.982	526.778	427.965	237.151	−813.771	−3.110	0.068
2500	126.447	531.930	432.021	249.773	−812.775	30.647	−0.640
2600	126.869	536.898	435.960	262.439	−811.792	64.364	−1.293
2700	127.255	541.693	439.787	275.146	−810.828	98.044	−1.897
2800	127.607	546.328	443.510	287.889	−809.885	131.689	−2.457
2900	127.929	550.811	447.133	300.666	−808.968	165.300	−2.977
3000	128.225	555.153	450.662	313.474	−808.082	198.881	−3.463
3100	128.496	559.362	454.101	326.310	−807.230	232.432	−3.916
3200	128.746	563.446	457.454	339.173	−806.417	265.956	−4.341
3300	128.977	567.411	460.727	352.059	−805.646	299.455	−4.740
3400	129.190	571.265	463.921	364.967	−804.921	332.933	−5.115
3500	129.388	575.012	467.042	377.896	−804.248	366.389	−5.468
3600	129.571	578.660	470.092	390.845	−803.630	399.827	−5.801
3700	129.740	582.212	473.075	403.810	−803.073	433.248	−6.116
3800	129.898	585.675	475.992	416.792	−802.580	466.656	−6.415
3900	130.046	589.051	478.848	429.789	−802.156	500.052	−6.697
4000	130.183	592.345	481.645	442.801	−801.808	533.436	−6.966
4100	130.311	595.561	484.384	455.826	−801.540	566.814	−7.221
4200	130 431	598.703	487.069	468.863	−801.354	600.186	−7.464
4300	130.543	601.773	489.701	481.912	−801.262	633.555	−7.696
4400	130.649	604.775	492.282	494.971	−801.184	666.915	−7.917
4500	130.748	607.713	494.815	508.041	−801.246	700.280	−8.129
4600	130.841	610.587	497.300	521.121	−801.428	733.648	−8.331
4700	130.928	613.402	499.741	534.209	−801.719	767.023	−8.525
4800	131.011	616.160	502.137	547.306	−802.123	800.405	−8.710
4900	131.089	618.862	504.492	560.411	−802.648	833.796	−8.888
5000	131.162	621.511	506.806	573.524	−803.283	867.199	−9.060
5100	131.231	624.109	509.081	586.643	−804.061	900.616	−9.224
5200	131.297	626.658	511.317	599.770	−804.976	934.048	−9.383
5300	131.359	629 159	513.517	612.903	−806.033	967.502	−9.535
5400	131.418	631.615	515.682	626.042	−807.238	1000.975	−9.683
5500	131.474	634.027	517.811	639.186	−808.595	1034.472	−9.825
5600	131.527	636.397	519.908	652.336	−810.111	1067.997	−9.962
5700	131.578	638.725	521.972	665.492	−811.790	1101.549	−10.095
5800	131.626	641.014	524.005	678.652	−813.636	1135.133	−10.223
5900	131.671	643.264	526.007	691.817	−815.655	1168.748	−10.347
6000	131.715	645.478	527.980	704.986	−817.534	1202.364	−10.468

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

$S°(298.15\ K) = 69.950 \pm 0.079\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -285\,830 \pm 0.042\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation and uncertainty are taken from the CODATA recommended values[1] which are, in turn, based on calorimetric measurements by Rossini[2] and King and Armstrong.[3]

Heat Capacity and Entropy

The adopted $C_p°$ data from 273.15 to 373.15 K are taken from the very accurate calorimetric measurements of Osborne *et al.*[4] Heat capacity data taken from the recent equation of state formulation of Haar *et al.*[5] agree with the adopted data to within 0.06% above 320 K with deviations up to 0.12% being noted near 305 K. In the latter region the experimental $C_p°$ data go through a single smooth minimum while data derived from the equation of state exhibit an incipient double minimum behavior. These deviations are very small and would lead to nearly negligible differences in the thermochemical functions.

We have made an approximate extrapolation of $C_p°$(l, p=1 bar) to temperatures where water is unstable with respect to vaporization by using data derived from Haar's equation of state formulation.[5] From 373 15 to 390 K the adopted $C_p°$(1 bar) data were taken directly from Haar *et al.*[5] while from 400 to 450 K the adopted $C_p°$ data were derived by taking advantage of the constant difference of $0.0090\ cal \cdot K^{-1} \cdot mol^{-1}$ between C_p(10 bar) and $C_p°$(1 bar) observed between 320 to 390 K using the data of Haar *et al*[5] Above 450 K the C_p(100 bar) data[5] were adjusted by a similar procedure although the difference is no longer constant. The $C_p°$ adjustment from 10 bar to 1 bar is less than 0.05% while that from 100 bar to 1 bar ranges from 0.9 to 1.2%.

The adopted value of $S°(298.15\ K) = 16.718 \pm 0.019\ cal \cdot K^{-1} \cdot mol^{-1}$ is taken from the CODATA recommended value.[1] This was calculated by CODATA from the entropy of the ideal gas with appropriate corrections for real gas behavior and vaporization.

Vaporization Data

The boiling point and enthalpy of vaporization to the real gas at p=1 bar are taken from the work of Haar *et al.*[5] see the H_2O (liquid–real gas at p=1 bar) JANAF Table[6] for further details. The enthalpy of vaporization, $\Delta_{vap}H°$, to the ideal gas is calculated as $\Delta_{vap}H° = \Delta_f H°(g)$ $\Delta_f H°$(l, p=1 bar) using JANAF data.[6] The temperature and enthalpy of vaporization at f=1 bar represent the calculated values at the point where $\Delta_f G° = 0$ for the process $H_2O(l) \rightarrow H_2O$(ideal gas). Thus, these values represent boiling to the (hypothetical) ideal vapor at a fugacity of 1 bar.

References

[1]ICSU CODATA Task Group, J Chem. Thermodyn. 4, 331 (1972); see also, CODATA Bulletin #17, "CODATA Recommended Key Values for Thermodynamics 1975," (1976).
[2]F. D. Rossini, J. Res. Nat. Bur. Stand. 6, 1 (1931); ibid 6, 36 (1931); ibid 22, 407 (1939).
[3]R. King and G. T. Armstrong, J. Res. Nat. Bur. Stand. 72A, 113 (1968).
[4]N. S. Osborne, H. F. Stimson and D. C. Ginnings, J. Res. Nat. Bur. Stand. 23, 197 (1939).
[5]L. Haar, J. Gallagher and G. S. Kell, Ninth International Conference on Properties of Steam, Sept. 1979, Munich; and personal communication from L. Haar and J. Gallagher, U. S. Nat. Bur. Stand., (May 1980).
[6]JANAF Thermochemical Tables: H_2O(liquid real gas at p=1 bar), H_2O(ideal gas) 3–31–79.

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0							
100							
200							
280	75.563	65.215	70.102	−1.368	−286.410	−240.123	44.796
298.15	75.351	69.950	69.950	0.	−285.830	−237.141	41.546
300	75.349	70.416	69.952	0.139	−285.771	−236.839	41.237
320	75.344	75.279	70.134	1.646	−285.137	−233.598	38.131
340	75.388	79.847	70.573	3.153	−284.506	−230.396	35.396
360	75.679	84.164	71.209	4.664	−283.874	−227.231	32.970
372.780	75.962	86.808	71.699	5.633	--- LIQUID <--> REAL GAS ---		
380	76.154	88.267	72.000	6.182	−283.237	−224.102	30.805
400	76.770	92.189	72.912	7.711	−282.591	−221.006	28.860
420	77.547	95.952	73.920	9.254	−281.934	−217.943	27.105
440	78.543	99.582	75.004	10.814	−281.262	−214.912	25.513
460	79.793	103 100	76.150	12.397	−280.569	−211.911	24.063
480	81.463	106.530	77.344	14.009	−279.850	−208.941	22.737
500	83 694	109.898	78.579	15.659	−279.095	−206.002	21.521

PREVIOUS March 1979 (1 atm) CURRENT March 1979 (1 bar)

$\Delta_a H°(0\ K) = 917\ 769 \pm 0.109\ kJ\cdot mol^{-1}$
$S°(298.15\ K) = 188.834 \pm 0.042\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -238.921 \pm 0.042\ kJ\cdot mol^{-1}$
$\Delta_f H°(298\ 15\ K) = -241\ 826 \pm 0.042\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies[a] ν, cm^{-1}
3651.1(1)
1594.7(1)
3755.9(1)

Point Group: C_{2v} $\sigma = 2$
Rotational Constants[a]: $A_0 = 27\ 8847\ cm^{-1}$ $B_0 = 14.5118\ cm^{-1}$ $C_0 = 9.2806\ cm^{-1}$
[a]See Wooley[4] for detailed molecular constants on which this table is based.

Enthalpy of Formaton

The adopted value of $\Delta_f H°(298.15\ K)$ is that recommended by CODATA[1] and was calculated by CODATA from the heat of formation of liquid water at 298.15 K using vaporization data given by Keenan *et al.*[2] The enthalpy of atomization, $\Delta_a H°(0\ K) = 219.352 \pm 0.026$ $kcal\cdot mol^{-1}$, is calculated using auxiliary JANAF data.[3]

Heat Capacity and Entropy

The adopted heat capacity and entropy data below 2000 K, which are for water with the natural isotopic abundance, are taken from recent calculations by Woolley.[4] Wooley has done detailed calculations on the thermodynamic functions of light isotopic water ($^1H_2{}^{16}O$) and then corrected those to functions appropriate for water of natural isotopic abundance. Below 240 K, his calculation was a direct summation over rotational levels of the group vibrational state, with small additions above 130 K for the ν_2=1 vibrational level Above 240 K, individual vibrational partition functions were summed to obtain the total partition function. During this summation the molecule was treated as a rigid rotator with modified corrections of Stripp–Kirkwood and centrifugal effect types, guided by the behavior found for the vibrational ground state. Details are given by Woolley.[4]

Between 2000 and 5000 K we adopt $C_p°$ data calculated by Friedman and Haar[5] for light isotopic water, after a small correction. Our correction consists of adding 0.021 $cal\cdot K^{-1}\cdot mol^{-1}$ to Friedman and Haar's $C_p°$ data. This correction arises from the constant difference of 0.021 ± 0.001 $cal\cdot K^{-1}\cdot mol^{-1}$ between Woolley's $C_p°$ data (natural abundance) and Friedman and Haar's $C_p°$ data (light isotopic water) in the temperature range 1300–2000 K. Above 5000 K, we have linearly extrapolated Friedman and Haar's corrected $C_p°$ data.

Below 2000 K there is good agreement among thermodynamic functions given by Woolley[4], Friedman and Haar[5] and Glushko *et al.*[6] Above 2000 K the $C_p°$ data from references[5] and[6] begin to deviate significantly; at 4000 and 6000 K the differences $[C_p°{}^6 - C_p°{}^5]$ are 0.57 and 1.07 $cal\cdot K^{-1}\cdot mol^{-1}$, respectively. Woolley is working on extending his calculations to higher temperature[7] and his initial results[4] yield $C_p°$ values slightly higher than[5] but not nearly so high as.[6]

Values of $S°(298.15\ K)$ and $H°(298.15\ K)-H°(0\ K)$ in the present table are in excellent agreement with CODATA values[1] of 45.106 ± 0.01 $cal\cdot K^{-1}\cdot mol^{-1}$ K) and 2.368 ± 0.002 $kcal\cdot mol^{-1}$, respectively.

References

[1]ICSU–CODATA Task Group, J. Chem. Thermodyn. 4, 331 (1972); also refer to, CODATA Bulletin #17,"CODATA Recommended Key Values for Thermodynamics – 1975," (1976).
[2]J. H. Keenan, F. G. Keyes, P. G. Hill and J. G. Moore, "Steam Tables," Wiley, New York, (1969).
[3]JANAF Thermochemical Tables: H(g), O(g), 3–31–77.
[4]H. W. Woolley, U. S. Nat. Bur. Stand., paper presented at the 9th International Conference on the Properties of Steam, Munich, Sept. 10–14, (1979).
[5]A. S. Friedman and L. Haar, J. Chem. Phys. 22, 2051 (1954).
[6]V. P. Glushko, L. V. Gurvich *et al.*, "Thermodynamic Properties of Individual Substances," Third edition, Volume I, Book 1, Nauka, Moscow, (1978).
[7]H. W. Woolley, U. S. Nat. Bur. Stand., personal communication, (August 1980).

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
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−9.904	−238.921	−238.921	INFINITE
100	33.299	152.388	218.534	−6.615	−240.083	−236.584	123.579
200	33.349	175.485	191.896	−3.282	−240.900	−232.766	60.792
298.15	33.590	188.834	188.834	0.	−241.826	−228.582	40.047
300	33.596	189.042	188.835	0.062	−241.844	−228.500	39.785
400	34.262	198.788	190.159	3.452	−242.846	−223.901	29.238
500	35.226	206.534	192.685	6.925	−243.826	−219.051	22.884
600	36.325	213.052	195.550	10.501	−244.758	−214.007	18.631
700	37.495	218.739	198.465	14.192	−245.632	−208.812	15.582
800	38.721	223.825	201.322	18.002	−246.443	−203.496	13.287
900	39.987	228.459	204.084	21 938	−247.185	−198.083	11.496
1000	41.268	232.738	206.738	26.000	−247.857	−192.590	10.060
1100	42.536	236.731	209.285	30.191	−248.460	−187.033	8.881
1200	43.768	240.485	211.730	34.506	−248.997	−181.425	7.897
1300	44.945	244.035	214.080	38.942	−249.473	−175.774	7.063
1400	46.054	247.407	216.341	43.493	−249.894	−170.089	6.346
1500	47.090	250.620	218.520	48.151	−250.265	−164.376	5.724
1600	48.050	253.690	220.623	52.908	−250.592	−158.639	5.179
1700	48.935	256.630	222.655	57.758	−250.881	−152.883	4.698
1800	49.749	259.451	224.621	62.693	−251.138	−147.111	4.269
1900	50.496	262.161	226.526	67.706	−251.368	−141.325	3.885
2000	51.180	264.769	228.374	72.790	−251.575	−135.528	3.540
2100	51.823	267.282	230.167	77.941	−251.762	−129.721	3.227
2200	52.408	269 706	231.909	83.153	−251.934	−123.905	2.942
2300	52.947	272.048	233.604	88.421	−252.092	−118.082	2.682
2400	53.444	274.312	235.253	93.741	−252.239	−112.252	2.443
2500	53.904	276.503	236.860	99.108	−252.379	−106.416	2.223
2600	54.329	278.625	238.425	104.520	−252.513	−100.575	2.021
2700	54.723	280.683	239.952	109.973	−252.643	−94.729	1.833
2800	55.089	282.680	241.443	115.464	−252.771	−88.878	1.658
2900	55.430	284.619	242.899	120.990	−252.897	−83.023	1.495
3000	55.748	286.504	244.321	126.549	−253.024	−77.163	1.344
3100	56.044	288.337	245.711	132.139	−253.152	−71.298	1.201
3200	56.323	290.120	247.071	137.757	−253.282	−65.430	1.068
3300	56.583	291.858	248.402	143 403	−253.416	−59.558	0.943
3400	56.828	293.550	249.705	149.073	−253.553	−53.681	0.825
3500	57.058	295.201	250.982	154.768	−253.696	−47.801	0.713
3600	57.276	296.812	252.233	160.485	−253.844	−41.916	0.608
3700	57.480	298.384	253 459	166.222	−253.997	−36.027	0.509
3800	57.675	299.919	254.661	171.980	−254.158	−30.133	0.414
3900	57.859	301.420	255.841	177.757	−254.326	−24.236	0.325
4000	58.033	302.887	256.999	183.552	−254.501	−18.334	0.239
4100	58.199	304.322	258.136	189.363	−254.684	−12.427	0.158
4200	58.357	305.726	259.252	195.191	−254.876	−6.516	0.081
4300	58.507	307.101	260.349	201.034	−255.078	−0.600	0.007
4400	58.650	308.448	261.427	206.892	−255.288	5.320	−0.063
4500	58.787	309.767	262.486	212.764	−255.508	11.245	−0.131
4600	58.918	311.061	263.528	218.650	−255.738	17.175	−0.195
4700	59.044	312.329	264.553	224.548	−255.978	23.111	−0.257
4800	59.164	313.574	265.562	230.458	−256.229	29.052	−0.316
4900	59.275	314.795	266.554	236.380	−256.491	34.998	−0.373
5000	59.390	315.993	267.531	242.313	−256.763	40.949	−0.428
5100	59.509	317.171	268.493	248.258	−257.046	46.906	−0.480
5200	59.628	318.327	269.440	254.215	−257.338	52.869	−0.531
5300	59.746	319.464	270.373	260.184	−257.639	58.838	−0.580
5400	59.864	320.582	271.293	266.164	−257.950	64.811	−0.627
5500	59.982	321.682	272.199	272.157	−258.268	70.791	−0.672
5600	60.100	322.764	273.092	278.161	−258.595	76.777	−0.716
5700	60.218	323.828	273.973	284.177	−258.930	82.769	−0.758
5800	60.335	324.877	274 841	290.204	−259.272	88.767	−0.799
5900	60.453	325.909	275.698	296.244	−259.621	94.770	−0.839
6000	60.571	326.926	276.544	302.295	−259.977	100.780	−0.877

PREVIOUS· March 1961 (1 atm) CURRENT March 1979 (1 bar)

$S°(298.15\ K) = 69.950 \pm 0.079\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -285.830 \pm 0.042\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Refer to the H_2O(l, p=1 bar) table for details.[1]

Heat Capacity and Entropy

The adopted heat capacity data in the liquid region are taken from the very accurate calorimetric measurements of Osborne *et al.*[2] The adopted heat capacity data for the real gas at one bar pressure are taken from the recent equation of state formulation of Haar *et al.*[3] Refer to the JANAF Table for H_2O(l, p=1 bar) for details concerning the entropy.

Phase Data

Our table refers to the real fluid existing at the standard-state pressure of 1 bar. Since this pressure is below the critical pressure of water [$P_c = 217.6$ bar at $T_c = 647.14$ K][4] there is a first order transition at the normal boiling point. Therefore, this is a two phase (liquid real gas) table for the real fluid at p=1 bar.

Fugacity and Fugacity Coefficient Data

At temperature T the fugacity f for the real gas at p=1 bar is given by $f = \exp[\Delta_f G(\text{real gas})\ \Delta_f G°(\text{ideal gas})/(RT)]$ using real gas data from this table and ideal gas data from from JANAF.[1] Since p=1 bar, the fugacity coefficient (f/P) is equal to the fugacity. The fugacity coefficient is 0.986 at 400 K and approaches 1 as temperature increases, indicating nearly ideal behavior at all temperatures.

References

[1]JANAF Thermochemical Tables: H_2O(l, p=1 bar), H_2O(ideal gas), 3-31-79.
[2]N. S. Osborne, H. F. Stimson and D. C. Ginnings, J. Res. Nat. Bur. Stand., 197 (1939).
[3]L. Haar, J. Gallagher and G. S. Kell, Ninth International Conference on Properties of Steam, September 1979, Munich, and personal communication from L. Haar and J. Gallagher, U. S. Nat. Bur. Stand., (May 1980).
[4]J. F. Matthews, Chem. Rev. 2, 71 (1972).

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

	J·K⁻¹mol⁻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							
100							
200							
280	75.563	65.215	70.102	−1.368	−286.410	−240.123	44.796
298.15	75.351	69.950	69.950	0.	−285.830	−237.141	41.546
300	75.349	70.416	69.952	0.139	−285.771	−236.839	41.237
320	75.344	75.279	70.134	1.646	−285.137	−233.598	38.131
340	75.388	79.847	70.573	3.153	−284.506	−230.396	35.396
360	75.679	84.164	71.209	4.664	−283.874	−227.231	32.970
372.780	75.962	86.808	71.699	5.633	LIQUID <--> REAL GAS		
372.780	36.800	195.911	71.699	46.304	PRESSURE = 1 bar		
400	35.982	198.473	80.240	47.293	−243.009	−223.937	29.243
500	35.699	206.428	104.712	50.858	−243.896	−219.069	22.886
600	36.521	213.003	122.227	54.466	−244.797	−214.018	18.632
700	37.596	218.712	135.612	58.170	−245.658	−208.819	15.582
800	38.780	223.809	146.323	61.988	−246.461	−203.501	13.287
900	40.023	228.448	155.194	65.928	−247.198	−198.086	11.497
1000	41.292	232.730	162.736	69.994	−247.868	−192.593	10.060
1100	42.554	236.725	169.283	74.186	−248.468	−187.035	8.882
1200	43.781	240.481	175.061	78.504	−249.004	−181.426	7.897
1300	44.954	244.032	180.231	82.941	−249.479	−175.775	7.063
1400	46.062	247.404	184.910	87.492	−249.899	−170.090	6.346
1500	47.097	250.618	189.184	92.151	−250.269	−164.376	5.724
1600	48.057	253.689	193.120	96.909	−250.595	−158.639	5.179
1700	48.941	256.629	196.770	101.760	−250.884	−152.883	4.698
1800	49.753	259.450	200.175	106.695	−251.141	−147.111	4.269

Since the standard state for a gas is defined as the ideal gas at one bar pressure, the gas phase properties in this table are not standard state properties. The superscript zero, representing standard state, refers only to liquid-phase properties and not to gas-phase properties which are for the real gas at P=1 bar.

PREVIOUS. March 1979 (1 atm) CURRENT March 1979 (1 bar)

S(298.15 K, 10 bar) = 69.946 ± 0.084 J·K^{-1}·mol^{-1} $\Delta_f H$(298 15 K, 10 bar) = −285.815 ± 0.042 kJ·mol^{-1}

Enthalpy of Formation

The enthalpy of formation of H_2O at 298.15 K and p=10 bar [$\Delta_f H$ H(298.15 K, 10 bar)] is derived from the CODATA[1] enthalpy of formation of the liquid at 298.15 K and 1 bar [$\Delta_f H°$(l, 298.15 K) = −68 315 ± 0.010 kcal·mol^{-1}] by addition of the enthalpy increment [H(298.15 K, 10 bar)–$H°$(298.15 K)]. The enthalpy increment is taken from the recent equation of state formation of Haar *et al.*[2] which yields enthalpy data at any temperature and pressure referenced to the triple point of water. The values of $\Delta_f H°$, $\Delta_f G°$ and log $K°$ in this table refer to formation of H_2O at p=10 bar from H_2 and O_2 in their standard reference states (ideal gas at a pressure of 1 bar).

Heat Capacity and Entropy

The adopted heat capacity data are taken from the recent equation of state formulation of Haar *et al.*[2] The entropy and enthalpy are obtained by appropriate integration of the C_p data and differ from entropy and enthalpy data calculated directly from the equuccirclation of state formulation by less than 0.0001 cal·K^{-1}·mol^{-1} and 0.0001 kcal·mol^{-1}, respectively. The starting point for the entropy integration [S(298.15 K, 10 bar)] is obtained from the CODATA[1] entropy at standard conditions [$S°$(l, 298.15 K) = 16.7184 ± 0.019 cal·K^{-1}·mol^{-1})] by addition of the entropy increment [S(298.15 K, 10 bar) $S°$(298.15 K)]. The entropy increment is also taken from the equation of state formulation[2]

Phase Data

Our table refers to the real fluid phase existing at the nonstandard state pressure of 10 bar. Since this pressure is below the critical pressure of water [P_c = 217.6 bar at T_c = 647.14 K[3]] there is a first order transition at the boiling temperature. Therefore this is a two phase (liquid–real gas) table for the real fluid at p=10 bar.

Vaporization Data

The adopted boiling temperature (at 10 bar) and enthalpy of vaporization are taken from the equation of state formulation of Haar *et al.*[2]

Fugacity and Fugacity Coefficients Data

At temperature T the fugacity f of water at p=10 bar is given by f=$K/K°$ or f=exp[($\Delta_f G°$–$\Delta_f G°$)/(RT)], where K and $\Delta_f G°$ are values for H_2O(ideal gas, T).[4] The fugacity coefficient (f/P) at p = 10 bar is given by f/10. At p = 10 bar the fugacity coefficient is 0.99 at 800 K and the gas behaves in a nearly ideal manner above that temperature.

References

[1]ICSU CODATA Task Group, J. Chem. Thermodyn. 4, 331 (1972), see also, CODATA Bulletin #17, "CODATA Recommended Key Values for Thermodynamics 1975," (1976).

[2]L. Haar, J. Gallagher and G. S. Kell, Ninth International Conference on Properties of Steam, September 1979, Munich; and personal communication from L. Haar and J. Gallagher, U. S. Nat. Bur. Stand., (May 1980).

[3]J. F. Matthews, Chem. Rev. 72, 71 (1972).

[4]JANAF Thermochemical Tables: H_2O(ideal gas), 3–31–79.

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
	at P = 10 bar						
0							
100							
200							
298.15	75.313	69.946	69.946	0.	−285.815	−237.125	41.543
300	75.314	70.412	69.948	0.139	−285.756	−236.823	41.235
400	76.732	92.173	72.906	7.707	−282.580	−220.989	28.858
453.070	79.322	101.872	75.740	11.840	LIQUID <--> REAL GAS		
453.070	46.063	181.988	75.740	48.138	PRESSURE = 10 bar		
500	41.002	186.240	85.919	50.160	−244.579	−209.657	21.903
600	38.430	193.409	103.261	54.089	−245.159	−202.623	17.640
700	38.527	199.326	116.572	57.927	−245.886	−195.477	14.587
800	39.310	204.517	127.247	61.816	−246.618	−188.225	12.290
900	40.357	209.206	136.097	65.798	−247.314	−180.884	10.498
1000	41.517	213.517	143.626	69.891	−247.955	−173.468	9.061
1100	42.714	217.531	150.164	74.103	−248.537	−165.990	7.882
1200	43.900	221.298	155.937	78.434	−249.059	−158.462	6.898
1300	45.045	224.858	161.103	82.881	−249.524	−150.893	6.063
1400	46.134	228.236	165.778	87.441	−249.935	−143.291	5.346
1500	47.155	231.454	170.050	92.106	−250.299	−135.660	4.724
1600	48.104	234.528	173.985	96.869	−250.620	−128.007	4.179
1700	48.981	237.471	177.633	101.724	−250.904	−120.335	3.697
1800	49.786	240.294	181.037	106.663	−251.157	−112.647	3.269

Values of $\Delta_f H°$, $\Delta_f G°$, and Log $K_f°$ in this table refer to formation of H_2O at P = 10 bar from H_2 and O_2 in their standard reference states (Ideal gas at a pressure of 1 bar).

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

S(298 15 K, 100 bar) = 69.903 ± 0.105 J·K^{-1}·mol^{-1} $\Delta_f H$(298.15 K, 100 bar) = −285.666 ± 0.084 kJ·mol^{-1}

Enthalpy of Formation

The enthalpy of formation of H_2O at 298 15 K and p=100 bar [$\Delta_f H$(298.15 K, 100 bar)] is derived from the CODATA[1] enthalpy of formation of the liquid at 298.15 K and 1 bar [$\Delta_f H°$(l, 298.15 K) = −68.315 ± 0 10 kcal·mol^{-1}] by addition of the enthalpy increment [H(298.15 K, 100 bar)–$H°$(298.15 K)]The enthalpy increment is taken from the recent equation of state formulation of Haar *et al.*[2] which yields enthalpy data at any temperature and pressure referenced to the triple point of water. The values of $\Delta_f H*$, $\Delta_f G°$ and log $K°$ in this table refer to formation of H_2O at p=100 bar from H_2 and O_2 in their standard reference states (ideal gas at a pressure of 1 bar).

Heat Capacity and Entropy

The adopted heat capacity data are taken from the recent equation of state formulation of Haar *et al.*[2] The entropy and enthalpy are obtained by appropriate integration of the C_p data and differ from entropy and enthalpy data calculated directly from the equation of state formulation by less than 0 0012 cal·K^{-1}·mol^{-1} and 0.0008 kcal·mol^{-1}, respectively. The starting point for the entropy integration [S(298.15 K, 100 bar)] is obtained from the CODATA[1] entropy at standard conditions [$S°$(l, 298.15 K) = 16uccircl.7184 ± 0.019 cal·K^{-1}·mol^{-1}] by addition of the entropy increment [S(298.15 K, 100 bar)–$S°$(298.15 K)]. The entropy increment is also taken from the equation of state formulation.[2]

Phase Data

Our table refers to the real fluid phase existing at the nonstandard state pressure of 100 bar. Since this pressure is below the critical pressure of water [P_c = 217.6 bar at T_c = 647.14 K)[3] there is a first order transition at the boiling temperature. Therefore this is a two phase (liquid real gas) table for the real fluid at p=100 bar.

Vaporization Data

The adopted boiling temperature (at 100 bar) and enthalpy of vaporization are taken from the equation of state formulation of Haar *et al.*[2]

Fugacity and Fugacity Coefficient Data

At temperature T the fugacity f of water at p=100 bar is given by f=$K/K°$ or f=exp[$\Delta_f G°$–$\Delta_f G°$)/(RT)], where K and $\Delta_f G°$ are values for H_2O(ideal gas).[4] The fugacity coefficient (f/p) at p=100 bar is given by f/100. At p=100 bar the fugacity coefficient is 0.99 at 1200 K and the gas behaves in a nearly ideal manner above that temperature.

References

[1]ICSU CODATA Task Group, J. Chem. Thermodyn. 4, 331 (1972); see also, CODATA Bulletin #17, "CODATA Recommended Key Values for Thermodynamics 1975," (1976).

[2]L. Haar, J. Gallagher and G. S. Kell, Ninth International Conference on Properties of Steam, September 1979, Munich; and personal communication from L. Haar and J. Gallagher, U. S. Nat. Bur. Stand., (May 1980).

[3]J. F. Matthews, Chem. Rev. 72, 71 (1972).

[4] JANAF Thermochemical Tables: H_2O(ideal gas), 3–31–79.

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*
	at P = 100 bar						
0							
100							
200							
298.15	74.864	69.903	69.903	0.	−285.666	−236.963	41.515
300	74.878	70.366	69.905	0.139	−285.608	−236 661	41.206
400	76.313	92.021	72.848	7.669	−282.468	−220.816	28.836
500	82.696	109.578	78.481	15.548	−279.041	−205.789	21.499
584 180	110.330	123.855	83.972	23.299	___ LIQUID <--> REAL GAS ___		
584 180	124.260	164.476	83.972	47.029	PRESSURE = 100 bar		
600	92.684	167.317	86.134	48.710	−250.389	−192.197	16.732
700	51.828	177.340	98.532	55.165	−248.498	−182.699	13.633
800	45.622	183.761	108.802	59.968	−248.317	−173.320	11.317
900	44.071	189.023	117.430	64.434	−248.528	−163.934	9.514
1000	43.949	193.653	124.825	68.828	−248.869	−154.517	8 071
1100	44.414	197.861	131.276	73.244	−249.247	−145 064	6.889
1200	45.145	201 756	136.989	77.721	−249.623	−135.576	5.901
1300	45.991	205.403	142.113	82.277	−249.978	−126.057	5.065
1400	46.872	208.844	146.758	86.920	−250.306	−116.513	4.347
1500	47.745	212.108	151.007	91.651	−250.603	−106.945	3.724
1600	48.586	215.216	154.923	96.468	−250.871	−97.359	3.178
1700	49.380	218.186	158.558	101.367	−251.112	−87.757	2.696
1800	50.123	221.029	161.950	106.343	−251.328	−78.142	2.268

Values of $\Delta_f H*$, $\Delta_f G*$, and Log K_f* in this table refer to formation of H_2O at P = 100 bar from H_2 and O_2 in their standard reference states (Ideal gas at a pressure of 1 bar).

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

S(298.15 K, 500 bar) = 69.696 ± 0.167 J·K^{-1}·mol^{-1} $\Delta_f H$(298.15 K, 500 bar) = −285.014 ± 0.167 kJ·mol^{-1}

Enthalpy of Formation

The enthalpy of formation of H_2O at 298 15 K and p=500 bar [$\Delta_f H°$(298 15 K, 500 bar)] is derived from the CODATA[1] enthalpy of formation of the liquid at 298.15 K and 1 bar [$\Delta_f H°$(l, 298.15 K) = −68.315 ± 0 010 kcal·mol^{-1}] by addition of the enthalpy increment [H(298.15 K, 500 bar)–$H°$(298.15 K)]. The enthalpy increment is taken from the recent equation of state formulation of Haar *et al.*[2] which yields enthalpy data at any temperature and pressure referenced to the triple point of water. The values of $\Delta_f H°$, $\Delta_f G°$ and log $K°$ in this table refer to formation of H_2O (real fluid at p = 500 bar) from H_2 and O_2 in their standard reference states (ideal gas at a pressure of 1 bar).

Heat Capacity and Entropy

The adopted heat capacity data are taken from the recent equation of state formulation of Haar *et al.*[2] The entropy and enthalpy are obtained by appropriate integration of the C_p data and differ from entropy and enthalpy data calculated directly from the equation of state formulation by less than 0.0004 cal·K^{-1}·mol^{-1} and 0.0002 kcal·mol^{-1}, respectively. The starting point for the entropy integration [S(298.15 K, 500 bar)] is obtained from the CODATA[1] entropy at standard condtions [$S°$(l, 298.15 K) = 16.7184 ± 0.019 cal·K^{-1}·mol^{-1}] by addition of the entropy increment [S(298.15 K, 500 bar)–$S°$(298.15 K)]. The entropy increment is also taken from the equation of state formulation.[2]

There is a significant maximum in the C_p(500 bar) data which rises to 40.2 cal·K^{-1}·mol^{-1} near 730 K. In this temperature region the density is varying rapidly but continuously with temperature; the maximum in the C_p data is due to a change in sign of the derivative of the density temperature curve. These same density changes are also responsible for large effects on intermolecular interaction as measured by the fugacity coefficient which changes from 0.22 at 600 K to 0.69 at 800 K (refer below).

Phase Data

Our table refers to the fluid phase existing at the nonstandard state pressure of 500 bar. Since 500 bar exceeds the critical pressure of water (P_c = 217.6 bar at T_c = 647.14 K)[3] the properties of the fluid vary continuously with temperature. Thus our table is a single phase table for the compressed fluid. No first order phase transition occurs, even though labels such as compressed liquid and dense gas are sometimes used for the regions below and above T_c.

Fugacity and Fugacity Coefficient Data

At temperature T the fugacity f of water at p = 500 bar is given by $f = K/K°$ or f=exp[($\Delta_f G°$–$\Delta_f G°$)/(RT)], where K and $\Delta_f G°$ are values for H_2O(ideal gas).[4] The fugacity coefficient (f/p) at p =500 bar is given by f/500.

References

[1]ICSU CODATA Task Group, J. Chem. Thermodyn. 4, 331 (1972); see also, CODATA Bulletin #17, "CODATA Recommended Key Values for Thermodynamics–1975," (1976).

[2]L. Haar, J. Gallagher and G. S. Kell, Ninth International Conference on Properties of Steam, September 1979, Munich; and prersonal communication from L. Haar and J. Gallagher, U. S. Nat. Bur. Stand., (May 1980).

[3]J. F. Matthews, Chem. Rev. 72, 71 (1972).

[4]JANAF Thermochemical Tables: H_2O(ideal gas), 3–31–79.

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 $K_f°$
	at P = 500 bar						
0							
100							
200							
298.15	73.198	69.696	69.696	0.	−285.014	−236.249	41.390
300	73.249	70.149	69.698	0.135	−284.959	−235.947	41.082
400	74.726	91.395	72.585	7.524	−281.962	−220.060	28.737
500	78.518	108.401	78.098	15.152	−278.786	−204.945	21.410
600	90.964	123.595	84.422	23.504	−274.943	−190.519	16.586
700	149.910	140.724	91.172	34.686	−268.326	−176.895	13.200
800	104.930	160.611	98.728	49.507	−258.126	−164 609	10.748
900	67.740	170.291	106.191	57.690	−254.620	−153.167	8.890
1000	57.261	176.794	112.941	63.853	−253.192	−141.981	7.416
1100	53.101	182.029	118.990	69.342	−252.497	−130.897	6.216
1200	51.274	186.560	124.436	74.549	−252.143	−119.860	5.217
1300	50.530	190.631	129.374	79.634	−251.970	−108.845	4.373
1400	50.349	194.367	133.885	84.675	−251.899	−97.838	3.650
1500	50.479	197.844	138.034	89.715	−251.888	−86.835	3.024
1600	50.781	201.111	141.875	94.778	−251.910	−75.831	2.476
1700	51.174	204.201	145.451	99.875	−251.952	−64.824	1.992
1800	51.611	207.138	148.797	105.014	−252.005	−53.816	1.562

Values of $\Delta_f H°$, $\Delta_f G°$, and Log $K_f°$ in this table refer to formation of H_2O at P = 500 bar from H_2 and O_2 in their standard reference states (Ideal gas at a pressure of 1 bar).

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

S(298.15 K, 5000 bar) = 69.627 ± 0.209 $J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H$(298.15 K, 5000 bar) = −278.394 ± 0.418 $kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of H_2O at 298.15 K and p=5000 bar [$\Delta_f H°$(298.15 K, 5000 bar)] is derived from the CODATA[1] enthalpy of formation of the liquid at 298.15 K and 1 bar [$\Delta_f H°$(l, 298.15 K) = −68.315 ± 0.010 $kcal \cdot mol^{-1}$] by addition of the enthalpy increment [H(298.15 K, 5000 bar)–$H°$(298.15 K)]. The enthalpy increment is taken from the recent equation of state formulation of Haar *et al.*[2] which yields enthalpy data at any temperature and pressure referenced to the triple point of water. The values of $\Delta_f H°$, $\Delta_f G°$ and log K in this table refer to formation of H_2O (real fluid at p=5000 bar) from H_2 and O_2 in their standard reference states (ideal gas at a pressure of 1 bar).

Heat Capacity and Entropy

The adopted heat capacity data are taken from the recent equation of state formulation of Haar *et al* [2] The entropy and enthalpy are obtained by appropriate integration of the C_p data and differ from entropy and enthalpy data calculated directly from the equation of state formulation by less than 0.0002 $cal \cdot K^{-1} \cdot mol^{-1}$ and 0.0001 $kcal \cdot mol^{-1}$, respectively. The starting point for the entropy integration [S(298.15 K, 5000 bar)] is obtained from the CODATA[1] entropy at standard condtions [$S°$(l, 298.15 K) = 16.7184 ± 0.019 $cal \cdot K^{-1} \cdot mol^{-1}$] by addition of the entropy increment [S(298.15 K, 5000 bar)–$S°$(298.15 K)]. The entropy increment is also taken from the equation of state formulation.[2]

There are two rather small maximum in the C_p(5000 bar) data near 420 and 780 K.

Phase Data

Our table refers to the fluid phase existing at the nonstandard–state pressure of 5000 bar. Since 5000 bar exceeds the critical pressure of water (P_c = 217.6 bar at T_c = 647.14 K)[3] the properties of the fluid vary continuously with temperature. Thus our table is a single phase table for the compressed fluid. No first–order phase transition occurs, even though labels such as compressed liquid and dense gas are sometimes used for the regions below and above T_c.

Fugacity and Fugacity Coefficient Data

At temperature T the fugacity f of water at p = 5000 bar is given by $f = K/K°$ or $f = \exp[(\Delta_f G° - \Delta_f G°)/(RT)]$, where K and $\Delta_f G°$ are values for H_2O(ideal gas).[4] The fugacity coefficient (f/p) at p=5000 bar is given by f/5000.

References

[1]ICSU CODATA Task Group, J. Chem. Thermodyn. 4, 331 (1972); also refer to, CODATA Bulletin #17, "CODATA Recommended Key Values for Thermodynamics–1975," (1976).

[2]L. Haar, J. Gallagher and G. S. Kell, Ninth International Conference on Properties of Steam, September 1979, Munich; and prersonal communication from L. Haar and J. Gallagher, U. S. Nat. Bur. Stand., (May 1980).

[3]J. F. Matthews, Chem. Rev. 72, 71 (1972).

[4]JANAF Thermochemical Tables: H_2O(ideal gas), 3–31–79.

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 $K_f°$
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
	at P = 5000 bar						
0							
100							
200							
298.15	62.350	66.927	66.927	0.	−278.394	−228.804	40.086
300	63.153	67.316	66.929	0.116	−278.358	−228.496	39.785
400	67.912	86.697	69.552	6.858	−276.008	−212.226	27.714
500	67.526	101.838	74.553	13.642	−273.676	−196.553	20.534
600	67.186	114.105	80.154	20.370	−271.457	−181.338	15.787
700	67.489	124.482	85.764	27.102	−269.290	−166.490	12.424
800	67.633	133.510	91.180	33.863	−267.150	−151 951	9.921
900	67.178	141.455	96.334	40.609	−265.082	−137.676	7.991
1000	66.153	148.483	101.205	47.278	−263.148	−123.625	6.458
1100	64 807	154.725	105.792	53.826	−261.393	−109.759	5.212
1200	63.396	160.303	110.106	60.236	−259.836	−96.045	4.181
1300	62.089	165.324	114.164	66.508	−258.475	−82.452	3.313
1400	60.968	169.883	117.984	72.659	−257.295	−68.957	2.573
1500	60.056	174.057	121.585	78.709	−256.274	−55.541	1.934
1600	59.344	177.910	124.986	84.678	−255.391	−42.188	1.377
1700	58.804	181.490	128.206	90.584	−254.624	−28.887	0.888
1800	58.408	184.840	131.260	96.443	−253.956	−15.628	0.454

Values of $\Delta_f H°$, $\Delta_f G°$, and Log $K_f°$ in this table refer to formation of H_2O at P = 5000 bar from H_2 and O_2 in their standard reference states (Ideal gas at a pressure of 1 bar).

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

Hydrogen Peroxide (H_2O_2) IDEAL GAS M_r = 34.01468 Hydrogen Peroxide (HOOH) H_2O_2(g)

$S°(298\ 15\ K) = 232.991\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -129.808\ kJ\ mol^{-1}$
$\Delta_f H°(298\ 15\ K) = -136.106\ kJ·mol^{-1}$

Point Group: C_2

Enthalpy of Formation

The adopted enthalpy of formation is taken from Giguere and Lin[1] This value was based on the measured enthalpy of decomposition of the liquid,[2] and the enthalpy of vaporization[2].

Heat Capacity and Entropy

$C_p°$ from Giguere and Lin.[1] $C_p°$ below 298.15 K estimated.

Reference

[1]P. A. Giguere and I. D. Lin, J. Amer. Chem. Soc. 77, 6477 (1955).
[2]P. A. Giguere, B. G. Morissette, A. W. Olmos, and O. Knop, Can J. Chem. 33, 804 (1955).

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⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−10.853	−129.808	−129 808	INFINITE
100	33.526	186.540	261.768	−7.523	−132.382	−123.632	64.579
200	36.874	210.632	228.978	−3.669	−134.133	−113.680	29.690
298 15	43.116	232.991	232.991	0.	−136.106	−105.445	18.474
300	43.221	233.258	232.992	0.080	−136.133	−105.255	18.326
400	48 451	246.435	234.753	4.673	−137.417	−94.757	12.374
500	52.551	257.705	238.243	9.731	−138.341	−83.978	8.773
600	55.689	267.576	242.326	15.150	−139.011	−73.039	6.359
700	57.990	276.339	246.571	20.838	−139.515	−62.002	4 627
800	59.831	284.205	250.792	26.731	−139.912	−50.901	3.324
900	61.463	291.349	254.908	32.797	−140.225	−39.755	2.307
1000	62.844	297.897	258.884	39.013	−140.475	−28.578	1.493
1100	64.141	303.949	262.709	45.364	−140.673	−17.378	0.825
1200	65.312	309.580	266.383	51.837	−140.827	−6.162	0.268
1300	66.400	314.852	269.911	58.423	−140.944	5.065	−0.203
1400	67.404	319.810	273.300	65.114	−141.031	16.299	−0.608
1500	68.325	324.492	276.558	71.901	−141.093	27.539	−0.959

PREVIOUS December 1960 (1 atm) CURRENT: December 1960 (1 bar)

$S°(298.15\ K) = [97.069 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 783.15 \pm 15\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -968.89 \pm 9.2\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 21.020 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = -231.57 \pm 2.2\ kcal \cdot mol^{-1}$ is obtained from the enthalpy of formation adopted for the liquid[1] minus enthalpy of melting and the enthalpy difference of the liquid and the crystal between the melting point and 298.15 K. The dissociation pressure measurements by Johnston[2] and by Tamaru and Shiomi[3] span the melting point, but there is not a definite break in the log P vs 1/T curve at the melting point. The temperatures of the dissociation pressures determined by Sano[4] are all below the melting point. For 2nd and 3rd law analysis, using auxiliary data from the JANAF Thermochemical Tables,[1] the dissociation pressures below the melting point are considered to pertain to the equilibrium $Sr(OH)_2(cr) = SrO(cr) + H_2O(g)$.

Source	Data Points	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Johnston[2]	4	703–776	18.7	31.65 ± 1.06	17.5 ± 1.4	−230.9 ± 1.9
Tamaru and Shiomi[3]	10	667–782	28.0	31.50 ± 0.42	4.9 ± 0.3	−230.8 ± 1.2
Sano[4]	5	613–743	26.0	31.27 ± 0.75	7.6 ± 0.2	−230.6 ± 1.6

These three 3rd law values for $\Delta_f H°$(cr, 298.15 K) are in excellent agreement, are in reasonable agreement with the adopted value, and are closer to another recent evaluation[5] of −229.2 kcal·mol^{-1} than is the adopted value. The route taken to derive the adopted value is presently preferred because dissociation pressure measurements of the liquid are judged to be better than those of the solid.

Heat Capacity and Entropy

The heat capacities are derived from a curve fit of the drop calorimeter enthalpy measurements of Powers and Blalock,[6] (545–783 K), extrapolated and forced through zero relative enthalpy at 273.15 K. The change in heat capacity with temperature is larger than it is for the other alkaline earth dihydroxides.[1] There appears to be no definite explanation for this. The purity of the $Sr(OH)_2$ sample, as indicated by total alkalinity, did change more during the enthalpy measurement than other samples in the same report.[6] The total alkalinity of the $Sr(OH)_2$ sample changed from 99.80 to 94.1% while for $Ba(OH)_2$ the change was 100.4 to 99.81%, for NaOH the change was 99.97 to 99.46%, and for KOH the change was 100.00 to 98.68%.[6] The known existence of crystalline allotropy in some of the alkaline earth halides and hydroxides suggests this possibility for $Sr(OH)_2$ crystal also.

The adopted entropy, $S°(298.15\ K) = [23.2 \pm 2]\ cal \cdot K^{-1} \cdot mol^{-1}$, is calculated from Kelley's additive entropy constants for cations and anions.[7]

Fusion Data

From their drop calorimetry, Powers and Blalock[6] selected a melting point of 783.15 K where they derived $\Delta_{fus} H° = 5.23\ kcal \cdot mol^{-1}$. Our smoothing of their data leads to the adopted $\Delta_{fus} H° = 5.024 \pm 0.50\ kcal \cdot mol^{-1}$. Brcic and Jernejcic[8] determined a melting point of 771 K and Berggren and Brown,[9] 723 K. The latter dihydroxide sample contained 5 mole percent $SrCO_3$. $T_{fus} = 783.15 \pm 15\ K$ is adopted.

References

[1]JANAF Thermochemical Tables: SrO(cr), 12-31-72; $H_2O(g)$, 3-31-61, $Be(OH)_2$ (β-c), $Mg(OH)_2$(cr), $Ca(OH)_2$(cr), $Ba(OH)_2$(cr), $Sr(OH)_2$(l), 12-31-75.
[2] J. Johnston, Z. Physik. Chem. 62, 330 (1908).
[3]S. Tamaru and K. Shiomi, Z. Physik. Chem. A171, 221 (1935).
[4]K. Sano, J. Chem. Soc. Japan 60, 758 (1939).
[5]U. S. Nat. Bur. Stand. Tech. Note 270-6, (1971).
[6]W. D. Powers an G. C. Blalock, U. S. Atomic Energy Comm., ORNL-1653 (1954).
[7]K. K. Kelley in Chap. 13, D. R. Stull and H. Prophet, "The Characterization of High Temperature Vapors," J. L. Margrave, ed., John Wiley and Sons, New York, (1967).
[8]B. S. Brcic and J. Jernejcic, Vestn. Sloven. Kem. Drustva 9, 65 (1962).
[9]G. Berggren and A. Brown, Acta Chem. Scand. 25, 1377 (1971).

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°	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	74.894	97.069	97.069	0.	−968.889	−881.098	154.365
300	75.145	97.533	97.070	0.139	−968.907	−880.553	153.318
400	88.450	120.970	100.176	8.318	−969.335	−851.006	111.130
500	101.755	142.137	106.481	17.828	−968.634	−821.482	85.820
600	115.018	161.859	114.083	28.666	−966.815	−792.204	68.967
700	128.323	180.589	122.256	40.833	−963.874	−763.319	56.960
783	150 139.370	195.601	129.251	51.963	--- CRYSTAL <--> LIQUID ---		
800	141.628	198.592	130.680	54.330	−959.806	−734.933	47.986
900	154.934	216.041	139.199	69.158	−955.232	−707.052	41.036
1000	168.239	233.054	147.737	85.316	−948.573	−679.822	35.510

PREVIOUS: CURRENT December 1975

Strontium Hydroxide ($Sr(OH)_2$) LIQUID M_r = 121.63468

$S°(298.15\ K) = [108.739]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 783.15 \pm 15\ K$

$\Delta_f H°(298.15\ K) = [-957.304]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 21.020 \pm 2.1\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = -228.8 \pm 1.7\ kcal·mol^{-1}$ is the average of values derived from the 3rd law analysis of the dissociation pressure measurements of Johnston[1] and of Tamaru and Shiomi.[2] The data from both sources[1,2] span the melting point, only those data above the melting point are used for the 2nd and 3rd law analysis of the reaction $Sr(OH)_2(l) = SrO(cr) + H_2O(g)$.

Source	Data Points	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}
Johnston[1]	11[a]	806–1038	28.5	30.06 ± 0.28[b]	1.6 ± 0.4	−229.36 ± 1.1
Tamaru and Shioni[2]	6	880–942	30.9	29.93 ± 0.26[b]	−2.3 ± 0.2	−228.23 ± 1.1

[a]One point rejected due to a failure of a statistical test.
[b]Considering all of the data as liquid data (733–1038 K,[1] 667–942 K),[2] yields 3rd law enthalpies of reaction of 29.97 ± 0.48 kcal·mol^{-1} for[1] and 29.08 ± 0.16 kcal·mol^{-1} for[2] leading to standard state enthalpies of formation at 298.15 K of −229.27 ± 1.3 and −228.38 ± 1.0 kcal·mol^{-1}, respectively.

Heat Capacity and Entropy

$C_p°$ is derived from the drop ice calorimeter measurements of Powers and Blalock (789–1187 K)[4] and is assumed constant at 27.7 cal·K^{-1}·mol^{-1} over the range of 520 to 1600 K. A glass transition is assumed at 520 K below which $C_p°$ is that of the crystal. The entropy of 298.15 K is calculated from the value adopted for the crystal.[3]

Decomposition Data

T_{dcm} = 1017 K is calculated as the temperature at which the fugacity of $H_2O(g)$ is 1 atm for the reaction $Sr(OH)_2(l) = SrO(cr) + H_2O(g)$. Auxiliary data used in the calculations are from the JANAF Thermochemical Tables.[3]

References

[1]J. Johnston, Z. physik. Chem. 62, 330 (1908).
[2]S. Tamaru and K. Shiomi, Z. physik. Chem. A171, 221 (1935).
[3]JANAF Thermochemical Tables· SrO(cr), 12–31–72, $H_2O(g)$, 3–31–61; $Sr(OH)_2(cr)$, 12–31–75.
[4]W. D. Powers and G. C. Blalock, U. S. Atomic Energy Comm. ORNL-1653 (1954).

Strontium Hydroxide ($Sr(OH)_2$) $H_2O_2Sr_1(l)$

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

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	74.894	108 739	108.739	0.	−957.304	−872.993	152.945
300	75.145	109.203	108.740	0.139	−957.323	−872.470	151 910
400	88.450	132.640	111.846	8.318	−957.750	−844.090	110.227
500	101.755	153.807	118.151	17.828	−957.049	−815.732	85.219
520.000	104.392	157.850	119.600	19.890	GLASS <--> LIQUID TRANSITION		
520.000	157.737	157.850	119.600	19.890			
600	157.737	180.422	126.241	32.509	−951.387	−787.914	68.594
700	157.737	204.737	135.762	48.282	−944.839	−761.189	56.801
783 150	157.737	222.442	144.043	61.398	--- CRYSTAL <--> LIQUID ---		
800	157.737	225.800	145.730	64.056	−938.495	−735.388	48.016
900	157.737	244.379	155.679	79.830	−932.976	−710.299	41.225
1000	157.737	260.998	165.395	95.603	−926.701	−685.895	35.827
1100	157 737	276.032	174.780	111.377	−928 412	−661.749	31.424
1200	157 737	289.757	183.798	127.151	−923.211	−637.737	27.760
1300	157.737	302.382	192.441	142.924	−918.088	−614.156	24 677
1400	157.737	314.072	200.716	158.698	−913.038	−590.966	22.049
1500	157.737	324.955	208.640	174.472	−908.060	−568.135	19.784
1600	157.737	335.135	216.231	190.245	−903.151	−545.634	17.813
1700	157.737	344.697	223.510	206.019	−1035.223	−522.258	16.047
1800	157.737	353.713	230.495	221.793	−1028.585	−492.276	14.285
1900	157.737	362.242	237.207	237.566	−1022.015	−462.660	12.719
2000	157.737	370.333	243.663	253.340	−1015.513	−433.389	11.319

PREVIOUS CURRENT. December 1975

Strontium Hydroxide ($Sr(OH)_2$) $H_2O_2Sr_1(l)$

0 to 783.15 K crystal
above 783.15 K liquid

Refer to the individual tables for details.

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⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	74.894	97.069	97.069	0.	−968.889	−881.098	154.365
300	75.145	97.533	97.070	0.139	−968.907	−880.553	153.318
400	88.450	120.970	100.176	8.318	−969.335	−851.006	111.130
500	101.755	142.137	106.481	17.828	−968.634	−821.482	85.820
600	115.018	161.859	114.083	28.666	−966.815	−792.204	68.967
700	128.323	180.589	122.256	40.833	−963.874	−763.319	56.960
783.150	139 .370	195.601	129.251	51.963	CRYSTAL <--> LIQUID TRANSITION		
783.150	157 .737	222.442	129.251	72.983			
800	157.737	225.800	131.249	75.641	−938.495	−735.388	48.016
900	157.737	244.379	142.807	91.415	−932.976	−710.299	41.225
1000	157.737	260.998	153.810	107.188	−926.701	−685.895	35.827
1100	157.737	276.032	164.248	122.962	−928.412	−661.749	31.424
1200	157.737	289.757	174.144	138.736	−923.211	−637.737	27.760
1300	157.737	302.382	183.529	154.509	−918.088	−614.156	24.677
1400	157.737	314.072	192.441	170.283	−913.038	−590.966	22.049
1500	157.737	324.955	200.917	186.057	−908.060	−568.135	19.784
1600	157.737	335.135	208.991	201.830	−903.151	−545.634	17.813
1700	157.737	344.697	216.695	217.604	−1035.223	−522.258	16.047
1800	157.737	353.713	224.059	233.378	−1028.585	−492.276	14.285
1900	157.737	362.242	231.110	249.151	−1022.015	−462.660	12.719
2000	157.737	370.333	237.870	264.925	−1015.513	−433.389	11.319

PREVIOUS. CURRENT December 1975

Strontium Hydroxide ($Sr(OH)_2$) IDEAL GAS M_r = 121.63468

$S°(298.15\ K) = [305.042 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -588.31 \pm 41.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -595.80 \pm 41.8\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[442](1)
[82](1)
[443](1)
[3650](2)
[438](4)

Ground State Quantum Weight: [1] σ = [2]
Point Group: [C_{2v}]
Bond Distances: Sr–O = [2.22] Å O–H = [0.96] Å
Bond Angles: O–Sr–O = [108]° Sr–O–H = [180]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [3.824302] × 10^{-114} $g^3 \cdot cm^6$

Enthalpy of Formation

Dissociation energies for the reaction $Sr(OH)_2(g) = Sr(g) + 2\ OH(g)$ have been derived from flame spectral measurements.[1-3] Ryabova and Gurvich[1] believed the dominant reaction to be $Sr(g) + H_2O(g) = SrOH(g) + H(g)$ but they also considered the possibility that the reaction $Sr(g) + 2\ H_2O(g) = Sr(OH)_2 + 2\ H(g)$ was dominant and derived $D_0° = 180 \pm 20\ kcal \cdot mol^{-1}$. Sugden and Schofield[2] considered the dihydroxide to be the dominant product and derived $D_0° = 215 \pm 12\ kcal \cdot mol^{-1}$. Cotton and Jenkins[3] found both SrOH and $Sr(OH)_2$ to be present in significant amounts in fuel–rich hydrogen–oxygen–nitrogen flames and derived $D_0° = 202.2 \pm 5\ kcal \cdot mol^{-1}$. Cotton and Jenkins[3] recalculated the work of Ryabova and Gurvich[1] and of Sugden and Schofield[2] considering both SrOH and $Sr(OH)_2$ to be present and obtained the recalculated $D_0°$ values of 196 and 200 kcal mol^{-1}, respectively.

A 3rd law analysis of the experimental equilibrium constants tabulated by Cotton and Jenkins[3] using current JANAF auxiliary data[4] leads to $D_0° = 204.8\ kcal \cdot mol^{-1}$ which is 2.6 $kcal \cdot mol^{-1}$ higher than the 202.2 $kcal \cdot mol^{-1}$ derived by Cotton and Jenkins.[3] Applying this difference to the data of Ryabova and Gurvich[1] and of Sugden and Schofield[2] as recalculated by Cottonand Jenkins[3] gives $D_0° = 198\ 6$ and 202 $kcal \cdot mol^{-1}$, respectively.

For $Ba(OH)_2(g)$[4] the corrected dissociation energy of Ryabova and Gurvich,[4] $D_0° = 208.8\ kcal \cdot mol^{-1}$, is in better agreement with the "adopted" value of 209.6 $kcal \cdot mol^{-1}$, based on good Knudsen cell mass spectrometric measurements, than are the corrected dissociation energies of Sugden and Schofield or Cotton and Jenkins.[4] We adopt $D_0° = 198\ 6\ kcal \cdot mol^{-1}$ for the dissociation of $Sr(OH)_2$ from which $\Delta_f H°(Sr(OH)_2) = -140\ 66 \pm 6.0\ kcal \cdot mol^{-1}$ is calculated.

The enthalpy of dissociation listed by Jackson[8] leads to $\Delta_f H°(Sr(OH)_2, g, 298\ 15\ K) = -143.82\ kcal \cdot mol^{-1}$. Another recent compilation[9] lists $\Delta_f H°(298.15\ K) = -135\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The analogy between gaseous mono– and dihydroxides and gaseous mono– and dihalides, particularly the mono– and difluorides, has been recognized.[5-8] The O–Sr–O bond angle is assumed to be the same as the F–Sr–F bond angle;[4] the Sr–O–H bond angle is considered to be linear as in SrOH.[4] The Sr–O bond distance is estimated to be slightly larger, 0 02 Å, than the Sr–F distance in SrF_2[4] after noting the close similarity in the bond distance of the alkali metal fluorides and hydroxides The O–H bond distance is taken to be the same as in water.[4]

The vibrational frequencies are assumed to be the same as in SrF_2 (O–Sr–O symmetrical and asymmetrical stretch, and bend)[4] and as in SrOH (O–H stretch and Sr–O–H bend).[4] The principal moments of inertia are: $I_A = 7.3880 \times 10^{-39}$, $I_B = 19.3556 \times 10^{-39}$, and $I_C = 26.7436 \times 10^{-39}\ g \cdot cm^2$.

Jackson[8] has used a different molecular configuration and different vibrational frequencies to estimate $S°(298.15\ K) = 74.057\ cal \cdot K^{-1} \cdot mol^{-1}$. We assign an uncertainty of $\pm 2.0\ cal \cdot K^{-1} \cdot mol^{-1}$ to the adopted entropy.

References

[1]V. G. Ryabova and L. V. Gurvich, Teplofiz. Vysokikh Temperatur, Akad. Nauk SSSR 3, 318 (1965).
[2]T. M. Sugden and K. Schofield, Trans. Faraday Soc. 62, 566 (1966).
[3]D. H. Cotton and D. R. Jenkins, Trans Faraday Soc. 64, 2988 (1968).
[4]JANAF Thermochemical Tables. Sr(g), HO(g), 12–31–70; $H_2O(g)$, 31–31–61, H(g), 6–30–74, SrOH(g), $Sr(OH)_2(g)$, $Ba(OH)_2(g)$, 12–31–75, $SrF_2(g)$, 31–31–72
5R. C. Schoonmaker and R. F Porter, J. Chem. Phys. 31, 830 (1959).
[6]J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).
[7]F E. Stafford and J. Berkowitz, J. Chem. Phys. 33, 2963 (1964).
[8]D D Jackson, Lawrence Livermore Laboratory, Univ of Calif., UCRL–51137, (December 8, 1971).
[9]U S. Nat. Bur. Stand. Tech. Note 270–6, (1971).

Strontium Hydroxide ($Sr(OH)_2$) $H_2O_2Sr_1(g)$

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	S° (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻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	−16.235	−588.313	−588.313	INFINITE
100	44.263	239.906	364.080	−12.417	−591.898	−585.681	305.928
200	64.366	276.853	311.694	−6.968	−594.542	−578.292	151.034
250	71.457	292.025	306.273	−3.562	−595.293	−574.142	119.960
298.15	76.209	305.042	305.042	0.	−595.797	−570.013	99.864
300	76.360	305.514	305.044	0.141	−595.813	−569.853	99.220
350	79.769	317.557	305.987	4.049	−596.183	−565.496	84.396
400	82.195	328.375	308.121	8.102	−596.458	−561.092	73.271
450	83.972	338.164	310.924	12.258	−596.681	−556.658	64.615
500	85.321	347.085	314.101	16.492	−596.878	−552.200	57.688
600	87.261	362.823	320.945	25.127	−597.261	−543.229	47.292
700	88.697	376.386	327.918	33.928	−597.687	−534.190	39.862
800	89.938	388.313	334.737	42.860	−598.183	−525.087	34.285
900	91.109	398.974	341.293	51.913	−599.385	−515.844	29.939
1000	92.247	408.632	347.551	61.081	−599 716	−506.544	26.459
1100	93.355	417.477	353.512	70.361	−607.920	−496.846	23.593
1200	94.420	425.645	359.187	79.751	−609.104	−486.696	21.185
1300	95.430	433.243	364.594	89.244	−610.261	−476.448	19.144
1400	96.378	440.351	369.754	98.835	−611.394	−466.112	17.391
1500	97.259	447.030	374.686	108.517	−612.507	−455.696	15.869
1600	98.071	453.334	379.406	118.284	−613.605	−445.206	14.534
1700	98.817	459.302	383.932	128.129	−751.606	−433.468	13.319
1800	99 498	464.970	388.278	138.045	−750.825	−414.777	12.037
1900	100 120	470.366	392.457	148.027	−750.047	−396 129	10.890
2000	100.687	475.516	396.483	158.068	−749.279	−377.521	9.860
2100	101.203	480.442	400.364	168.162	−748.526	−358 952	8.928
2200	101.674	485.161	404.112	178.307	−747.797	−340.418	8.083
2300	102.102	489.690	407.735	188.496	−747.100	−321.917	7.311
2400	102.493	494.044	411.241	198.726	−746.443	−303.445	6 604
2500	102.851	498.235	414.638	208.993	−745.836	−284.999	5 955
2600	103 177	502.275	417.931	219.295	−745.288	−266.577	5.356
2700	103.476	506.175	421 128	229.628	−744.810	−248.174	4.801
2800	103 751	509 943	424.233	239.989	−744.412	−229.787	4.287
2900	104 003	513.588	427.251	250.377	−744.104	−211.414	3.808
3000	104.235	517.118	430.188	260.789	−743.899	−193.049	3.361
3100	104.449	520.540	433.048	271.224	−743.805	−174.689	2.943
3200	104.646	523.859	435.834	281.679	−743.835	−156.331	2.552
3300	104.828	527.082	438.551	292.152	−743.996	−137.969	2.184
3400	104.997	530.214	441.201	302.644	−744.300	−119 600	1.837
3500	105.153	533.260	443.788	313.151	−744.755	−101.221	1.511
3600	105.299	536.224	446.315	323.674	−745.367	−82.826	1.202
3700	105.434	539.111	448.784	334.211	−746.145	−64 412	0.909
3800	105.560	541.924	451.198	344.760	−747.092	−45 974	0 632
3900	105.677	544.668	453.560	355.322	−748.214	−27.509	0.368
4000	105.787	547.345	455.871	365.896	−749.514	−9.014	0.118
4100	105.890	549.958	458.134	376.480	−750.993	9.517	−0 121
4200	105.986	552.511	460.351	387.073	−752.648	28.086	−0.349
4300	106.076	555.006	462.523	397.676	−754.486	46.696	−0.567
4400	106.160	557 446	464.653	408.288	−756.500	65.351	−0 776
4500	106.239	559.832	466.741	418.908	−758.688	84.053	−0.976
4600	106.314	562.168	468.791	429.536	−760 982	102.801	−1.167
4700	106.385	564.455	470.802	440.171	−763.487	121.606	−1.351
4800	106.451	566.696	472.776	450.813	−766.147	140.466	−1.529
4900	106.513	568.891	474 716	461.461	−768.957	159.383	−1.699
5000	106.573	571.044	476.621	472.115	−771.903	178.358	−1.863
5100	106.629	573 155	478.493	482.775	−774.963	197.391	−2.022
5200	106.681	575.226	480.333	493.441	−778.168	216.487	−2.175
5300	106.732	577.258	482 143	504.112	−781.489	235.648	−2.322
5400	106.779	579.254	483.923	514.787	−784.918	254 870	−2.465
5500	106 824	581.214	485.674	525 467	−788 447	274 157	−2.604
5600	106 867	583.139	487.397	536.152	−792.068	293.511	−2.738
5700	106.908	585 031	489.094	546.841	−795.772	312.929	−2.868
5800	106.947	586.890	490 764	557.534	−799.552	332.414	−2.994
5900	106.984	588 719	492.409	568.230	−803.189	351.937	−3.116
6000	107.019	590.517	494.029	578.930	−807 067	371.549	−3.235

PREVIOUS December 1975 (1 atm) CURRENT December 1975 (1 bar)

Strontium Hydroxide ($Sr(OH)_2$) $H_2O_2Sr_1(g)$

$S°(298.15\ K) = 156.895 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 283.46 \pm 0.05\ K$

$\Delta_f H°(0\ K) = -811.969 \pm 0.67\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -813.989 \pm 0.67\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 10.711 \pm 0.13\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of combustion, $\Delta_c H°(298.15\ K)$, of rhombic sulfur to aqueous sulfuric acid, S(cr, rhombic) + 3/2 O_2(g) + H_2O(l) = H_2SO_4 (n H_2O), has been determined by many investigators. Based on the reported combustion data, values of $\Delta_f H°(298.15\ K)$ for liquid H_2SO_4 are derived using tabulated enthalpy of solution and enthalpy of dilution data.[1,2] The value adopted, $\Delta_f H°(H_2SO_4, l, 298.15\ K) = -194.548 \pm 0.16\ kcal \cdot mol^{-1}$, is that recommended by NBS.[2] The uncertainty of $\pm 0.16\ kcal \cdot mol^{-1}$ not only accounts for the scatter in the combustion data but also the uncertainty arising from conversion of these data to be consistent with the current atomic weights and fundamental constants (~tens of calories/mol). An uncertainty of $-0.08\ kcal \cdot mol^{-1}$ may exist due to the difference in the heat of formation of SO_4^{2-}(aq) as reported by CODATA[11] and NBS.[2]

Source	Product	$\Delta_c H°(298.15\ K)$, $kcal \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$, $kcal \cdot mol^{-1}$
McCullough *et al.*[3]	H_2SO_4 (70 H_2O)	−143.58 ± 0.09	−194.400
Scott *et al.*[4]	H_2SO_4 (75 H_2O)	−143.98 ± 0.22	−194.775
Good *et al.*[5]	H_2SO_4 (115 H_2O)	−143.85 ± 0.06	−194.521
Mansson and Sunner[6]	H_2SO_4 (115 H_2O)	−143.93 ± 0.07	−194.601

Heat Capacity and Entropy

The heat capacity has been measured experimentally[7] in the range 15–300 K and has been summarized by Giauque *et al.*[1] Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda[8] based on experimental data (0–300°C). These temperature-dependent values are corrected to current atomic weights, converted from IPTS–48 to IPTS–68, and adjusted graphically in the region 290–350 K so as to provide smoothly varying heat capacity values. In the region above 350 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data), this linear dependence is used for extrapolation of the heat capacity values to 1000 K.

Other heat capacity studies on sulfuric acid and its aqueous solutions are too numerous to mention. However, a recent compilation[9] summarizes much of the work and shows that our adopted heat capacity values for sulfuric acid and its hydrates from room temperature to ~80°C are consistent with the available literature.

The entropy at 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, $S°(15\ K) = 0.269\ cal \cdot K^{-1} \cdot mol^{-1}$ and addition of the entropy of melting.

Fusion Data

The melting point and enthalpy of melting have been measured calorimetrically by Rubin and Giauque.[7] The value for T_{fus} used by Giauque *et al.*[1] in their re evaluation and correlation of aqueous sulfuric acid properties was slightly different; the change was 0.07 K. Many other studies have also reported melting data but they are too numerous to mention.

Vaporization Data

$T_{vap} = 610\ K$ is the temperature at which the fugacity of H_2SO_4(g) is one atm for the reaction H_2SO_4(l) = H_2SO_4(g). $\Delta_{vap} H° = 13.9\ kcal \cdot mol^{-1}$ is calculated as the difference in the respective $\Delta_f H°$ values at T_{vap}.

According to Luchinskii[10] the total pressure over H_2SO_4(l) reaches one atmosphere at 553 K with a vapor composition of 76.6 mole% SO_3, 22.6 mole% H_2SO_4, and 0.8 mole% H_2O.

References

[1] W. F. Giauque, E. W. Horning, J. E. Kunzler, and T. R. Rubin, J. Amer. Chem. Soc. 82, 62 (1960).
[2] U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[3] J. P. McCullough, S. Sunner, H. L. Finke, W. N. Hubbard, J. E. Gross, R. E. Pennington, J. F. Messerly, W D. Good, and G. Waddington, J. Amer. Chem. Soc. 75, 5075 (1953).
[4] D. W. Scott, J. P. McCullough, W. N. Hubbard, J. F. Messerly, I. A. Hossenlopp, F. R. Frow, and G. Waddington, J. Amer. Chem. Soc. 78, 5463 (1956).
[5] W. D. Good, J. L. Lacina, and J. P. McCullough, J. Amer. Chem. Soc. 82, 5589 (1960).
[6] M. Mansson and S. Sunner, Acta Chem. Scand. 17, 723 (1963).
[7] T. R. Rubin and W. F. Giauque, J. Amer. Chem. Soc. 74, 800 (1952).
[8] Om. P. Kharbanda, Ind. Chemist 31, 538 (1955).
[9] Landolt–Bornstein, "Numerical Data and Functional Relationships in Science and Technology," New Series, Group IV, Vol. 1, Part 6, Springer–Verlag, New York, (1977).
[10] G. P. Lucinskii, Zh. Foz. Khim. 30, 1207 (1956).
[11] ICSU CODATA Task Group, J. Chem. Thermodyn. 4, 331 (1972).

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻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	−28.226	−811.969	−811.969	INFINITE
100	45.142	42.586	300.474	−25.789	−819.030	−777.302	406.021
200	73.587	82.684	181.887	−19.841	−823.240	−733.773	191.642
283.456	96.902	112.175	157.073	−12.727	CRYSTAL <--> LIQUID		
283.456	135 .770	149.962	157.073	−2.016	TRANSITION		
298.15	138.584	156.895	156.895	0.	−813.989	−689.918	120.871
300	138.940	157.753	156.897	0.257	−813.936	−689.149	119.991
400	158.205	200.356	162.576	15.112	−812.526	−647.968	84.616
500	177.619	237.744	173.938	31.903	−808.704	−607.248	63.439
600	197.033	271.844	187.451	50.636	−802.804	−567.476	49.403
700	216.447	303.674	201.804	71.310	−794.924	−528.851	39.463
800	235.860	333.844	216.438	93.925	−785.146	−491.486	32.091
900	255.274	362.745	231.099	118.482	−826.632	−454.377	26.371
1000	274.688	390.646	245.666	144.980	−811.918	−413.788	21.614

PREVIOUS December 1966 CURRENT September 1977

$S°(298.15\ K) = [298.796 \pm 2.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -721.22 \pm 8.4\ kJ\ mol^{-1}$
$\Delta_f H°(298.15\ K) = -735.13 \pm 8.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[3500](1)	[380](1)	883 (1)
1223 (1)	[265](1)	[400](1)
1138 (1)	[390](1)	1450 (1)
834 (1)	3610 (1)	[265](1)
550 (1)	1159 (1)	568 (1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: C_{2v}
Bond Distances. S–O = [1.42] Å S–OH = [1.55] Å O–H = [0.97] Å
Bond Angles: O–S–O = [109.47122]° S–O–H = [105]°
Product of the Moments of Inertia: $I_A I_B I_C = [4.510247 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The vapor phase equilibria of the H_2SO_4, H_2O and SO_3 system have been determined by *PVT* studies by Bodenstein and Katayama[5] and Suvorov *et al.*[4] and by vapor pressure measurements by Luchinskii.[3] Using the reported equilibrium values (after correcting a few typographical errors) for the reaction $H_2SO_4(g) = H_2O(g) + SO_3(g)$, we calculate $\Delta_f H°(298.15\ K)$ using a 2nd and 3rd law analysis and auxiliary data.[6] The results are tabulated below We adopt $\Delta_f H°(H_2SO_4, g, 298.15\ K) = -175.7 \pm 2\ kcal \cdot mol^{-1}$ which is the median of the three values derived from the 3rd law $\Delta_f H°(298.15\ K)$. The analysis of vaporization data of Thomas and Ramsey[1] and Abel[2] leads to $\Delta_f H°(298.15\ K)$ values within 2 $kcal \cdot mol^{-1}$ of our adopted value.

Source	T/K	Data Points	Reaction*	$\Delta_r H°(298.15\ K)$, $kcal \cdot mol^{-1}$ 2nd law	3rd law	Drift $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal^{-1} \cdot mol^{-1}$
1	463–493	4	A	18.1 ± 0.1	20.5 ± 0.1	4.9 ± 0.2	−174.0
2	523–673	7	A	17.7 ± 0.2	19.7 ± 0.4	3.3 ± 0.3	−174.8
2	298–603	9	B	24.2 ± 0.3	23.4 ± 0.5	−1.6 ± 0.1	−175.8
3	333–473	8	B	23.7 ± 0.1	23.5 ± 0.1	−0.6 ± 0.3	−175.9
4	583–785	40	B	25.1 ± 0.4	23.3 ± 0.3	−2.7 ± 0.7	−175.7
5	596–756	53	B	23.3 ± 0.6	23.0 ± 0.5	−0.4 ± 0.9	−175.4

*Reactions: A) $H_2SO_4(l) = H_2SO_4(g)$ B) $H_2SO_4(g) = H_2O(g) + SO_3(g)$

Heat Capacity and Entropy

The molecular structure of $H_2SO_4(g)$ is assumed to be tetrahedral with differing bond lengths for S–O and S–OH This adopted structure is consistent with the X-ray and electron diffraction studies on $H_2SO_4(cr)$ by Pascard[7] and Pascard-Billy,[8] respectively, and the X-ray scattering study on $H_2SO_4(l)$ by Weidner *et al.*[9] The latter study gave results which could be interpreted by models having point symmetry C_2 and C_{2v}. In both models, the sulfur–oxygen bond distance are equivalent within the experimental uncertainty. For the C_{2v} model, the O–S–O bond angles coincide with the tetrahedral angle. In the C_2 model these angles are split, but not as extremely as in $H_2SO_4(cr)$.[7,8] The OH distance and the S–O–H angle are taken from those for $H_2O(g)$. The principal moments of inertia are: $I_A = 14.9802 \times 10^{-39}$, $I_B = 17.0080 \times 10^{-39}$ and $I_C = 17.7023 \times 10^{-39}\ g \cdot cm^2$.

The vibrational frequencies are from the infrared studies of Chackalackal and Stafford[10] and the comparisons of Giguere and Savoie.[11] The infrared studies led to the assignement of nine vibrational frequencies while the remaining six were estimated[10] by comparison with the infrared frequencies for the crystal and Raman frequencies for the liquid.

References

[1]J. S. Thomas and A. G. Ramsey, J. Chem. Soc. 123, 3256 (1923).
[2]E. ABel, J. Phys. Chem. 50, 260 (1946); J. Phys. Chem. 52, 908 (1948).
[3]G. P. Luchinskii, Zh. Fiz. Khim. 30, 1207 (1956).
[4]A. V. Suvorov, R. B. Dobrotin, and S. M. Gadzhiev, Russ. J. Inorg. Chem. 10, 710 (1965).
[5]B. Bodenstein and M. Katayama, Z. Elektrochem. 15, 244 (1909); Z. Physik. Chem. 69, 26 (1909).
[6]JANAF Thermochemical Tables: $H_2SO_4(l)$, 9–30–77; $SO_3(g)$, 9–30–65, $H_2O(g)$, 3–31–61.
[7]R. Pascard, Compt. Rend. 240, 2162 (1955).
[8]C. Pascard-Billy, Acta Cryst. 18, 829 (1965).
[9]J. U. Weidner, H. Geisenfelder, and H. Zimmerman, Ber. Bunsenges; Phys. Chem. 75, 800 (1971).
[10]S. M. Shackalackal and F. E. Stafford, J. Amer. Chem. Soc. 88, 723 (1966).
[11]P. A. Giguere and R. Savoie, J. Amer Chem. Soc. 85, 287 (1963).

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻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	−16.340	−721.223	−721.223	INFINITE
100	42.100	232.305	360.452	−12.815	−727.196	−704.440	367.962
200	65 850	269.002	305.914	−7.382	−731.922	−679.718	177.524
250	75.588	284.768	300.131	−3.841	−733.711	−666.453	139.248
298.15	83.761	298.796	298.796	0.	−735.129	−653.366	114.467
300	84.054	299.315	298.798	0.155	−735.178	−652.859	113.673
350	91.435	312.840	299.849	4.547	−736.354	−639.042	95.372
400	97.833	325.477	302.271	9.282	−739.496	−624.986	81.615
450	103.344	337.327	305.515	14.315	−740.883	−610.596	70.876
500	108.076	348.466	309.259	19.604	−742.143	−596.048	62.269
600	115.661	368.875	317.527	30.809	−743 771	−566.661	49.332
700	121.411	387.155	326.191	42.675	−744.699	−537.062	40.076
800	125.932	403.674	334.860	55.051	−745.161	−507.364	33.127
900	129.611	418.725	343.355	67.833	−798.420	−476.548	27.658
1000	132.690	432.545	351.592	80.953	−797 084	−440.854	23.028
1100	135.316	445.318	359.540	94.356	−795.609	−405.301	19.246
1200	137.583	457 192	367.188	108.004	−794.025	−369.888	16.101
1300	139.557	468.284	374.543	121.863	−792.355	−334.610	13.445
1400	141.285	478 691	381.614	135 907	−790 620	−299.464	11.173
1500	142.803	488.492	388.416	150 113	−788.838	−264.444	9.209
1600	144 143	497 751	394.963	164 462	−787.023	−229.543	7.494
1700	145.328	506.526	401.269	178 937	−785.188	−194.756	5.984
1800	146.380	514.863	407.351	193.523	−783.344	−160.079	4.645
1900	147.315	522.803	413.220	208.209	−781.499	−125.503	3.450
2000	148.150	530.381	418.890	222 983	−779 661	−91.024	2.377
2100	148.897	537.628	424.373	237.836	−777.837	−56.638	1.409
2200	149.567	544.570	429.680	252 760	−776.031	−22.336	0.530
2300	150.169	551.232	434.821	267.747	−774.248	11.882	−0.270
2400	150.713	557.635	439.805	282 792	−772.491	46.023	−1.002
2500	151.204	563.798	444.643	297.888	−770.764	80.092	−1.673
2600	151.649	569 737	449.340	313.031	−769.067	114.093	−2.292
2700	152.054	575.468	453.906	328.216	−767.402	148.030	−2.864
2800	152.422	581.005	458.347	343 441	−765 771	181.905	−3.393
2900	152.759	586.359	462.670	358 700	−764 174	215.721	−3.886
3000	153.067	591.543	466.879	373.991	−762.612	249.484	−4.344
3100	153.349	596.567	470.982	389.312	−761.086	283.196	−4.772
3200	153.608	601.440	474.983	404.660	−759.595	316.858	−5.172
3300	153.847	606.170	478.887	420.033	−758.140	350.474	−5.548
3400	154.067	610.766	482.699	435 429	−756.720	384.048	−5.900
3500	154.270	615.235	486.422	450.846	−755.336	417.579	−6.232
3600	154.459	619.584	490.061	466.283	−753.987	451.072	−6.545
3700	154.633	623.818	493.619	481 737	−752.674	484.527	−6.840
3800	154.796	627.944	497.100	497.209	−751.396	517.949	−7.120
3900	154 947	631 967	500.507	512.696	−750 154	551.337	−7.384
4000	155.087	635.892	503.842	528 198	−748 947	584.692	−7.635
4100	155.219	639.723	507.110	543.713	−747.776	618.019	−7.874
4200	155.341	643.465	510.312	559.241	−746.641	651.317	−8.100
4300	155.456	647.121	513.451	574.781	−745.542	684.590	−8.316
4400	155.564	650.697	516.530	590.332	−744.480	717.835	−8.522
4500	155.665	654.194	519.551	605.894	−743.454	751.057	−8.718
4600	155.759	657.616	522.515	621.465	−742.467	784.256	−8.906
4700	155.849	660.967	525.425	637.045	−741.517	817.437	−9.085
4800	155.933	664.249	528.283	652.634	−740.607	850.596	−9.256
4900	156.012	667.465	531.091	668.232	−739.736	883.738	−9.421
5000	156.086	670.618	533.850	683.837	−738.906	916.863	−9.578
5100	156.157	673.709	536.562	699.449	−738.117	949.970	−9.730
5200	156.224	676.742	539.229	715.068	−737.371	983.061	−9.875
5300	156.287	679.718	541.852	730.693	−736.668	1016.141	−10.015
5400	156.347	682.640	544.432	746.325	−736.010	1049 206	−10.149
5500	156.403	685.510	546.971	761.963	−735.398	1082.258	−10.278
5600	156.457	688.328	549.470	777.606	−734.833	1115.303	−10.403
5700	156.508	691.098	551.931	793.254	−734.316	1148.336	−10.523
5800	156.557	693.820	554.354	808.907	−733.848	1181.363	−10.639
5900	156.603	696.497	556.740	824.565	−733.432	1214.376	−10.751
6000	156.647	699.129	559.091	840.228	−733.068	1247.389	−10.859

PREVIOUS September 1977 (1 atm) CURRENT September 1977 (1 bar)

$S°(298.15\ K) = [144.766 \pm 25.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -1131.77 \pm 1.7\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Spitsyn and Patsukova[1] have measured calorimetrically the enthalpy of reaction (1) and (2) at 298.15 K as -13.80 ± 0.01 and -13.05 ± 0.02 kcal·mol^{-1}, respectively. The reactions are given as follows:

$$(1)\ WO_3(cr) + 2\ NaOH(66H_2O) \rightarrow Na_2WO_4(4200\ H_2O) + H_2O(l)$$
$$(2)\ H_2WO_4(cr) + 2\ NaOH(66H_2O) \rightarrow Na_2WO_4(4200\ H_2O) + 2\ H_2O(l)$$

Combination of reactions (1) and (2) gives $\Delta_f H°(298.15\ K) = -0.75 \pm 0.04$ kcal·mol^{-1} for $WO_3(cr) + H_2O(l) \rightarrow H_2WO_4(cr)$, which leads to $\Delta_f H°(H_2WO_4, cr, 298.15\ K) = -270.5 \pm 0.4$ kcal·mol^{-1}.

To obtain WO_3(cr) in a form soluble in the calorimetric solution, Spitsyn and Patsukova dehydrated H_2WO_4(cr) at the relatively low temperature of 250°C. The resulting WO_3(cr) was a very fine lemon yellow powder which may have excess surface free energy compared with the JANAF standard state. The latter is WO_3 formed at high temperature in a calorimetric bomb. The actual enthalpy of formation of tungstic acid should be less negative if this effect is significant.

The previously accepted value (2, 3, 4) -280.2 ± 0.4 kcal·mol^{-1}, was based on the pressure temperature composition studies of Huttig and Kurre[5] for the WO_3 H_2O system. We suspect that the data do not correspond to equilibrium (see entropy section) for the reaction $H_2WO_4(cr) = WO_3(cr) + H_2O(g)$.

Heat Capacity and Entropy

$C_p°(300\ K) = 27.0$ cal·K^{-1}·mol^{-1} is estimated using Kopp's rule. Since the decomposition temperature of H_2WO_4(cr) is approximately 400 K, which is relatively low for hydrogen and oxygen to reach their maximum $C_p°$ contribution, we estimate $C_p°(400\ K) = 31.0$ cal·K^{-1}·mol^{-1} for H_2WO_4(cr).

The entropy, $S°(298.15\ K) = 34.6$ cal·K^{-1}·mol^{-1}, is estimated so that the decomposition pressure of water is one atmosphere at 120°C. This value is quite uncertain as suggested by comparison with the following estimates. A lower limit may be obtained from $S°(283.5\ K) = 26.8$ cal·K^{-1}·mol^{-1} for H_2SO_4(cr). Summation of the entropies for WO_3(cr) and H_2O(cr) [10.7 cal·K^{-1}·mol^{-1}] yields 28.8 cal·K^{-1}·mol^{-1}, and estimate which is somewhat larger than the lower limit. An upper limit may be obtained by assuming that the pressure of about 14 mm at 190 °C corresonds to equilibrium for the reaction $H_2WO_4(cr) = WO_3(cr) + H_2O(g)$. This pressure, base,uccircld on the plateau in the temperature composition data of Huttig and Kurre[5] yields $S°(298.15\ K) = 46.5$ cal·K^{-1}·mol^{-1} when combined with the adopted $\Delta_f H°(298.15\ K)$ and JANAF auxiliary data. Since the estimate appears to be unreasonably large, we suggest that this region of the curve may correspond to the reaction $WO_3 \cdot 0.5\ H_2O(cr) = WO_3(cr) + 0.5\ H_2O(g)$. In contrast, the observed pressures[5] for samples having mole ratios (H_2O/WO_3) of 1.2 1.35 leads to $S°(298.15\ K) = 34$ cal·K^{-1}·mol^{-1}, if the reaction is $WO_3 \cdot H_2O(cr) = WO_3(cr) + H_2O(g)$.

Decomposition Data

$T_{dcm} = 393$ K is calculated as the temperature at which the fugucity of water is 1 atmosphere for the reaction $H_2WO_4(cr) \rightarrow WO_3(cr) + H_2O(g)$ approaches zero.

Spitsyn and Patsukova[1] observed that some dehydration of stoichiometric H_2WO_4(cr) occurs at temperature as low as 90°C. Thermal studies[6,7] on tungstic acid containing some exces water indicated the start of dehydration somewhere in the region of 60–120°C. These temperatures yield a lower limit for T_{dcm} on the presumption that the experiments correspond to a partial pressure of water of less than one atmosphere.

References

[1]V. I. Spitsyn and N. N. Patsukova, Russ. J. Inorg. Chem. 10, 1304 (1965).
[2]D. D. Wagman, U. S. Nat. Bur. Stand. Report 8919, (1965).
[3]M. F. Kohler, L. B. Parkratz and R. Barany, U. S. Bur. Mines RI 5973, (1962).
[4]U. S. Nat. Bur. Stand. Circ. 500, (1952).
[5]G. F. Huttig and B. Kurre, Z. Anorg Chem. 122, 44 (1922); 126, 167 (1923).
[6]W. Wanek, Silikaty 6, 70 (1962).
[7]P. F. Kerr and F. Young, Amer. Mineral. 29, 192 (1944).

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							
100							
200							
298.15	112.633	144.766	144.766	0.	−1131.772	−1003.905	175.880
300	112.968	145.464	144.769	0.209	−1131.770	−1003.112	174.657
400	129.704	180.255	149.399	12.342	−1130.949	−960.310	125.404
500	146.440	211.003	158.697	26.153	−1128.693	−917.882	95.890
600	159.829	238.972	169.783	41.513	−1125.138	−876.036	76.266
700	170.707	264.509	181.518	58.094	−1120.606	−834.865	62.298
800	176.565	287.724	193.367	75.485	−1115.486	−794.391	51.868
900	182.422	308.889	205.044	93.461	−1109.985	−754.580	43.795
1000	186.606	328.326	216.414	111.912	−1104.195	−715.399	37.369

PREVIOUS June 1963 CURRENT March 1967

Tungstic Acid ($O_2W(OH)_2$) IDEAL GAS M_r = 249.86348 Tungstic Acid ($O_2W(OH)_2$) $H_2O_4W_1(g)$

$S°(298.15\ K)$ = [351.999] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -896.09 \pm 4.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -905.84 \pm 4.2\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[2200](1)	[100](1)	[570](1)
[1000](1)	[225](1)	[120](1)
[620](1)	[100](1)	[1100](1)
[560](1)	[2500](1)	[300](1)
[500](1)	[630](1)	[540](1)

Ground State Quantum Weight: 1 σ = [2]
Point Group: [C_{2v}]
Bond Distances: W–O = [1.81] Å O–H = [0.97] Å
Bond Angles: O–W–O = [109.47]° W–O–H = [105]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [$1.442326 \times 10^{-113}$] $g^3·cm^6$

Enthalpy of Formation

The adopted enthalpy of formation, $\Delta_f H°(298.15\ K) = -216.5 \pm 1.0\ kcal·mol^{-1}$, is derived from equilibrium data[1-5] obtained by the transpiration method. The data are in reasonable agreement and they are summarized below. Belton and McCarron[1] have concluded that $WO_3·H_2O$ is the species responsible for the increased volatilization of W(cr) and WO_3(cr) in the presence of water vapor. Based on their data for W(cr) and the earlier data for WO_3(cr), Belton and McCarron[1] ruled out the possibility of significant amounts of $(WO_3)_2·H_2O$ and $WO_3·2H_2O$.

Source	Reaction*	T/K	Data Points	$\Delta_r H°$(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}
Belton & McCarron[1]	A	1473–1773	Equation	14.70	14.63	−0.1 ± 1.1	−216.56
Glemser & Ackermann[2]	B	673–1173	6	38.56	41.67	3.2 ± 0.9	−217.59
Glemser & Haeseler[3]	B	1173–1373	Equation	38.27	42.27	1.6	−216.99
Glemser & Volz[4]	B	1373	1	–	43.44	–	−215.82
Meyer *et al.*[5]	B	1393–1518	Equation	26 14	43.51	11.9	−215.75

*Reactions: A) $W(cr) + 4H_2O(g) \rightarrow H_2WO_4(g) + 3H_2(g)$ B) $WO_3(cr) + H_2O(g) \rightarrow H_2WO_4(g)$

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with those for H_2SO_4(g) reported by Giguere and Savoie,[6] and Chackalackal and Stafford.[7] These frequencies are also adjusted so that $S°(H_2WO_4, g, 1600\ K)$ is 136.7 cal·K^{-1}·mol^{-1} as reported by Belton and McCarron.[1] This entropy was derived a 2nd law analysis of the equilibrium constants for reaction A.

The configuration of WO_4^- group is assumed to be tetrahedral. The bond angle W–O–H is estimated to be the same as the angle of H_2O(g). The bond distances are assumed to be the same as those in WO_3(g) and H_2O(g). The principal moments of inertia are: $I_A = 23.2705 \times 10^{-39}$, $I_B = 24.8660 \times 10^{-39}$, and $I_C = 24.9259 \times 10^{-39}$ g·cm^2.

References

[1]G. R. Belton and R. L. McCarron, J. Phys. Chem. 68, 1852 (1964).
[2]O. Glemser and H. Ackermann, Z. anorg. allg. Chem. 325, 281 (1963).
[3]O. Glemser and R. V. Haeseler, Z. anorg. allg. Chem. 316, 168 (1962).
[4]O. Glemser and H. G. Volz, Naturwissenschaften 43, 33 (1956).
[5]G. Meyer, J. F. Oosterom and W J. V. Oeveren, Rev. Trav Chim. 78, 417 (1959).

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	−21.062	−896.091	−896.091	INFINITE
100	60.677	265.197	430.296	−16.510	−901.000	−881.824	460.618
200	84 476	314.672	360.846	−9.235	−904.248	−861.251	224.936
250	94.555	334.639	353.644	−4.751	−905.233	−850.380	177.677
298.15	102.527	351.999	351.999	0.	−905.836	−839.756	147.122
300	102.802	352.634	352.001	0.190	−905.853	−839.346	146.143
350	109.449	368.999	353.278	5.502	−906.167	−828.233	123.607
400	114.836	383.977	356.193	11.114	−906.241	−817.091	106.701
450	119.269	397.767	360.056	16.970	−906.131	−805.953	93.553
500	122.986	410.531	364.473	23.029	−905.881	−794.834	83.036
600	128.916	433.504	374.107	35.638	−905.077	−772.694	67.269
700	133.483	453.733	384.066	48.767	−903.996	−750.713	56.019
800	137.120	471.804	393.924	62.304	−902.731	−728.900	47.592
900	140.070	488.130	403.499	76.168	−901.341	−707.253	41.048
1000	142.491	503.017	412.717	90.300	−899.871	−685.766	35.821
1100	144.492	516.695	421.557	104.652	−898.355	−664.429	31.551
1200	146.159	529.341	430.018	119.187	−896.820	−643.230	27.999
1300	147.555	541.097	438.116	133.875	−895.289	−622.160	24.999
1400	148 733	552.076	445.868	148.691	−893.780	−601.207	22.431
1500	149.733	562.373	453.296	163.616	−892.309	−580.361	20.210
1600	150.587	572.064	460.419	178.633	−890.887	−559.611	18.269
1700	151.320	581.216	467.258	193.729	−889.525	−538.948	16.560
1800	151 954	589.884	473.832	208.894	−888.231	−518.364	15.043
1900	152.504	598.114	480.158	224 117	−887.011	−497.850	13.687
2000	152.985	605.949	486.253	239.392	−885.872	−477.397	12.468
2100	153.407	613.424	492.132	254.712	−884.818	−457.000	11.367
2200	153.779	620.569	497.809	270.072	−883.853	−436.649	10.367
2300	154.109	627.412	503.297	285.467	−882.979	−416.342	9.455
2400	154.402	633.978	508.606	300.892	−882.199	−396.072	8.620
2500	154.664	640.286	513.748	316.346	−881.513	−375.831	7.853
2600	154 898	646.357	518.732	331.824	−880.921	−355.615	7.144
2700	155 109	652.207	523.568	347.325	−880.448	−335.420	6.489
2800	155.300	657.851	528.263	362.846	−880.131	−315.240	5.881
2900	155.472	663.304	532.826	378.384	−880.008	−295.069	5.315
3000	155.628	668.577	537.264	393.939	−880.106	−274.897	4.786
3100	155.771	673.683	541.583	409.509	−880.467	−254 718	4.292
3200	155.901	678.630	545.789	425.093	−881.123	−234.524	3.828
3300	156.020	683.429	549.887	440.689	−882.098	−214.304	3.392
3400	156.129	688.089	553.884	456.297	−883.426	−194.048	2.981
3500	156.229	692.616	557.783	471.915	−885.171	−173.748	2.593
3600	156.321	697.018	561.590	487.542	−887.428	−153.391	2.226
3700	156.407	701.303	565.308	503.179	−925.062	−132 773	1.874
3800	156.486	705.475	568.942	518.823	−925.055	−111.359	1.531
3900	156.559	709.540	572.495	534 476	−925.087	−89 945	1.205
4000	156.627	713.505	575.971	550 135	−925 157	−68.531	0.895
4100	156 690	717.373	579.373	565.801	−925.266	−47 114	0.600
4200	156.749	721.150	582.704	581.473	−925 412	−25 694	0.320
4300	156.804	724.839	585.967	597.151	−925.595	−4.269	0.052
4400	156.856	728.444	589.164	612.834	−925.816	17 158	−0.204
4500	156.904	731.970	592.299	628.522	−926 073	38.591	−0.448
4600	156.949	735.419	595.372	644.214	−926.368	60.031	−0.682
4700	156.991	738.795	598.388	659.911	−926.699	81.479	−0.906
4800	157.031	742.100	601.348	675.612	−927.068	102.933	−1.120
4900	157.068	745.339	604.254	691.317	−927.475	124.397	−1.326
5000	157.103	748.512	607.107	707.026	−927.920	145.869	−1.524
5100	157.137	751.624	609.910	722.738	−928.403	167.349	−1.714
5200	157.168	754.675	612.665	738.453	−928.926	188.838	−1.897
5300	157 198	757.669	615.373	754.172	−929.488	210.340	−2.073
5400	157.226	760.608	618.035	769.893	−930.092	231.851	−2.243
5500	157.252	763.493	620.654	785.617	−930.737	253.373	−2.406
5600	157.278	766.327	623.230	801.343	−931.425	274.911	−2.564
5700	157.301	769 111	625.765	817.072	−932.156	296.458	−2.717
5800	157.324	771.847	628.260	832.803	−932.933	318.021	−2.864
5900	157.346	774.536	630.716	848.537	−933.755	339.592	−3.007
6000	157.366	777.181	633 136	864.272	−934.625	361 184	−3 144

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

$S°(298.15\ K)$ = [212.652] $J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = [112.3 ± 96.2] $kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [108.5 ± 96.2] $kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[2327](1)
[1020](1)
[2322](1)

Ground State Quantum Weight: [2] σ = [2]
Point Group = [C_{2v}]
Bond Distance: P–H = [1.419] Å
Bond Angle: H–P–H = [93.7]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [0.0695×10^{-117}] $g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was estimated by DiStefano *et al.*[1]. The $\Delta_f H°(298.15\ K)$ was estimated by taking 63% of the dissociation energy of PH_3 and using it as the dissociation energy of PH_2. Willes and Winkler[2] have estimated $\Delta_f H°(PH_2, g, 298.15\ K)$ to be 30 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The vibratonal spectra of PH_2 from the flash photolysis of PH_3 has been reported by Ramsey[3] and in.[4] Similarities between the spectra of NH_2 and PH_2 were found. For NH_2 and NH_3 bond angles and bond distances were reported to be about the same. Byanalogy then the bond angles and bond distances of PH_2 and PH_3 should be nearly the same. The moments of inertia for PH_2 were therefore calculated from the molecular constants for PH_3. The principal moments of inertia are: $I_A = 0.2960 \times 10^{-39}$, $I_B = 0.3588 \times 10^{-39}$, and $I_C = 0.6548 \times 10^{-39}$ $g \cdot cm^2$.

DiStefano *et al.*[1] have assumed the ground state degeneracy to be 2 because of the unpaired electron. The vibrational frequencies reported by DiStefano *et al.* have been used. They used a simple force field and the force constants of PH_3 to obtain the vibrational frequencies.

References

[1]V. N. DiStefano, R. L. Potter and S. N. Fox, "The Thermodynamic Functions of Some Combustion Products Containing Phosphorus–I.", American Cyanamid Company.
[2]D. Willes and C. Winkler, J. Phys. Chem. 61, 902 (1957).
[3]D A. Ramsey, Nature 178, 375 (1956).
[4]N. Y. Acad. Sci. 67, 485 (1957).

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
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	.000	.000	INFINITE	−10.006	112.321	112.321	INFINITE
100	33.258	175.957	242.760	−6.680	111.760	106.006	−55.372
200	33.549	199.055	215.787	−3.347	110.136	100.633	−26.283
250	34.075	206.593	213.221	−1.657	109.338	98.348	−20.549
298.15	34.774	212.652	212.652	.000	108.499	96.306	−16.872
300	34.804	212.868	212.653	.064	108.466	96.231	−16.755
350	35.641	218.295	213.080	1.825	106.842	94.334	−14.079
400	36.535	223.112	214.038	3.629	105.873	92.614	−12.094
450	37.468	227.468	215.292	5.479	104.947	91.012	−10.564
500	38.430	231.466	216.712	7.377	104.065	89.512	−9.351
600	40.400	238.646	219.783	11.318	102.445	86.756	−7.553
700	42.343	245.020	222.941	15.456	101.012	84.257	−6.287
800	44.169	250 796	226.067	19.783	99.754	81.952	−5.351
900	45.820	256.095	229.113	24.284	98.648	79.794	−4.631
1000	47.278	261.000	232.060	28.940	97.668	77.753	−4.061
1100	48.548	265.567	234.901	33.733	96.789	75.805	−3.600
1200	49.645	269.839	237.636	38.644	32.417	75.011	−3.265
1300	50.590	273.851	240.269	43.657	32.452	78.560	−3.157
1400	51.403	277.631	242.804	48.758	32.525	82.104	−3.063
1500	52.104	281.202	245.246	53.934	32.627	85.642	−2.982
1600	52.711	284.584	247.600	59.175	32.747	89.172	−2.911
1700	53.238	287.796	249.871	64.473	32.878	92.695	−2.848
1800	53 696	290.852	252.063	69.821	33.015	96.210	−2.792
1900	54.097	293.767	254.182	75.211	33.153	99.717	−2.741
2000	54.450	296.551	256.231	80.638	33.290	103.217	−2.696
2100	54.760	299.215	258.215	86.099	33.422	106.710	−2.654
2200	55 035	301.769	260.137	91.589	33.548	110.197	−2.616
2300	55.280	304.221	262.001	97.105	33.665	113.678	−2.582
2400	55 498	306.578	263.810	102.644	33 774	117.154	−2.550
2500	55.693	308.848	265.566	108.204	33.873	120.627	−2.520
2600	55.869	311 036	267.273	113.782	33.961	124.095	−2.493
2700	56.027	313.147	268.933	119.377	34.037	127.560	−2.468
2800	56 170	315.187	270.549	124.987	34.102	131.023	−2.444
2900	56.299	317.161	272.122	130.611	34.154	134.483	−2.422
3000	56.417	319.071	273.656	136.247	34 194	137.942	−2.402
3100	56.524	320.923	275.151	141.894	34.221	141.400	−2.383
3200	56.622	322.719	276.609	147.551	34.235	144.857	−2.365
3300	56.712	324.463	278.033	153.218	34.236	148.314	−2.348
3400	56.795	326.157	279.424	158.893	34.222	151.771	−2.332
3500	56.871	327.805	280.783	164.577	34.195	155.229	−2.317
3600	56.941	329.408	282.111	170.267	34.154	158.687	−2.302
3700	57.005	330.969	283.411	175.965	34.098	162.147	−2.289
3800	57.065	332.490	284.682	181.668	34.028	165.609	−2.276
3900	57.121	333.973	285.927	187.377	33.944	169.073	−2.264
4000	57.172	335 419	287.146	193.092	33.844	172.539	−2.253
4100	57.220	336.832	288.341	198.812	33.729	176.008	−2.242
4200	57.265	338.211	289.512	204.536	33.600	179.479	−2.232
4300	57.307	339.559	290.660	210.265	33.455	182.954	−2.222
4400	57.346	340.877	291.787	215.997	33.295	186.433	−2.213
4500	57.383	342.166	292.892	221.734	33.121	189.915	−2.204
4600	57.417	343.428	293.977	227.474	32.931	193.401	−2.196
4700	57.449	344.663	295.042	233.217	32.726	196.892	−2.188
4800	57 480	345.873	296.089	238.964	32.507	200.388	−2.181
4900	57.508	347.058	297.117	244.713	32.274	203.887	−2.173
5000	57.535	348.220	298.127	250.465	32.027	207.392	−2.167
5100	57.560	349.360	299.121	256.220	31.766	210.902	−2.160
5200	57.584	350.478	300.098	261.977	31.491	214.417	−2.154
5300	57.607	351.575	301.059	267.737	31.205	217.938	−2.148
5400	57.628	352.652	302.004	273.499	30.906	221.464	−2.142
5500	57.649	353 710	302.935	279.263	30.596	224.995	−2.137
5600	57.668	354.749	303.851	285.028	30.275	228.533	−2.132
5700	57.686	355.769	304.753	290.796	29.944	232.076	−2.127
5800	57.703	356 773	305.641	296.566	29.604	235.626	−2.122
5900	57 720	357 759	306.516	302.337	29.255	239 180	−2.118
6000	57 736	358.730	307.378	308.110	28.899	242.741	−2.113

PREVIOUS March 1963 (1 atm) CURRENT. March 1963 (1 bar)

$S°(298.15\ K) = 205.757\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -17.584 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -20.502 \pm 0.8\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
2614.6(1)
1182.7(1)
2626.5(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond(ucircl Distance: S–H = 1.328 Å
Bond Angle: H–S–H = 92.2°
Product of the Moments of Inertia: $I_A I_B I_C = 0.0469 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation of H_2S(g) determined by various workers including those reviewed in the previous JANAF analysis[1] were recalculated with the results shown below. No weight was given to the work performed prior to 1934 and less weight was given to the work of Kapustinskii and Kankovskii[7] because of the difficulty of establishing the state of the products.

Source	Reaction*	$\Delta_f H°$(298.15 K), kcal·mol^{-1} [from (1)]	Recalculated
Thomsen[2]	$H_2S(g) + HI_3(aq) = 3\ HI(aq) + S(amorph)$	–	−4.4, −5.1 if S(rhombic)
Thomsen[3]	$*H_2S(g) + O_2(g) = SO_2(g) + H_2SO_4 \cdot H_2O$	–	−2.0
Pollitzer[4]	$H_2S(g) + I_2(cr) = 2\ HI(g) + S(rh)$	–	−4.7, −4.0 if S(amorph)
Lewis and Randall[5]	$3\ S(l) + 2\ H_2O(g) = SO_2(g) + 2\ H_2S(g)$	–	−3.6 ± 0.2
Zeumer and Roth[6]	$*H_2S(g) + O_2(g) = SO_2(g) + H_2SO_4 \cdot H_2O$	−4.80 ± 0.15	−4.89 ± 0.24
Kapustinskii and Kankovskii[7]	$*H_2S(g) + 3/2\ O_2(g) = SO_2(g) + H_2O(l) + S(rh)$	−4.9 ± 0.8	−4.92 ± 0.08

*Equations which are not balanced involve two reactions occurring in various proportions.

Heat Capacity and Entropy

The thermodynamic functions were taken from the JANAF table for H_2S(g) dated (December 31, 1965).[1] These in turn were taken from Gordon[8] except below 298 K were they were calculated by the rigid–rotor, harmonic–oscillator approximation. Gordon had calculated $C_p°$ from 298 K to 6000 K by a method which takes into account second–order corrections for vibrational anharmonicity, vibration–rotation interaction, and centrifugal stretching. The spectroscopic constants used were taken from Allen and Plyler.[9]

The National Bureau of Standards prepared this table[10] by critical analysis of data existing in 1972. Using $\Delta_f H°$ selected by NBS,[10] we recalculate the table in terms of current JANAF reference states for the elements.

References

[1]JANAF Thermochemical Tables, 2nd ed., NSRDS–NBS 37, (1971).
[2]J Thomsen, "Thermochemical Investigations," Vol. II, p. 60, J. A. Barth, Leipzig, (1882).
[3]J. Thomsen, "Thermochemical Investigations," Vol. IV, p. 188, J. A. Barth, Leipzig, (1882).
[4]F. Pollitzer, Z. Anorg. Chem. 64, 121 (1909).
[5]G. N. Lewis and M. Randall, J. Amer. Chem. Soc. 40, 362 (1918).
[6]H. Zeumer and W. A. Roth, Z. Elektrochem. 40, [11], 777 (1934).
[7]A. F. Kapustinskii and R. T. Kankovskii, Zhur. Fiz. Khim. 32, 2810 (1958).
[8]J. S. Gordon, Thiokol Chem. Corp., personal communication to D. R. Stull, (February 7, 1961).
[9]H. C. Allen and E. K. Plyler, J. Chem. Phys 25, 1132 (1956), 24, 35 (1956).
[10]S. Abramowitz *et al.*, U. S. Nat. Bur. Stand. Rept. 10904, 239, (July, 1972).

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	−9.962	−17.584	−17.584	INFINITE
100	33.259	168.972	235.330	−6.636	−17.947	−23.519	12.285
200	33.380	192.038	208.586	−3.310	−18.957	−28.754	7.510
298.15	34.192	205.757	205.757	0	−20.502	−33.329	5.839
300	34.208	205.969	205.758	0.063	−20.534	−33.408	5.817
400	35.581	215.992	207.115	3.551	−24.549	−37.343	4.876
500	37.192	224.102	209.726	7.188	−27.762	−40.179	4.197
600	38.936	231.037	212.713	10.994	−30.470	−42.399	3.691
700	40.740	237 174	215.777	14.978	−32.771	−44.201	3.298
800	42.518	242.731	218.804	19.142	−34.771	−45.694	2.984
900	44.212	247.838	221.750	23.479	−89.665	−45.870	2.662
1000	45.786	252.579	224.599	27.980	−90.024	−40.984	2.141
1100	47.200	257.011	227.346	32.631	−90.284	−36.066	1.713
1200	48.467	261.173	229.993	37.415	−90.465	−31.129	1.355
1300	49.593	265.098	232.544	42.320	−90.584	−26.179	1.052
1400	50.593	268.810	235.003	47.330	−90.656	−21.222	0.792
1500	51.476	272.331	237.375	52.434	−90.693	−16.261	0.566
1600	52.262	275.679	239.666	57.622	−90.705	−11.298	0.369
1700	52.961	278.869	241.879	62.883	−90.699	−6.336	0.195
1800	53.589	281.914	244.019	68.212	−90.681	−1.374	0.040
1900	54.145	284.827	246.091	73.599	−90.656	3.587	−0.099
2000	54.656	287.617	248.098	79.039	−90.627	8.547	−0.223
2100	55.107	290.295	250.044	84.528	−90.597	13.505	−0.336
2200	55.522	292.868	251.932	90.059	−90.566	18.461	−0.438
2300	55.898	295.345	253.766	95.631	−90.538	23.416	−0.532
2400	56.250	297.731	255.549	101.238	−90.512	28.370	−0.617
2500	56.568	300.034	257.282	106.879	−90.490	33.323	−0.696
2600	56.861	302.258	258.970	112.551	−90.472	38.275	−0.769
2700	57.133	304.409	260.613	118.251	−90 458	43.227	−0.836
2800	57.384	306.492	262.214	123.977	−90.450	48.178	−0.899
2900	57.618	308.510	263.776	129.727	−90.447	53.129	−0.957
3000	57.840	310.467	265.300	135.500	−90.450	58.080	−1.011
3100	58.049	312.367	266.788	141.294	−90.459	63.031	−1.062
3200	58.245	314.213	268.241	147.109	−90 473	67.982	−1 110
3300	58.430	316.008	269.662	152.943	−90.495	72.935	−1.154
3400	58.605	317.755	271.051	158.795	−90.524	77.887	−1.197
3500	58.773	319.456	272 409	164.664	−90.560	82.841	−1.236
3600	58.932	321.114	273.739	170.549	−90.604	87.796	−1.274
3700	59.086	322.731	275.042	176.450	−90.656	92.752	−1.309
3800	59.229	324.308	276.317	182.366	−90.717	97.710	−1.343
3900	59.371	325.849	277.568	188.296	−90.788	102.670	−1.375
4000	59.509	327.354	278.794	194.240	−90.868	107.631	−1.406
4100	59.639	328.825	279.996	200.197	−90.958	112.595	−1.434
4200	59.768	330.263	281.176	206.168	−91.058	117.561	−1.462
4300	59.890	331.671	282.334	212.151	−91.169	122.529	−1.488
4400	60.011	333.050	283.471	218.146	−91.290	127.500	−1.514
4500	60.128	334.399	284.588	224.153	−91.423	132.474	−1.538
4600	60.237	335 722	285.685	230.171	−91.568	137.451	−1.561
4700	60.346	337.019	286.763	236.200	−91.725	142.431	−1.583
4800	60.459	338.291	287.824	242.240	−91.893	147.416	−1.604
4900	60.563	339.538	288.866	248.292	−92.073	152.403	−1.625
5000	60.668	340.763	289.892	254.353	−92.265	157.394	−1.644
5100	60.764	341.965	290.901	260.425	−92.468	162.389	−1.663
5200	60.869	343.146	291.895	266.506	−92.682	167.388	−1.681
5300	60.965	344.306	292.873	272.598	−92.907	172.392	−1.699
5400	61.061	345.447	293.836	278.699	−93 143	177.400	−1 716
5500	61.153	346.568	294.785	284.810	−93.389	182.412	−1.732
5600	61.250	347 671	295.719	290.930	−93.644	187.429	−1.748
5700	61.342	348.756	296.640	297.060	−93.908	192.451	−1.764
5800	61.429	349.823	297.548	303.198	−94.180	197.477	−1.778
5900	61.526	350.874	298.443	309.346	−94.459	202.507	−1.793
6000	61.609	351 909	299.325	315.503	−94.745	207.543	−1.807

PREVIOUS June 1977 (1 atm) CURRENT June 1977 (1 bar)

$S°(298.15\ K) = 29.711\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-136.00 \pm 8.4]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-144.35 \pm 8.4]\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of combustion of $TiH_{1.73}$(cr), the stable species of titanium hydride, was reported to be 247.8 kcal·mol^{-1} by Sieverts and Gotta[1]). From this data the value of $\Delta_f H°(298.15\ K)$ for $TiH_{1.73}$(cr) was calculated to be 29.40 kcal·mol^{-1}. The enthalpy of dissociation of titanium hydride having compositions between the rough limits $TiH_{1.75}$ $TiH_{1.93}$ was given as 19.15 kcal·mol^{-1} of H_2 dissociated by Gibb.[2] Assuming this value is applicable to compositions between the limits $TiH_{1.73}$ TiH_2, the difference in the enthalpy of formation of titanium hydride between $TiH_{1.73}$ and TiH_2 was estimated to be 5.17 kcal·mol^{-1}. Thus the value of $\Delta_f H°(298.15\ K)$ for TiH_2(cr) was calculated.

Heat Capacity and Entropy

The low temperature $C_p°$ for $TiH_{1.97}$(cr) were measured by Stalinski and Bieganski[3] 24 363 K). This data were adopted for TiH_2(cr) due to lack of the measured $C_p°$ values. A small but well marked type anomaly with a maximal value of $C_p°$ at 288.5 K in the $C_p°$ vs T curve was observed. $S°(298.15\ K)$ was reported by Stalinski and Bieganski[3] based on $S°(extrap\ 25\ K) = 0.65\ cal·K^{-1}·mol^{-1}$.

References

[1]A. Sieverts and A. Gotta, Z. Anorg. Allg. Chem. 199, 384 (1931).
[2]T. R. P. Gibb, Jr., J. J. McSharry, and R. W. Bragdon, J. Amer. Chem. Soc. 73, 1751 (1951).
[3]B. Stalinski and Z. Bieganski, Bull. Acad. Polon. Sci., Ser. Sci. Chim. 8, No. 5, 243 (1960).

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	−4.945	−135.996	−135.996	INFINITE
100	12.678	6.745	51.513	−4.477	−139.087	−128.863	67.311
200	22.719	19.041	32.284	−2.648	−141.870	−117.550	30.701
298.15	30.087	29.711	29.711	0.	−144.348	−105.073	18.408
300	30.259	29.897	29.711	0.056	−144.392	−104.829	18.252
400	39.330	39.847	31.006	3.536	−146.431	−91.315	11.924
500	47.279	49.504	33.747	7.879	−147.752	−77.368	8.083
600	53.806	58.721	37.148	12.944	−148.441	−63.217	5.504
700	58.994	67.418	40.857	18.593	−148.618	−48.993	3.656
800	63.137	75.577	44.693	24.707	−148.381	−34 773	2.270
900	66.159	83.194	48.553	31.178	−147.877	−20.600	1.196
1000	68.534	90.294	52.376	37.918	−147.261	−6.491	0.339
1100	70.057	96.899	56.127	44.849	−146.684	7.557	−0.359
1200	71.337	103.051	59.784	51.921	−150.185	21.677	−0.944
1300	72.251	108.798	63.336	59.101	−149.106	35.955	−1.445
1400	73.046	114.182	66.777	66.367	−148.063	50.151	−1.871
1500	73.722	119.246	70.108	73.707	−147.082	64.274	−2.238
1600	74.279	124.022	73.330	81.108	−146.187	78.335	−2.557
1700	74.716	128.539	76.446	88.558	−145.402	92.343	−2.837
1800	75.034	132.819	79.460	96.047	−144.751	106.308	−3.085
1900	75.232	136.882	82.376	103.561	−144.257	120.242	−3.306
2000	75.312	140.743	85.199	111.089	−158.631	134.607	−3.516

PREVIOUS: CURRENT: June 1963

$S°(298.15\ K) = 271.022 \pm 0.25\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [8.35 \pm 16.7]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-2.09 \pm 16.7]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2192(1)	2206(2)
903(1)	941(2)
362(1)	592(2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances Si–H = 1.486 ± 0.008 Å Si–H = 2.437 Å
Bond Angles H–Si–H = 110.42° ± 0.5° H–Si–I = 108.5° ± 0.5°
Product of the Moments of Inertia: $I_A I_B I_C = 6.831704 \times 10^{-115}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H$ (298.15 K) is estimated by linear interpolation between the values[1] of SiI_4(g) and SiH_4(g). There are no experimental $\Delta_f H°$ data for SiH_3I, SiH_2I_2 and $SiHI_3$. It is difficult to justify a nonlinear interpolation scheme such as that adopted for the chlorosilanes.[1] A cubic interpolation fits $\Delta_f H°$ data for the chloromethanes and has been proposed for bromomethanes and iodomethanes.[2] Experimental $\Delta_f H°$ values do not seem to eixst for CI_4, CBr_4 and $CHBr_3$, while published values for CBr_4 and $CHBr_3$ are the subject of controversy (SiH_3Br, g).[1] Moreover, the cubic scheme proposed[2] for CH_nI_{4-n} is surprisingly different from those of the other halomethanes;[2] i.e., the first differences in $\Delta_f H°$ exhibit a minimum instead of a maximum. These uncertainties preclude use of the iodomethanes for predicting $\Delta_f H°$ of the iodosilanes. Hunt and Sirtl[3] also concluded that linear interpolation of $\Delta_f H°$ is all that is justified by available data.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Kewley *et al.*[4] for isotopic forms of the four monohalosilanes. The authors concluded that the silyl group is effectively the same in all four halides. We adopt effective (r_o) structural parameters rather than substitutional (r_s) parameters. These are in reasonable agreement with previous structural determinations.[5] The principal moments of inertia are $I_A = 0.9972 \times 10^{-39}$ and $I_B = I_C = 26.1748 \times 10^{-39}\ g \cdot cm^2$.

Vibrational frequencies are from gas-phase infrared spectra.[6,7] Assignments are consistent with liquid-phase Raman spectra[8,9] which yield slightly lower values for most of the frequencies.

We neglect excited states and assume the electronic ground state to be $^1A_1$ by analogy with CH_3I[10]. Comparison of the halosilanes[11] and halomethanes[10,11] suggests that the lowest excited state of SiH_3I is at ≥30000 cm^{-1}. Contributions from this state should be unimportant.

References

[1]JANAF Thermochemical Tables: ClH_3Si(g), BrH_3Si(g) 12-31-76; H_4Si(g), I_4Si(g) 6-30-76
[2]S. A. Kudchadker and A. P. Kudchadker, J. Phys. Chem. Ref. Data 4, 457 (1975).
[3]L. P. Hunt and E. Sirtl, J. Electrochem. Soc. 120, 806 (1973).
[4]R. Kewley, P. M. McKinney and A. G. Robiette, J. Mol. Spectrosc. 34, 390 (1970).
[5]L. E. Sutton, "Interatomic Distances," Spec. Publ. No. 11, 1958, "Interatomic Distances Supplement," Spec. Publ No. 18, The Chemical Society, London, (1965).
[6]R. N. Dixon and N. Sheppard, Trans. Faraday Soc. 53, 282 (1957); J. Chem. Phys. 23, 215 (1955).
[7]H. R. Linton and E. R. Nixon, Spectrochim. Acta 12, 41 (1958).
[8]D. F. Ball, M. J. Buttler and D. C. McKean, Spectrochim. Acta 21, 451 (1965), unpublished data from R. Taylor, Dissert., Oxford Univ., (1961).
[9]F. Feher, A. G. Wronka and B. Mostert, Monatsh. Chem. 104, 360 (1973).
[10]G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc. New York, (1966).
[11]G. C. Causley, J. B. Clark and B. R. Russell, Chem. Phys. Lett. 38, 602, (1976).

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
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−12.078	8.348	8.348	INFINITE
100	34.754	224.891	312.147	−8.726	5.410	1.463	−0.764
200	43.918	251.491	275.668	−4.835	1.615	−1.031	0.269
250	49.420	261.884	271.890	−2.501	−0.309	−1.469	0.307
298.15	54.401	271.022	271.022	0.	−2.092	−1.529	0.268
300	54.582	271.359	271.023	0.101	−2.159	−1.525	0.266
350	59.178	280.125	271.704	2.947	−3.927	−1.279	0.191
400	63.215	288.296	273.273	6.009	−13.550	−0.514	0.067
450	66.784	295.952	275.372	9.261	−15.629	1.242	−0.144
500	69.979	303.157	277.794	12.681	−37.638	5.122	−0.535
600	75.514	316.420	283.146	19.964	−39.001	13.809	−1.202
700	80.152	328.419	288.770	27.754	−39.950	22.691	−1.693
800	84.055	339.385	294.421	35.970	−40.561	31.685	−2.069
900	87.331	349.480	299.986	44.545	−40.906	40.739	−2.364
1000	90.075	358.827	305.408	53.419	−41.049	49.820	−2.602
1100	92.372	367.523	310.664	62.545	−41.046	58.908	−2.797
1200	94.299	375.646	315.745	71.881	−40.942	67.991	−2.960
1300	95.922	383.260	320.648	81.394	−40.778	77.062	−3.096
1400	97.295	390.420	325.379	91.057	−40.587	86.120	−3.213
1500	98.462	397.173	329.942	100.847	−40.398	95.163	−3.314
1600	99.460	403.561	334.346	110.744	−40.232	104.195	−3.402
1700	100.318	409.617	338.597	120.734	−90.285	113.665	−3.492
1800	101.059	415.372	342.704	130.804	−89.986	125.653	−3.646
1900	101.703	420.854	346.674	140.942	−89.711	137.625	−3.784
2000	102.265	426.085	350.514	151.141	−89.467	149.584	−3.907
2100	102.759	431.087	354.233	161.393	−89.257	161.531	−4.018
2200	103.194	435.877	357.836	171.691	−89.082	173.469	−4.119
2300	103.579	440.473	361.330	182.030	−88.941	185.400	−4.211
2400	103.922	444.889	364.720	192.406	−88.833	197.325	−4.295
2500	104.228	449.138	368.012	202.814	−88.752	209.247	−4.372
2600	104.502	453.231	371.212	213.250	−88.694	221.166	−4.443
2700	104.748	457.179	374.323	223.713	−88.656	233.082	−4.509
2800	104.970	460.993	377.351	234.199	−88.632	244.998	−4.570
2900	105.171	464.680	380.299	244.706	−88.617	256.913	−4.628
3000	105.354	468.249	383.171	255.233	−88.607	268.828	−4.681
3100	105.520	471.706	385.972	265.776	−88.600	280.742	−4.730
3200	105.672	475.059	388.704	276.336	−88.591	292.656	−4.777
3300	105.811	478.312	391.370	286.910	−88.578	304.570	−4.821
3400	105.938	481.473	393.974	297.498	−88.559	316.483	−4.862
3500	106.055	484.546	396.518	308.098	−88.533	328.396	−4.901
3600	106.163	487.535	399.005	318.709	−472.649	350.769	−5.090
3700	106.262	490.445	401.437	329.330	−472.190	373.635	−5.275
3800	106.354	493.280	403.817	339.961	−471.724	396.489	−5.450
3900	106.440	496.044	406.146	350.601	−471.249	419.331	−5.616
4000	106.519	498.740	408.427	361.248	−470.765	442.160	−5.774
4100	106.593	501.371	410.662	371.904	−470.273	464.977	−5.924
4200	106.661	503.940	412.853	382.567	−469.773	487.782	−6.066
4300	106.725	506.451	415.000	393.236	−469.265	510.575	−6.202
4400	106.785	508.905	417.107	403.912	−468.750	533.356	−6.332
4500	106.841	511.305	419.174	414.593	−468.228	556.125	−6.455
4600	106.894	513.654	421.202	425.280	−467.699	578.882	−6.573
4700	106.943	515.954	423.194	435.972	−467.164	601.628	−6.686
4800	106.990	518.206	425.150	446.669	−466.624	624.364	−6.794
4900	107.033	520.412	427.071	457.370	−466.079	647.086	−6.898
5000	107.074	522.575	428.960	468.075	−465.530	669.799	−6.997
5100	107.113	524.696	430.816	478.784	−464.976	692.500	−7.093
5200	107.149	526.776	432.642	489.498	−464.419	715.190	−7.184
5300	107.184	528.817	434.437	500.214	−463.857	737.869	−7.272
5400	107.217	530.821	436.204	510.934	−463.292	760.538	−7.357
5500	107.248	532.789	437.942	521.658	−462.722	783.196	−7.438
5600	107.277	534.721	439.653	532.384	−462.150	805.844	−7.517
5700	107.305	536.620	441.338	543.113	−461.573	828.482	−7.592
5800	107.331	538.487	442.996	553.845	−460.992	851.110	−7.665
5900	107.356	540.322	444.631	564.579	−460.407	873.727	−7.735
6000	107.380	542.126	446.240	575.316	−459.817	896.334	−7.803

PREVIOUS: December 1976 (1 atm) CURRENT December 1976 (1 bar)

$S°(298.15\ K) = 192.774 \pm 0.025\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -38.907 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -45.898 \pm 0.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies			
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
3506(1)	1022(1)	3577(2)	1691(2)

Ground State Quantum Weight: 1 σ(internal) = 2
Point Group: C_{3v} σ(external) = 3
Bond Length: N–H = 1.0124 Å
Bond Angle: 106.67°
Product of the Moments of Inertia: $I_A I_B I_C = 0.0348 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

2nd and 3rd law analyses of equilibrium data for the reaction $1/2N_2(g)+3/2H_2(g) = NH_3(g)$ cited in the previous JANAF evaluation[1] plus more recent work of Schulz and Schaefer[6] were made using the revised thermal functions for NH_3(g). All of the previously cited work in reaction calorimetry plus the early work of Berthelot[7,8] and Thomsen[9] were reevaluated. No significant differences in the 3rd law calculations of the equilibrium data or in the corrections to the flow calorimetry data of Haber and Tamaru[12] and Wittig and Schmatz[13] were found. Thus, the 0.1 kcal discrepancy between the results of the equilibrium and reaction calorimetry measurements remains unresolved. The previous JANAF selection[1] for $\Delta_f H°(298.15\ K)$ of NH_3(g) was adopted. A recent evaluation[14] which includes new indirect calorimetry (unpublished) further confirms this selection.

Source	Method	$\Delta_f H°(298.15\ K)$ $kcal \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal \cdot mol^{-1}$*	$\Delta S°$(obs.–calc. 298.15 K)* $cal \cdot K^{-1} \cdot mol^{-1}$
Larson, Dodge[2]	K_p^{o4} from K_p^o(10–1,000 atm, 600–800 K)	−10.88	−10.70 ± 0.11	+0.24 ± 0.15[a]
Haber *et al.*[3]	K_p^{o4} from K_p^o(30 atm, 800–1200 K)	−10.86	−10.88 ± 0.15	−0.02 ± 0.15[b]
Haber, Maschke[5]	K_p^o(1 atm, 900–1400 K)	−10.85	−10.62 ± 0.22	0.20 ± 0.19[c]
Schulz, Schaefer[6]	K_p^o(1 atm, 567–673 K)	−10.87	−10.78 ± 0.20	0.14 ± 0.3[d]
Berthelot[7]	Indirect, Reaction of Br_2(aq) and NH_3(aq)	−11.4		
Berthelot[8]	Indirect; Reaction of O_2(g) with NH_3(g)	−12.1		
Thomsen[9]	Indirect; Reaction of O_2(g) with NH_3(g)	−11.9		
Becker, Roth[10]	Indirect; Heat of combustion oxalates	−11.00 ± 0.15		
Haber *et al.*[11]	Flow calorimetry at 298 K	−11.10 ± 0.05		
Haber, Tamaru[12]	Flow calorimetry (739–932 K)	−10.97 ± 0.008		
Wittig, Schmatz[13]	Flow calorimetry at 832 K	−10.99 ± 0.05		

*2nd law analysis assuming $\Delta C_p°(cal \cdot K^{-1}\ mol^{-1})$ equals (a)−2.672+0.00591(T−700), (b)−1.236+0.00404(T−1000), (c) − 0.855+0.00305(T−1100), (d) 3.287+0.00651(T−600).

Heat Capacity and Entropy

The thermodynamic functions differ from those of the 1965 JANAF table[1] in being taken directly form the later and more complete work of Haar.[15] Haar treated in detail the contribution of the highly anharmonic out-of-plane vibrational mode, including its large coupling with rotation and its coupling with the other vibrational modes. Haar's values of $C_p°$ pass through a shallow maximum between 4000 and 5000 K, they were extrapolated from 5000 to 6000 K by assuming a constant value (19.300 $cal \cdot K^{-1} \cdot mol^{-1}$). A summary of Haar's estimated uncertainties and of the differences of the 1965 table from the present table (in $cal \cdot K^{-1}\ mol^{-1}$) is as follows:

	Uncertainities (Haar, 15)		1965 Table minus This Table	
T,K	$C_p°$	$S°$	$C_p°$	$S°$
1000	0.006	0.006	−0.034	−0.033
3000	0.10	0.06	+0.142	−0.122
5000	0.6	0.04	+1.775	+0.265

The National Bureau of Standards prepared this table[16] by critical analysis of data existing in 1972. Using the results of Haar[15] and $\Delta_f H°$ selected by NBS,[16] we recalculate the table in terms of R=1.987192 $cal \cdot K^{-1} \cdot mol^{-1}$ [17] and current JANAF reference states for the elements.

References

[1]JANAF Thermochemical Tables, 2nd ed., NSRDS–NBS 37, (1971).
[2]A. T. Larson and R. L. Dodge, J. Amer. Chem. Soc. 45, 2918 (1923).

Continued on page 1359

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
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−10.045	−38.907	−38.907	INFINITE
100	33.284	155.840	223.211	−6.737	−41.550	−34.034	17.777
200	33.757	178.990	195.962	−3.394	−43.703	−25.679	6.707
298.15	35.652	192.774	192.774	0.	−45.898	−16.367	2.867
300	35.701	192.995	192.775	0.066	−45.939	−16.183	2.818
400	38.716	203.663	194.209	3.781	−48.041	−5.941	0.776
500	42.048	212.659	197.021	7.819	−49.857	4.800	−0.501
600	45.293	220.615	200.302	12.188	−51.374	15.879	−1.382
700	48.354	227.829	203.727	16.872	−52.618	27.190	−2.029
800	51.235	234.476	207.160	21.853	−53.621	38.662	−2.524
900	53.948	240.669	210.543	27.113	−54.411	50.247	−2.916
1000	56.491	246.486	213.849	32.637	−55.013	61.910	−3.234
1100	58.859	251.983	217.069	38.406	−55.451	73.625	−3.496
1200	61.048	257.199	220.197	44.402	−55.746	85.373	−3.716
1300	63.057	262.166	223.236	50.609	−55.917	97.141	−3.903
1400	64.893	266.907	226.187	57.008	−55.982	108.918	−4.064
1500	66.564	271.442	229.054	63.582	−55.954	120.696	−4.203
1600	68.079	275.788	231.840	70.315	−55.847	132.469	−4.325
1700	69.452	279.957	234.549	77.193	−55.672	144.234	−4.432
1800	70.695	283.962	237.184	84.201	−55.439	155.986	−4.527
1900	71.818	287.815	239.748	91.328	−55.157	167.725	−4.611
2000	72.833	291.525	242.244	98.561	−54.833	179.447	−4.687
2100	73.751	295.101	244.677	105.891	−54.473	191.152	−4.755
2200	74.581	298.552	247.048	113.309	−54.084	202.840	−4.816
2300	75.330	301.884	249.360	120.805	−53.671	214.509	−4.872
2400	76.009	305.104	251.616	128.372	−53.238	226.160	−4.922
2500	76.626	308.220	253.818	136.005	−52.789	237.792	−4.968
2600	77.174	311.236	255.969	143.695	−52.329	249.406	−5.011
2700	77.672	314.158	258.070	151.438	−51.860	261.003	−5.049
2800	78.132	316.991	260.124	159.228	−51.386	272.581	−5.085
2900	78.529	319.740	262.132	167.062	−50.909	284.143	−5.118
3000	78.902	322.409	264.097	174.933	−50.433	295.689	−5.148
3100	79.228	325.001	266.020	182.840	−49.959	307.218	−5.177
3200	79.521	327.521	267.903	190.778	−49.491	318.733	−5.203
3300	79.785	329.972	269.747	198.744	−49.030	330.233	−5.227
3400	80.011	332.358	271.554	206.734	−48.578	341.719	−5.250
3500	80.216	334.680	273.324	214.745	−48.139	353.191	−5.271
3600	80.400	336.942	275.060	222.776	−47.713	364.652	−5.291
3700	80.550	339.147	276.763	230.824	−47.302	376.101	−5.310
3800	80.684	341.297	278.433	238.886	−46.908	387.539	−5.327
3900	80.793	343.395	280.072	246.960	−46.534	398.967	−5.344
4000	80.881	345.441	281.680	255.043	−46.180	410.385	−5.359
4100	80.956	347.439	283.260	263.136	−45.847	421.795	−5.374
4200	81.006	349.391	284.811	271.234	−45.539	433.198	−5.388
4300	81.048	351.297	286.335	279.337	−45.254	444.593	−5.401
4400	81.065	353.161	287.833	287.442	−44.996	455.981	−5.413
4500	81.073	354.983	289.305	295.550	−44.764	467.364	−5.425
4600	81.057	356.765	290.752	303.656	−44.561	478.743	−5.436
4700	81.032	358.508	292.175	311.761	−44.387	490.117	−5.447
4800	80.990	360.213	293.575	319.862	−44.242	501.488	−5.457
4900	80.931	361.882	294.952	327.958	−44.129	512.856	−5.467
5000	80.856	363.517	296.307	336.048	−44.047	524.223	−5.477
5100	80.751	365.117	297.641	344.127	−43.999	535.587	−5.486
5200	80.751	366.685	298.954	352.202	−43.979	546.951	−5.494
5300	80.751	368.223	300.246	360.277	−43.982	558.315	−5.503
5400	80.751	369.732	301.519	368.352	−44.006	569.680	−5.511
5500	80.751	371.214	302.773	376.428	−44.049	581.044	−5.518
5600	80.751	372.669	304.008	384.503	−44.112	592.410	−5.526
5700	80.751	374.098	305.225	392.578	−44.193	603.778	−5.533
5800	80.751	375.503	306.425	400.653	−44.291	615.147	−5.540
5900	80.751	376.883	307.607	408.728	−44.404	626.516	−5.547
6000	80.751	378.240	308.773	416.803	−44.531	637.889	−5.553

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

Hydronium, Ion (H_3O^+) — IDEAL GAS — M_r = 19.022671

$S°(298.15\ K)$ = [192.257] $J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = 581.99 ± 12.6 $kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 581.16 ± 12.6 $kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[3760](1)	[3870](2)
[1050](1)	[1550](2)

Ground State Quantum Weight: 1 — σ = [3]
Point Group: [C_{3v}]
Bond Distance: H–O = [0.95] Å
Bond Angle: H–O–H = [109]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [0.0240×10^{-117}] $g^3\ cm^6$

Enthalpy of Formation

The proton affinity of water has been measured by the ion impact method as −169 kcal mol^{-1} by Tal'rose and Frankevitch.[1] The selected enthalpy of formation of hydronium ion, $\Delta_f H°(H_3O^+, g, 0\ K)$ = 139.1 $kcal \cdot mol^{-1}$, was derived from the $\Delta_r H°(0\ K)$ = −169 $kcal \cdot mol^{-1}$ for $H_2O(g) + H^+(g) \rightarrow H_3O^+(g)$, using the JANAF $\Delta_f H°(H_2O, g, 0\ K)$ = −57.1 and $\Delta_f H°(H^+, g, 0\ K)$ = 365.2 $kcal \cdot mol^{-1}$.

The values of 195 and 207 $kcal \cdot mol^{-1}$ for the enthalpy of formation of $H_3O^+(g)$ have also been reported by Field and Franklin[2] and Bernecker and Long,[3] respectively. These two values were based on the electron impact studies which may involve unaccounted excitations and excess energy in the fragments. Other literature values have been reviewed by Bishop.[4]

Green and Sugden,[5] based on the studies of the positive ions in flames by mass spectrometry, prefer the value derived from the proton affinity of water obtained by Tal'rose and Frankevitch, rather than the electron impact data. From the approximate equilibrium constant calculations for the reaction $HCO^+(g) + H_2O(g) = H_3O^+(g) + CO(g)$, Clifton[6] has also found that the heat of formation of $H_3O^+(g)$ derived from the proton affinity of water, not from the electron impact data, leads to agreement with the experimental data given by Green and Sugden.

Heat Capacity and Entropy

Since the molecule $H_3O^+(g)$ has the same number of valence electrons as $NH_3(g)$, a pyramidal molecular configuration (C_{3v}) is assumed for $H_3O^+(g)$ in the tabulation. Clifton[7] has obtained a bond distance O–H of 0.95 Å from an application of covalent bond radii and the effect of electric charge, and a bond angle H–O–H of 109° by extrapolating a plot of bond length versus bond angle for $NH_3(g)$ and $PH_3(g)$ to 0.95 Å. Both values are adopted in the tabulation. The principal moments of inertia are: $I_A = I_B 0.2446 \times 10^{-39}$, $I_C = 0.4005 \times 10^{-39}$ $g \cdot cm^2$. Bishop[4] has calculated theoretically the bond distance OH of 0.95 Å and the bond angle H–O–H of 114° 26' with a planar D_{3h} molecular configuration. The vibrational frequencies were calculated by the valence force method from the estimated stretching and bending force constants of Clifton.

References

[1] V. L. Tal'rose and E. L. Frankevitch, Doklady Akad. Nauk SSSR **111**, 376 (1956), J. Amer. Chem Soc. **80**, 2344 (1958).
[2] F. M. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, (1957).
[3] R. R. Bernecker and F. A. Long, J. Phys. Chem. **65**, 1565 (1961).
[4] D. M. Bishop, J. Chem. Phys. **43**, 4453 (1965).
[5] J. A. Green and T. M. Sugden, Ninth Symposium (International) on Combustion, Academic Press, New York, (1963).
[6] D. G. Clifton, AD444078, G. M. Defense Research Laboratory, General Motors Corp., Santa Barbara, Calif., (July 1964).
[7] D. G. Clifton, J. Chem. Phys. **41**, 3656 (1964).

Hydronium, Ion (H_3O^+) — $H_3O^+(g)$

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
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0	INFINITE	−10.016	581.986		
100	33.258	155.526	222.432	−6.691			
200	33.536	178.619	195.407	−3.358			
250	34.159	186.161	192.829	−1.667			
298.15	35.146	192.257	192.257	0.	581.158	606.607	−106.275
300	35.190	192.474	192.257	0.065	581.154	606.765	−105.647
350	36.540	197.997	192.691	1.857	581.074	611.040	−91.193
400	38.081	202.975	193.670	3.722	581.045	615.324	−80.353
450	39.697	207.554	194.961	5.667	581.080	619.607	−71.922
500	41.309	211.820	196.436	7.692	581.180	623.883	−65.177
600	44.368	219.626	199.663	11.978	581.571	632.391	−55.055
700	47.158	226.678	203.026	16.556	582.194	640.815	−47.818
800	49.727	233.145	206.392	21.402	583.021	649.135	−42.384
900	52.131	239.142	209.702	26.496	584.029	657.341	−38.151
1000	54.401	244.753	212.929	31.824	585.199	665.426	−34.758
1100	56.542	250.040	216.065	37.372	586.513	673.386	−31.976
1200	58.553	255.047	219.107	43.128	587.955	681.221	−29.653
1300	60.428	259.808	222.056	49.078	589.512	688.930	−27.682
1400	62.164	264.351	224.916	55.209	591.168	696.517	−25.987
1500	63.763	268.695	227.691	61.506	592.911	703.981	−24.515
1600	65.229	272.858	230.385	67.957	594.730	711.327	−23.222
1700	66.569	276.853	233.001	74.548	596.614	718.557	−22.079
1800	67.790	280.693	235.545	81.267	598.552	725.674	−21.059
1900	68.903	284.389	238.019	88.102	600.537	732.682	−20.143
2000	69.915	287.949	240.427	95.044	602.561	739.585	−19.316
2100	70.837	291.383	242.772	102.082	604.618	746.386	−18.565
2200	71.676	294.698	245.058	109.209	606.700	753.088	−17.881
2300	72.440	297.901	247.286	116.415	608.803	759.695	−17.253
2400	73.138	300.999	249.460	123.694	610.923	766.210	−16.676
2500	73.775	303.998	251.582	131.041	613.055	772.637	−16.143
2600	74.358	306.903	253.654	138.448	615.196	778.977	−15.650
2700	74.891	309.719	255.678	145.911	617.343	785.236	−15.191
2800	75.381	312.452	257.657	153.424	619.492	791.415	−14.764
2900	75.831	315.105	259.593	160.985	621.642	797.517	−14.365
3000	76.245	317.683	261.486	168.589	623.790	803.545	−13.991
3100	76.626	320.189	263.340	176.233	625.935	809.502	−13.640
3200	76.979	322.628	265.155	183.914	628.074	815.389	−13.310
3300	77.304	325.001	266.932	191.628	630.207	821.210	−12.999
3400	77.606	327.314	268.674	199.374	632.331	826.966	−12.705
3500	77.886	329.567	270.382	207.149	634.445	832.659	−12.427
3600	78.146	331.765	272.057	214.950	636.548	838.293	−12.163
3700	78.387	333.910	273.700	222.777	638.639	843.868	−11.913
3800	78.612	336.003	275.312	230.627	640.718	849.387	−11.676
3900	78.823	338.048	276.894	238.499	642.782	854.852	−11.449
4000	79.019	340.046	278.448	246.391	644.832	860.263	−11.234
4100	79.202	342.000	279.975	254.302	646.866	865.624	−11.028
4200	79.374	343.910	281.474	262.231	648.884	870.935	−10.832
4300	79.535	345.780	282.948	270.177	650.885	876.198	−10.644
4400	79.687	347.610	284.397	278.138	652.869	881.415	−10.464
4500	79.829	349.402	285.822	286.114	654.835	886.586	−10.291
4600	79.962	351.158	287.223	294.103	656.782	891.715	−10.126
4700	80.088	352.880	288.602	302.106	658.712	896.801	−9.967
4800	80.207	354.567	289.958	310.121	660.622	901.847	−9.814
4900	80.319	356.222	291.294	318.147	662.513	906.853	−9.667
5000	80.425	357.846	292.609	326.185	664.386	911.821	−9.526
5100	80.526	359.439	293.904	334.232	666.239	916.751	−9.389
5200	80.621	361.004	295.179	342.290	668.074	921.645	−9.258
5300	80.710	362.540	296.435	350.356	669.890	926.504	−9.131
5400	80.796	364.050	297.674	358.431	671.687	931.329	−9.009
5500	80.877	365.533	298.894	366.515	673.467	936.120	−8.891
5600	80.953	366.991	300.097	374.607	675.228	940.881	−8.776
5700	81.027	368.425	301.283	382.706	676.972	945.609	−8.666
5800	81.096	369.834	302.453	390.812	678.699	950.307	−8.558
5900	81.162	371.221	303.607	398.925	680.410	954.974	−8.455
6000	81.225	372.586	304.745	407.044	682.104	959.614	−8.354

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

Hydronium, Ion (H_3O^+) — $H_3O^+(g)$

$S°(298.15\ K) = 110.544 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 315.5 \pm 5\ K$

$\Delta_f H°(0\ K) = -1265.9 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1284.4 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 13.389 \pm 0.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Recent calorimetric measurements[1,2,3] indicate the National Bureau of Standards' selected values quoted in reference[4] $\Delta_f H°(H_3PO_4, cr, 298.15\ K) = -305.7 \pm 0.3\ kcal \cdot mol^{-1}$, is probably in error. The value was taken from Holmes' work.[5] The data are summarized below, with heat values based on white phosphorus reference state.

Source	Method	n Moles of H_2O	$\Delta_f H°(H_3PO_4, aq, 298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Head[1]	a & b	40	-309.34 ± 0.38	-307.0 ± 0.4
Birley[2]	a	100	-309.8 ± 0.35	-307.18 ± 0.5
Irving[3]	a	0.6416	-305.9 ± 0.5	-307.36 ± 0.5
Holmes[5]	a & b	–	–	-307.4 ± 0.5*

a = solution calorimetry; b = combustion calorimetry
* see text

Head and Lewis[1] determined the enthalpy of combustion of phosphorus and enthalpy of hydrolysis of combustion products which led to $\Delta_f H°(H_3PO_4 \cdot 40\ H_2O, aq, 298.15\ K) = -309.34 \pm 0.38\ kcal \cdot mol^{-1}$. Birley and Skinner[2] measured the enthalpy of hydrolysis of PCl_5 and derived $\Delta_f H°(H_3PO_4 \cdot 100\ H_2O, aq, 298.15\ K) = -309.8 \pm 0.35\ kcal \cdot mol^{-1}$ based on $\Delta_f H°(PCl_5, cr, 298.15\ K) = -106.0\ kcal \cdot mol^{-1}$ obtained by direct chlorination of phosphorus.[4] Irving and McKerrell[3] measured the enthalpy of solution of P_4O_{10} from which they derived $\Delta_f H°(H_3PO_4 \cdot 0.6416\ H_2O, aq, 298.15\ K) = -305.9 \pm 0.5\ kcal \cdot mol^{-1}$. Using enthalpy of solution data for $H_3PO_4(cr) \rightarrow H_3PO_4(363\ H_2O, aq)$,[5] and enthalpy of dilution data for $H_3PO_4(363\ H_2O, aq) \rightarrow H_3PO_4(n\ H_2O, aq)$[6] we obtain enthalpy of formation of $H_3PO_4(cr)$ listed in the last column of the table. (These values are based on white phosphorus as the reference state.) Holmes[5] determined $\Delta_f H°(H_3PO_4, cr, 298.15\ K) = -305.7 \pm 0.3\ kcal \cdot mol^{-1}$ based on his enthalpy of combustion of white phosphorus and related enthalpy of solution data which were combined to form a thermal cycle. Using the white phosphorus based $\Delta_f H°(P_4O_{10}, cr, 298.15\ K) = -719.4\ kcal \cdot mol^{-1}$[7] (instead of his value $-713.2\ kcal \cdot mol^{-1}$, we have recalculated his thermal cycle and find $\Delta_f H°(H_3PO_4, cr, 298.15\ K) = -307.4 \pm 0.5\ kcal \cdot mol^{-1}$ which is in good agreement with the recent calorimetric measurements.[1,2,3]

The value, $307.0 \pm 0.5\ kcal \cdot mol^{-1}$, is tentatively selected for the enthalpy of formation of $H_3PO_4(cr)$, based on white phosphorus as reference state.

Heat Capacity and Entropy

Low temperature heat capacity from 10 to 300 K were measured by Egan and Wakefield.[8] Their smooth $C_p°$ are adopted to the tabulation. Heat capacities above 300 K are estimated graphically based on the measured $C_p°$ curve.

The entropy $S°(298.15\ K)$ is derived from heat capacity data, using $S°(10\ K) = 0.04\ cal\ K^{-1} \cdot mol^{-1}$.

Fusion Data

Egan and Wakefield[8] measured calorimetrically the heat of fusion $\Delta_{fus} H° = 3.1 \pm 0.2\ kcal \cdot mol^{-1}$, but failed to determine the exact melting point due to continuous fusion between 301 to 319 K in their measurements. They suggested the melting point 315.5 K which was found by Ross and Jones.[9]

Holmes[5] derived the enthalpy of fusion $\Delta_{fus} H°(298.15\ K) = 3.2 \pm 0.5\ kcal \cdot mol^{-1}$ from his enthalpy of solution data for crystalline and liquid H_3PO_4 in water and in aq. $HClO_4$ solution, which corresponds to $\Delta_{fus} H° = 3.36\ kcal \cdot mol^{-1}$. We adopt an intermediate value of $\Delta_{fus} H° = 3.2 \pm 0.2\ kcal \cdot mol^{-1}$.

References

[1]A. J. Head and G. B. Lewis, J. Chem. Thermodyn. 2, 701 (1970).
[2]G. I. Birley and H. A. Skinner, Trans. Faraday Soc. 64, 3232 (1968).
[3]R. J. Irving and H. McKerrell, Trans. Faraday Soc. 63, 2582 (1967).
[4]U. S. Nat. Bur. Stand. Tech. Note 270-3, 1968; personal communication D. D. Wagman, (October 1971).
[5]W. S. Holmes, Trans. Faraday Soc. 58, 1916 (1962).
[6]E. P. Egan and B. B. Luff, J. Phys. Chem. 65, 523 (1961).
[7]JANAF Thermochemical Table: P_4O_{10}(cr), 12-31-65.
[8]E. P. Egan, Jr., and Z. T. Wakefield, J. Phys. Chem. 61, 1500 (1957).
[9]W. H. Ross and R. M. Jones, J. Amer. Chem. Soc 47, 2165 (1925).

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	−16.980	−1265.927	−1265.927	INFINITE
100	42.844	34.528	183.578	−14.905	−1275.048	−1226.961	640.899
200	75.856	74.598	119.270	−8.935	−1281.203	−1176.480	307.265
298.15	106.064	110.544	110.544	0.	−1284.375	−1124.314	196.975
300	106.608	111.202	110.546	0.197	−1284.411	−1123.321	195.588
315.500	111.303	116.688	110.713	1.885	--- CRYSTAL <--> LIQUID ---		
400	136.900	146.019	115.089	12.372	−1285.789	−1069.271	139.633
500	167.193	179.822	124.668	27.577	−1283.719	−1015.323	106.070
600	197.485	212.982	136.631	45.811	−1278.830	−962.056	83.754
700	227.777	245.700	149.880	67.074	−1271.116	−909.831	67.892
800	258.069	278.092	163.885	91.366	−1260.559	−858.906	56.081
900	288.361	310.238	178.363	118.688	−1247.143	−809.475	46.981
1000	318.653	342.187	193.149	149.038	−1230.854	−761.692	39.787

PREVIOUS: June 1962 CURRENT: December 1971

$S°(298.15\ K) = [150.775]\ J\ K^{-1}\cdot mol^{-1}$
$T_{fus} = 315.5\ K$

$\Delta_f H°(298\ 15\ K) = [-1271\ 663]\ kJ\ mol^{-1}$
$\Delta_{fus}H° = 13.389 \pm 0.8\ kJ\cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ (H_3PO_4, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(315.5\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Heat capacities of the liquid are estimated by comparison with those of H_2SO_4(cr. l)[1] and H_3PO_4(cr) $S°(298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.[2]

Decomposition Data

The phosphoric acid tends to be dehydrated to pyro– and meta–phosphoric acids when it is heated.

References

[1]W. F. Giauque, E. W Hornung, J. E. Kunzler and T. R Rubin, J Amer. Chem. Soc 82, 62 (1960).
[2]JANAF Thermochemical Tables H_3PO_4(cr), 12–30–71.

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⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	145 047	150 775	150 775	0.	−1271.663	−1123.597	196.849
300	145 603	151.673	150 777	0.269	−1271.627	−1122.678	195.476
315.500	150.273	159.125	151.005	2.562	--- CRYSTAL <--> LIQUID ---		
400	175 728	197.687	156.848	16.335	−1269.114	−1073.263	140.154
500	205.853	240.135	169.306	35.414	−1263.169	−1024.930	107.074
600	235.978	280.330	184.486	57.506	−1254.423	−978.057	85 147
700	266.102	318 968	200.954	82.610	−1242.867	−932.871	69.612
800	296.227	356.468	218.059	110.726	−1228.486	−889.534	58.081
900	326.352	393.097	235.480	141.855	−1211.263	−848.169	49.226
1000	356.477	429.041	253.044	175 997	−1191.183	−808.875	42.251

PREVIOUS June 1962 CURRENT December 1971

0 to 315.5 K crystal
above 315.5 K liquid

Refer to the individual tables for details.

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

	J·K⁻¹mol⁻¹			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	−16.980	−1265.927	−1265.927	INFINITE
100	42.844	34.528	183.578	−14.905	−1275.048	−1226.961	640.899
200	75.856	74.598	119.270	−8.935	−1281.203	−1176.480	307.265
298.15	106.064	110.544	110.544	0.	−1284.375	−1124.314	196.975
300	106.608	111.202	110.546	0.197	−1284 411	−1123.321	195.588
315.500	111.303	116.688	110.713	1.885	____ CRYSTAL <--> LIQUID ____		
315.500	150.273	159.125	110.713	15.274	TRANSITION		
400	175.728	197.687	125.068	29.048	−1269 114	−1073.263	140.154
500	205.853	240.135	143.882	48.127	−1263.169	−1024.930	107.074
600	235.978	280.330	163.299	70.218	−1254.423	−978.057	85.147
700	266.102	318.968	182.794	95.322	−1242.867	−932.871	69.612
800	296.227	356.468	202.169	123.439	−1228.486	−889.534	58 081
900	326.352	393.097	221.356	154.568	−1211.263	−848.169	49.226
1000	356.477	429.041	240.332	188.709	−1191.183	−808.875	42.251

PREVIOUS: CURRENT: December 1971

$S°(298.15\ K) = 210.243\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 7.2 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 5.4 \pm 1.7\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2322.9(1)	2327.7(2)
992 (1)	1122.4(2)

Ground State Quantum Weight: 1 $\sigma = 3$
Point Group: C_{3v}
Bond Distance: P–H = 1.42 Å
Bond Angle: H–P–H = 93° 50'
Product of the Moments of Inertia: $I_A I_B I_C = 0.2826 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation was derived by Gunn and Green.[1] In order to obtain the $\Delta_f H°(298.15\ K)$ they measured the enthalpy of explosive decomposition of phosphine gas. There is a good deal of uncertainty about the enthalpy of formation of PH_3(g), for instance:

$\Delta_f H°(298.15\ K)$	Source
+3.6 $kcal \cdot mol^{-1}$	The enthalpy of reaction between gaseous PH_3 and saturated bromine water[2]
+6.3 $kcal \cdot mol^{-1}$	The enthalpy of combustion of PH_3(g) in O_2(g) to form H_3PO_4[3].
−2.34 $kcal \cdot mol^{-1}$	Equilibrium data of.[4] Their data showed a wide variation in $\Delta_f H°$, as much as 11 $kcal \cdot mol^{-1}$.
+1.6 $kcal \cdot mol^{-1}$	U.S. Nat. Bur. Stand.[5]

The enthalpy of formation have been reviewed by Cottrell[6] and by Bichowsky and Rossini.[7]

The enthalpy of formation selected was, +1.3 ± 0.4 $kcal \cdot mol^{-1}$, as reported by Gunn and Green.[1] The selected enthalpy of formation was based on white (α) phosphorus.

Heat Capacity and Entropy

The fundamental wave number and degeneracy assignments are from the infrared spectral data by McConaghie and Nielsen.[8] The molecular constants are those obtained from infrared data by Nielsen.[9] Nielsen[9] has reported the molecular constants after calculating the Coriolis coupling effect between the wave numbers 2 and 4, or (992 cm^{-1}) and (1122.4 cm^{-1}).

The principal moments of inertia are: $I_A = I_B = 0.6264 \times 10^{-39}\ g \cdot cm^2$ and $I_C = 0.7201 \times 10^{-39}\ g \cdot cm^2$.

References

[1]S. R. Gunn and L. G. Green, J. Phys. Chem. 65, 779 (1961).
[2]M. J. Ogier, Ann. Chim. Phys. 20, 5 (1880).
[3]M. P. Lemoult, Compt. Rend. 145, 374 (1907).
[4]W. N. Ipatiew, and A. W. Frost, Ber. dtsch. Chem. Ges. 63B, 1104 (1930).
[5]U.S. Nat. Bur. Stand. Report No. 7437, pp. 80–91, (1962).
[6]T. L. Cottrell, "The Strength of Chemical Bonds," Butterworth's Scientific Publications, London, (1958).
[7]F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York (1936).
[8]V. N. McConaghie and H. H. Nielsen, J. Chem. Phys. 21, 1836, (1953).
[9]H. H. Nielsen, J. Chem. Phys. 20, 759 (1952).

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

	J·K⁻¹mol⁻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	.000	.000	INFINITE	−10.136	7.166	7.166	INFINITE
100	33.259	173.027	241.134	−6.811	7.185	6.760	−3.531
200	33.933	196.180	213.516	−3.467	6.303	6.780	−1.771
298.15	37.102	210.243	210.243	.000	5.439	7.191	−1.260
300	37.180	210.473	210.244	.069	5.422	7.202	−1.254
350	39.422	216.370	210.704	1.983	4.266	7.605	−1.135
400	41.782	221.787	211.755	4.013	3.834	8.112	−1.059
450	44.151	226.845	213.154	6.161	3.515	8.668	−1.006
500	46.478	231.618	214.764	8.427	3.310	9.252	−.967
600	50.905	240.489	218.323	13.299	3.235	10.455	−.910
700	54.935	248.644	222.080	18.595	3.570	11.637	−.868
800	58.511	256.218	225.879	24.271	4.263	12.746	−.832
900	61.623	263.294	229.648	30.282	5.258	13.750	−.798
1000	64.300	269.929	233.348	36.581	6.498	14.629	−.764
1100	66.585	276.167	236.960	43.128	7.932	15.374	−.730
1200	68.532	282.047	240.474	49.887	−54.053	17.060	−.743
1300	70.191	287.599	243.888	56.825	−51.575	22.886	−.920
1400	71.608	292.854	247.199	63.917	−49.013	28.518	−1.064
1500	72.822	297.837	250.411	71.140	−46.390	33.965	−1.183
1600	73.867	302.571	253.524	78.476	−43.723	39.235	−1.281
1700	74.770	307.077	256.543	85.909	−41.025	44.337	−1.362
1800	75.554	311.374	259.470	93.426	−38.306	49.280	−1.430
1900	76.238	315.477	262.311	101.016	−35.576	54.071	−1.487
2000	76.837	319.404	265.068	108.671	−32.839	58.719	−1.534
2100	77.365	323.165	267.746	116.381	−30.101	63.230	−1.573
2200	77.831	326.775	270.347	124.142	−27.366	67.610	−1.605
2300	78.244	330.244	272.877	131.946	−24.637	71.866	−1.632
2400	78.612	333.582	275.337	139.789	−21.916	76.003	−1.654
2500	78.942	336.798	277.732	147.667	−19.206	80.028	−1.672
2600	79.237	339.900	280.063	155.576	−16.507	83.943	−1.686
2700	79.504	342.896	282.335	163.514	−13.822	87.756	−1.698
2800	79.744	345.792	284.550	171.476	−11.150	91.469	−1.706
2900	79.962	348.594	286.711	179.462	−8.494	95.087	−1.713
3000	80.160	351.308	288.819	187.468	−5.854	98.614	−1.717
3100	80.340	353.939	290.877	195.493	−3.230	102.053	−1.720
3200	80.505	356.493	292.888	203.535	−.624	105.407	−1.721
3300	80.655	358.972	294.853	211.593	1.965	108.681	−1.720
3400	80.794	361.382	296.775	219.666	4.535	111.876	−1.719
3500	80.921	363.726	298.654	227.752	7.087	114.996	−1.716
3600	81.039	366.007	300.494	235.850	9.619	118.043	−1.713
3700	81.147	368.229	302.294	243.959	12.132	121.020	−1.709
3800	81.247	370.395	304.058	252.079	14.624	123.930	−1.704
3900	81.340	372.506	305.786	260.208	17.097	126.774	−1.698
4000	81.427	374.567	307.480	268.347	19.548	129.555	−1.692
4100	81.507	376.578	309.141	276.494	21.979	132.275	−1.685
4200	81.582	378.544	310.770	284.648	24.389	134.936	−1.678
4300	81.652	380.464	312.369	292.810	26.777	137.540	−1.671
4400	81.718	382.342	313.938	300.978	29.144	140.088	−1.663
4500	81.779	384.179	315.478	309.153	31.490	142.583	−1.655
4600	81.836	385.977	316.991	317.334	33.814	145.026	−1.647
4700	81.890	387.738	318.478	325.520	36.118	147.419	−1.638
4800	81.941	389.462	319.939	333.712	38.400	149.763	−1.630
4900	81.988	391.152	321.375	341.908	40.663	152.060	−1.621
5000	82.033	392.809	322.787	350.110	42.905	154.311	−1.612
5100	82.076	394.434	324.176	358.315	45.128	156.516	−1.603
5200	82.116	396.028	325.543	366.525	47.333	158.679	−1.594
5300	82.153	397.593	326.887	374.738	49.519	160.799	−1.585
5400	82.189	399.129	328.211	382.955	51.689	162.879	−1.576
5500	82.223	400.637	329.514	391.176	53.842	164.917	−1.566
5600	82.255	402.119	330.798	399.400	55.980	166.918	−1.557
5700	82.286	403.575	332.062	407.627	58.104	168.880	−1.548
5800	82.315	405.006	333.307	415.857	60.215	170.806	−1.538
5900	82.342	406.414	334.534	424.090	62.314	172.694	−1.529
6000	82.368	407 798	335.744	432.325	64.403	174.547	−1.520

PREVIOUS· June 1962 (1 atm) CURRENT. June 1962 (1 bar)

Ammonium Iodide (NH_4I) CRYSTAL

M_r = 144.94296 Ammonium Iodide (NH_4I) $H_4I_1N_1$(cr)

$S°(298.15\ K) = 112.968 \pm 6.3\ kJ \cdot mol^{-1}$
$T_{trs} = 260\ K$
$T_{fus} = 824\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -202.087\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 2.929\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [20.920]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The $\Delta_f H$, T_{trs} and T_{fus} was taken from U. S. Nat. Bur. Stand.[1] Sublimation data from Luft;[3] $\Delta_{sub} H°(798\ K) = 40.28\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Data extrapolated from Simon *et al.*[4] $S°(298\ 15\ K)$ was taken from Kelley.[2]

References

[1]U. S. Nat. Bur. Stand. Circ. 500, (1952).
[2]K. K. Kelley, U. S. Bur. Mines Bull. 584, (1960).
[3]N. W. Luft, Ind. Chemist, **31**, 502 (1955).
[4]Simon, Simson, and Ruhemann, Z. Phys. Chemie, **129**, 339 (1927).

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0							
100							
200							
298.15	81.755	112.968	112.968	0.	−202.087	−111.966	19.616
300	81 881	113.474	112.970	0.151	−202.120	−111.407	19.398
400	88.998	138.004	116.266	8.695	−211.666	−80.646	10.531
500	96.148	158.632	122.727	17.953	−233.822	−45.736	4 778
600	103.261	176.789	130.252	27.922	−233.079	−8.177	0.712
700	110.458	193.247	138.093	38.608	−231.674	29.204	−2.179
800	117.696	208.468	145.949	50.015	−229.616	66.340	−4.332
900	124.976	222.753	153.697	62.150	−226.914	103.179	−5.988
1000	132.089	236.288	161.285	75.003	−223.590	139.683	−7.296
1100	139.327	249.217	168.695	88.574	−219.652	175.825	−8.349
1200	146.440	261.656	175.927	102.875	−215.099	211.581	−9.210
1300	152.030	273.609	182.984	117.812	−210.029	246.935	−9.922
1400	156.098	285.034	189.869	133.231	−204.598	281.884	−10.517
1500	158.643	295.899	196.579	148.980	−198.962	316.437	−11.019
1600	159.666	306.178	203.110	164.909	−193.275	350.611	−11.446
1700	159.166	315.851	209.461	180.863	−187.688	384.432	−11.812
1800	157 144	324.898	215.626	196.691	−182.352	417.931	−12.128
1900	153.599	333.307	221 601	212.241	−177.418	451.143	−12.403
2000	148.532	341.063	227.383	227.360	−173.034	484 109	−12.644

PREVIOUS. CURRENT March 1962

Hydrazine (N_2H_4) LIQUID M_r = 32.04516 Hydrazine (N_2H_4) H_4N_2(l)

$S°$(298 15 K) = 121.544 ± 0.4 J·K^{-1}·mol^{-1}
T_{fus} = 274.69 K

$\Delta_f H°$(298.15 K) = 50.626 ± 0.4 kJ·mol^{-1}
$\Delta_{fus}H°$ = 12.657 kJ·mol^{-1}

Enthalpy of Formation

Hughes *et al.*[1] measured the enthalpies of combustion of hydrazine and hydrazine monohydrate The data, adjusted as suggested by Cole and Gilbert[2] are summarized below Enthalpies of solution determined by Bushnell *et al* interrelate N_2H_4(l). An intermediate value was selected from the resulting enthalpies of formation.

Source	Reaction	$\Delta_r H°$(298.15 K) kcal·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Hughes[1]	$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)$	−148 68 ± 0.06	12.05
Hughes[1]	$N_2H_4{\cdot}H_2O(l) + O_2(g) \rightarrow N_2(g) + 3H_2O(l)$	−147.00 ± 0 06	–
Bushnell[3]	$N_2H_4(l) + H_2O(l) \rightarrow N_2H_4{\cdot}H_2O(l)$	−1 80	12.17*

*From combination of second and third reactions.

Heat Capacity and Entropy

Heat capacities (12–340 K) of hydrazine crystal and liquid were determined by Scott *et al.*[4] Values beyond the experimental range for the liquid were extrapolated linearly The entropy was obtained from the enthalpy of melting and the smoothed heat capacities of the crystal using $S°(12)$ = 0.023 cal·K^{-1}·mol^{-1}.

Fusion Data

Taken from Scott *et al.*[4]

Vaporization Data

The normal boiling point and enthalpy of vaporization are those calculated for the ideal gas from these tables The boiling point found for the real gas (387.3 K) by Hieber and Woerner is in good agreement. The selected enthalpy of vaporization, $\Delta H°$(298.15 K) = 10.69 kcal mol^{-1}, is based on the vapor pressure data of Scott *et al.*,[4] series III. Vapor pressure measurements of Hieber and Woerner[5] are in satisfactory agreement as shown below.

Source	T/K	$\Delta_{vap}H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1} mol^{-1}
Scott, *et al.*[4]	273–343	10.683 ± 0.003	10.696	0.05 ± 0.01
Chang, Gockcen[6]	276–325	10.40 ± 0.03	10.68	0.91 ± 0.09
Hieber, Woerner[5]	293–387	10.82 ± 0.03	10.71	−0.33 ± 0.07

The 2nd law 3rd law consistency of Scott *et al.* reflects the use of these data in selection of the gas phase functions (refer to H_4N_2 gas).

References

[1]A. M. Hughes, R J. Corruccini and E. C. Gilbert, J. Amer. Chem Soc 61, 2639 (1939).
[2]L. G Cole and E. C. Gilbert, J. Amer. Chem. Soc. 73, 5423 (1951).
[3]V. C. Bushnell, A. M. Hughes and E. C. Gilbert, J. Amer. Chem. Soc. 59, 2142 (1937).
[4]D. W Scott, G. D. Oliver, M E. Gross, W. N. Hubbard and H. M. Huffman, J. Amer Chem. Soc. 71, 2293 (1949).
[5]W. Hieber and A. Woerner, Z. Elektrochem. 40, 252 (1934).
[6]E. T. Chang and N. A. Gokcen, AD 458288, Defense Documentation Center, (January 1964).

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							
100	87.236	21.037	205.395	−18 436	48.895	82.918	−43 312
200	93.094	83.302	130.399	−9.419	49.613	116 715	−30.483
298 15	98.840	121.544	121.544	0	50 626	149 440	−26.181
300	98.952	122.156	121.546	0 183	50.649	150.054	−26.127
400	107.361	151.693	125.516	10 471	52.208	182 975	−23.894
500	116.566	176.639	133.305	21 667	54.619	215.406	−22.503
600	125.771	198.705	142.398	33.784	57.895	247.270	−21.527
700	134 976	218 784	151.896	46.822	62.013	278.518	−20.783
800	144.181	237.409	161.435	60.779	66.957	309.120	−20.183

PREVIOUS. CURRENT December 1965

$S°(298.15\ K) = 238.719 \pm 1.7\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 109.43\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 95.35 \pm 0.8\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
3350(1)	875(1)	3280(1)
3261(1)	780(1)	1275(1)
1312(1)	377(1)	[933](1)
1098(1)	3330(1)	966(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_2
Bond Distances: N–H = 1.022 Å N–N = 1.449 Å
Bond Angles: H–N–H = 109.47° H–N–N = 112.0°
Torsional angle between two NH_2 groups ≥ 90° from eclipsed position.
Product of the Moments of Inertia: $I_A I_B I_C = 7.3095 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

This was obtained from the enthalpy of formation of the liquid and the selected enthalpy of vaporization, $\Delta_f H°(298.15\ K) = 10\ 69$ kcal mol^{-1}, derived from the vapor pressure data (Series III) of Scott *et al.*[1] Other vapor pressure data from Hieber and Woerner[2] and Chang and Gokcen[3] are in satisfactory agreement (refer to the N_2H_4 liquid table).

Heat Capacity and Entropy

Functions were calculated from the constants given above using the rigid rotator harmonic oscillator method. The entropy ws increased by R ln 2 because two rotameric forms are implied by use of the torsional frequency. Small but arbitrary adjustments were made in the assignment of the bending mode frequencies in order to reproduce the vapor pressure data of Scott *et al.*[1] as closely as possible. Calculated values of $S°(298.15\ K) = 57.03$ and $S°(340\ K) = 58.70\ cal \cdot K^{-1} \cdot mol^{-1}$ may be compared with 56.99 and 58.69, respectively, derived from the data of Scott *et al.* Internal rotation calculations would require a complex potential function in order to fit the data. The barrier to inversion (990 cm^{-1} ~2.8 $kcal \cdot mol^{-1}$) is slightly less than the barrier to internal rotation at the trans position (1110 cm^{-1} ~3.2 $kcal \cdot mol^{-1}$) according to analyses of the microwave data by Kasuya[4] and Kasuya and Kojima.[5]

From matrix isolation and gas phase infrared studies, Catalano *et al.*[6] have suggested possible uncertainties in the assignment of the bending mode frequencies in the region from 1630 to 740 cm^{-1}. The question hinges on the uncertain existence of a gas phase fundamental at about 1600 cm^{-1} as observed by Giguere and Liu.[7] No corresponding matrix band was found and the gas phase band appeared to be due to absorption on the cell windows. A vapor phase Raman frequency at 1564 cm^{-1} was observed, however, by Kotov and Tatevskii.[8] Catalano *et al.* suggest one assignment based on the uncertain fundamental and a tentative alternative assignment excluding it The two assignments give entropies that are 0.26 $cal \cdot K^{-1} \cdot mol^{-1}$ lower and 0.12 higher than the 3rd law value The lower calculated entropy is probably more reasonable, but the higher value could be more easily modified to agree with the 3rd law value. Thus the alternative assignment was adopted with ν_{11} arbitrarily increased from ~810 to 933 cm^{-1}.

The structural constants are based primarily on the electron diffraction study of Morino *et al* [9] Related analyses of the infrared fine structure of the torsional frequency (377 cm^{-1}), Yamaguchi *et al.*[10] and of the microwave spectra, Kasuya and Kojima[5] are in close agreement. The microwave data give an H–N–H angle of 106° and a torsional angle of 90°2'. Principal moments of inertia of the adopted structure are: $I_A = 0.5741 \times 10^{-39}$, $I_B = 3.5633 \times 10^{-39}$, and $I_C = 3.5734 \times 10^{-39}\ g \cdot cm^2$.

References

[1]D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, J. Amer Chem. Soc. 71, 2293 (1949).
[2]W. Hieber and A. Woerner, Z. Elektrochem. 40, 252 (1934).
[3]E. T. Chang and N. A. Gokcen, AD–458288, Defense Documentation Center, (January 1964).
[4]T. Kasuya, Sci Papers Inst. Phys. Chem. Res. (Tokyo) 56, No. 1, 1–39 (1962).
[5]T. Kasuya and T. Kojima, J. Phys. Soc. Japan 18, 364–8 (1963).
[6]E. Catalano, R. H. Sanborn and J. W. Frazer, J. Chem. Phys. 38, 2265 (1963).
[7]P A Giguere and I. D. Liu, J. Chem. Phys. 20, 136 (1952).
[8]Yu. I. Kotov and V. M. Tatevskii, Opt. i Spektroskopiya 15, 65 (1963).
[9]Y Morino, T. Iijima and Y. Murata, Bull. Chem. Soc. Japan 33, 46 (1960).
[10]A. Yamaguchi, I. Ichishima, T. Shimanouchi and S. Mizushima, Spectrochim Acta 16, 1471 (1960).

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

	J·K⁻¹mol⁻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	−11.528	109.430	109.430	INFINITE
100	34.368	195.185	277.002	−8.182	103.876	120.484	−62.934
200	40 658	220.673	243.020	−4.469	99.290	138.917	−36.281
250	45.534	230.252	239.526	−2.318	97.193	149 070	−31.146
298.15	50.813	238.719	238.719	0.	95.353	159.232	−27.897
300	51.019	239.034	238.720	0.094	95.287	159.628	−27.794
350	56.531	247.315	239.362	2.784	93.621	170.487	−25.444
400	61.702	255.207	240.853	5.742	92.205	181.567	−23.710
450	66.379	262.749	242.870	8.946	91.023	192.811	−22.381
500	70.544	269.963	245.221	12.371	90.050	204.175	−21.330
600	77.562	283.469	250.487	19.789	88.626	227.144	−19.775
700	83.302	295.869	256.096	27.841	87.760	250.305	−18.678
800	88.202	307.320	261.793	36.422	87.326	273.560	−17.862
900	92.511	317.962	267.449	45.462	87.240	296.848	−17.229
1000	96.356	327.912	273.004	54.908	87.439	320.130	−16.722
1100	99.803	337.260	278.424	64.720	87.875	343.379	−16.306
1200	102.891	346.079	283.698	74.857	88.507	366.581	−15.957
1300	105.653	354.426	288.821	85.287	89.302	389.722	−15.659
1400	108.119	362.348	293.792	95.978	90.231	412.797	−15.402
1500	110.318	369.884	298.616	106.902	91.270	435.802	−15.176
1600	112.279	377.067	303.296	118.034	92.401	458.734	−14 976
1700	114.026	383.928	307.839	129.350	93.606	481.594	−14 798
1800	115.586	390 490	312.250	140.833	94.871	504.380	−14.637
1900	116.980	396.778	316.534	152 462	96.185	527 095	−14.491
2000	118.227	402.810	320.698	164.224	97.538	549 740	−14.358
2100	119.346	408.606	324.747	176.103	98.922	572.316	−14.236
2200	120.352	414.182	328.687	188.089	100.330	594 826	−14.123
2300	121.257	419.552	332.521	200 170	101.756	617.271	−14 019
2400	122.075	424.730	336.256	212.338	103 195	639.654	−13 922
2500	122.815	429.729	339.896	224.583	104.644	661.977	−13.831
2600	123.486	434.559	343.444	236.898	106.097	684.241	−13.747
2700	124 096	439.231	346.906	249.278	107.553	706 450	−13.667
2800	124.652	443.754	350.284	261 716	109.007	728.604	−13.592
2900	125.159	448 137	353.583	274.207	110.459	750.707	−13.522
3000	125.624	452.388	356.806	286 746	111.904	772.760	−13.455
3100	126.050	456.515	359 956	299.330	113.342	794.765	−13.392
3200	126.441	460.523	363.037	311.955	114.770	816.723	−13.332
3300	126.802	464 419	366.050	324.617	116.187	838.638	−13.275
3400	127.134	468.210	368.999	337.314	117.591	860.509	−13.220
3500	127.441	471.899	371.887	350.043	118.980	882.339	−13.168
3600	127.726	475.493	374.715	362.802	120.354	904.130	−13.119
3700	127.989	478.997	377.487	375.588	121.711	925.883	−13.071
3800	128.234	482.413	380.203	388.399	123.050	947.599	−13.026
3900	128.462	485 747	382.867	401.234	124.370	969.281	−12.982
4000	128.675	489.002	385.480	414.091	125.669	990.928	−12.940
4100	128.873	492.182	388.043	426.968	126.948	1012.544	−12.900
4200	129.058	495.290	390.560	439.865	128.205	1034.129	−12.861
4300	129.232	498.329	393.031	452.780	129.440	1055.684	−12.824
4400	129.394	501.302	395.458	465.711	130.652	1077.210	−12.788
4500	129.546	504.211	397.843	478.658	131.841	1098 709	−12.753
4600	129.690	507.060	400.186	491.620	133.007	1120.182	−12.720
4700	129.824	509.851	402.490	504.596	134.149	1141.630	−12.688
4800	129.951	512.585	404.755	517.585	135.268	1163 055	−12.657
4900	130.071	515.266	406.983	530.586	136.364	1184.455	−12.626
5000	130.183	517.895	409.175	543.599	137.436	1205.835	−12.597
5100	130.290	520.474	411.332	556.622	138.487	1227 191	−12.569
5200	130.391	523.005	413.456	569.656	139.515	1248.529	−12.542
5300	130.486	525.489	415.546	582.700	140.522	1269.846	−12.515
5400	130.576	527.929	417.605	595.753	141.509	1291.145	−12.489
5500	130.662	530.326	419.632	608.815	142.477	1312.425	−12.464
5600	130.743	532.681	421 630	621.886	143.426	1333.689	−12.440
5700	130.820	534.996	423.599	634.964	144.359	1354.935	−12.417
5800	130.894	537.272	425.539	648.050	145.275	1376.166	−12.394
5900	130.964	539.510	427.452	661.142	146.177	1397.379	−12.371
6000	131.030	541.712	429.338	674.242	147.065	1418.579	−12.350

PREVIOUS December 1965 (1 atm) CURRENT December 1965 (1 bar)

$S°(298.15\ K) = 211.510 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 281.63 \pm 0.05\ K$

$\Delta_f H°(0\ K) = -1126.433 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1127.621 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 19.464 \pm 0.042\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the monohydrate of sulfuric acid is derived from the enthalpy of solution data of Giauque *et al*.[1] We calculate $\Delta_f H°(298.15\ K)$ using $\Delta_r H°(298.15\ K) = -6.645\ kcal \cdot mol^{-1}$ for the solution process $H_2SO_4(l) + H_2O(l) = H_2SO_4\ H_2O(l)$ and auxiliary data for H_2SO_4[2] and H_2O.[3]

Heat Capacity and Entropy

The heat capacity has been measured experimentally[4] in the range 15–300 K and has been re-analyzed and summarized by Giauque *et al*.[1] Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda[5] based on experimental data (273–573 K). These temperature-dependent values are corrected to current atomic weights, converted from IPTS–48 to IPTS–68, and adjusted graphically in the region 290–390 K so as to provide smoothly varying heat capacity values. In the region above 390 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data); this linear dependence is used to obtain heat capacity data by extrapolation to 1000 K.

The entropy of 298 15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and $S°(15\ K) = 0.190\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

The melting point and enthalpy of melting have been measured calorimetrically by Rubin and Giauque.[4] The values used by Giauque *et al*.[1] in their re-evaluation and correlation of aqueous sulfuric acid properties were slightly different from those reported by Rubin and Giauque[4] the changes were 0.01 K in the melting point and 6 cal $K^{-1} \cdot mol^{-1}$ in the enthalpy of melting. In addition, the value for T_{fus} is corrected from IPTS–48 to IPTS–68.

References

[1]W. F. Giauque, E. W. Hornung, J. E. Kinzler, and T. R. Rubin, J. Amer. Chem. Soc. 82, 62 (1960).
[2]JANAF Thermochemical Tables. $H_2SO_4(l)$, 9–30–77.
[3]ICSU CODATA Task Group, J. Chem. Thermodyn. 4, 331 (1972).
[4]T. R. Rubin and W. F. Giauque, J. Amer. Chem. Soc. 74, 800 (1952).
[5]Om. P. Kharbanda, Ind. Chemist 31, 538 (1955).

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻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	−41.866	−1126.433	−1126.433	INFINITE
100	54.220	43.699	436.019	−39.232	−1137.748	−1077.394	562.773
200	92.914	93.433	252.619	−31.837	−1144.661	−1014.113	264.859
281.626	123.973	130.247	211.864	−22.985	CRYSTAL <--> LIQUID TRANSITION		
281.626	211 961	199.360	211.864	−3.521			
298 15	214.264	211.510	211.510	0.	−1127.621	−950.290	166.487
300	214.523	212.836	211.514	0.397	−1127.510	−949.190	165.269
400	228.538	276.470	220.096	22.550	−1123.193	−890.620	116.303
500	243.601	329.085	236.772	46.157	−1117.007	−833.180	87.042
600	258.663	374.830	256.047	71.270	−1109.236	−777.118	67.654
700	273.726	415.834	275.992	97.889	−1099.975	−722.477	53.912
800	288.788	453.369	295.850	126.015	−1089.308	−669.261	43 698
900	303.850	488.253	315.312	155.647	−1130.396	−616.382	35.774
1000	318.913	521.046	334.261	186.785	−1115.776	−560.042	29.254

PREVIOUS: CURRENT September 1977

$S°(298.15\ K) = 204.653\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 43.92 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 34.31 \pm 2.1\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
2185.7 (1)
972.1 (2)
2189.08(3)
913.28 (3)

Ground State Quantum Weight: [1] $\sigma = 12$
Point Group: T_d
Bond Distance: Si–H = 1.4806 ± 0.001 Å
Bond Angle H–Si–H = 109.47122°
Product of the Moments of Inertia: $I_A I_B I_C = 0.9367 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted $\Delta_f H°(SiH_4, g, 298.15\ K) = 8.2 \pm 0.5\ kcal \cdot mol^{-1}$ is derived from the enthalpy of decomposition measurements by Gunn and Green.[1] We have taken the average of the three measurements, $\Delta E = -7.83\ kcal \cdot mol^{-1}$, to obtain $\Delta H = -7.24\ kcal \cdot mol^{-1}$ for the decomposition. Some question exists about the final state of the silicon, we choose to consider it as amorphous and apply a correction of 1 $kcal \cdot mol^{-1}$ to convert to the crystalline state[2] (the authors chose to neglect this correction) The results of Gunn and Green[1] are in good agreement with the value of $\Delta_f H°(SiH_4, g, 298.15\ K) = 7.8 \pm 3.5\ kcal \cdot mol^{-1}$ determined by Brimm and Humphreys[3] from high temperature (680°C) enthalpy of decomposition measurements. We question the earlier negative values for the enthalpy of formation of $SiH_4(g)$[4-6] which range from − 8.7 to −14.8 $kcal \cdot mol^{-1}$ and the later result of Feher, *et al.*[7], −11.3 $kcal \cdot mol^{-1}$, because of suspected uncertainty in the final states and/or corrections for the final states.

Heat Capacity and Entropy

The four fundamental vibrational frequencies and the Si–H bond distance are the result of gas–phase infrared and Raman spectral studies by Kattenberg and Oskam.[8] They are in excellent agreement with values selected from earlier work as given in the compilations of Janz and Mikawa[9] and Shimanouchi.[10] The heat capacity and entropy calculations are based on a tetrahedral structure. The $S°(298.15\ K) = 48.89 \pm 0.01\ cal \cdot K^{-1} \cdot mol^{-1}$ is in good agreement with another evaluation.[2]

The principal moments of inertia are $I_A = I_B = I_C = 0.9784 \times 10^{-39}\ g \cdot cm^2$.

References

[1] S. R. Gunn and L. H. Green, J. Phys. Chem. 65, 779 (1961).
[2] U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[3] E. O. Brimm and H. M. Humphreys, J. Phys. Chem. 61, 829 (1957).
[4] H. Von Wartenberg, Z. anorg. allgem. Chem. 79, 71 (1913).
[5] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold, New York, (1936).
[6] U. S. Nat. Bur. Stand. Circ. 500, (1952).
[7] F. Feher, G. Jansen, and H. Rohmer, Z. anorg. allg. Chem. 329, 31 (1964).
[8] H. W. Kattenberg and A. Oskam, J. Mol. Spectrosc. 49, 52 (1974).
[9] G. J Janz and Y. Mikawa, Bull. Chem. Soc. Japan 34, 1495 (1961).
[10] T. Shimanouchi, NSRDS–NBS 39, (1972).

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻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	−10.538	43.923	43.923	INFINITE
100	33.269	165.774	237.899	−7.212	40.984	44.936	−23.472
200	35.520	189.213	208.310	−3.819	37.811	50.067	−13.076
250	38.857	197.475	205.335	−1.965	36.023	53.336	−11.144
298.15	42.827	204.653	204.653	0.	34.309	56.827	−9.956
300	42.985	204.918	204.654	0.079	34.244	56.967	−9.919
350	47.291	211.868	205.193	2.336	32.568	60.888	−9.087
400	51 473	218.458	206.442	4.806	31.038	65.040	−8.493
450	55.431	224 752	208.130	7.480	29.667	69.374	−8.053
500	59.148	230.786	210.096	10.345	28.454	73.853	−7.715
600	65.877	242.179	214.505	16.604	26.478	83.128	−7.237
700	71.715	252.784	219.225	23.491	25.042	92.690	−6.917
800	76.713	262.695	224.046	30.919	24.056	102.426	−6.688
900	80.948	271.982	228.862	38.808	23.433	112.263	−6.516
1000	84.513	280.701	233.614	47.086	23.093	122.153	−6.381
1100	87.507	288.900	238.271	55.692	22.965	132.067	−6.271
1200	90.024	296.625	242.815	64.572	22.989	141.986	−6.180
1300	92.146	303.917	247.238	73.683	23.119	151.897	−6.103
1400	93.942	310.814	251.535	82.990	23.315	161.796	−6.037
1500	95.470	317.348	255.706	92.463	23.548	171.680	−5.978
1600	96.777	323.553	259.755	102.077	23.793	181.547	−5.927
1700	97.901	329.454	263.682	111.812	−26.143	191.846	−5.895
1800	98.872	335.078	267.494	121.652	−25.691	204 656	−5.939
1900	99.716	340 447	271 193	131.582	−25.226	217.440	−5 978
2000	100 454	345.581	274.785	141.592	−24 756	230.200	−6.012
2100	101.101	350 498	278 274	151.670	−24.288	242.937	−6.043
2200	101.671	355.215	281.665	161.809	−23.826	255.651	−6.070
2300	102.176	359.746	284.962	172.002	−23.375	268.344	−6.094
2400	102.625	364.104	288.170	182.243	−22.936	281.018	−6.116
2500	103.026	368.302	291.291	192.526	−22.513	293.674	−6.136
2600	103.385	372.350	294.332	202 847	−22.108	306.313	−6.154
2700	103.708	376.258	297.294	213.202	−21.720	318.937	−6.170
2800	104.000	380.035	300.182	223.587	−21.353	331.548	−6.185
2900	104.264	383 689	302.999	234.001	−21.007	344.145	−6.199
3000	104.503	387.228	305.748	244.439	−20.683	356.731	−6.211
3100	104 721	390.658	308.432	254.900	−20.381	369.306	−6.223
3200	104.920	393.986	311 054	265.383	−20.102	381.872	−6.233
3300	105.102	397.217	313.616	275.884	−19.847	394 430	−6.243
3400	105.269	400.357	316.121	286.402	−19.617	406.980	−6.252
3500	105.422	403 411	318.572	296.937	−19.412	419.524	−6.261
3600	105.564	406.383	320 970	307.486	−403.383	442.523	−6.421
3700	105.694	409.277	323.318	318.049	−402.815	466.013	−6.579
3800	105.815	412.097	325.617	328.625	−402.275	489.488	−6.728
3900	105.927	414.847	327 870	339.212	−401.764	512.949	−6.870
4000	106.031	417.530	330.078	349.810	−401.280	536.396	−7.005
4100	106.127	420.150	332.243	360.418	−400.824	559.833	−7.132
4200	106.217	422 708	334.367	371.035	−400.397	583.258	−7.254
4300	106.302	425.209	336.450	381.661	−399.997	606.674	−7.370
4400	106.380	427.653	338.495	392.295	−399.625	630.080	−7.480
4500	106.454	430.045	340.503	402.937	−399.280	653.478	−7.585
4600	106.522	432.385	342.475	413.586	−398.963	676.869	−7.686
4700	106.587	434 677	344.413	424.242	−398.672	700.254	−7.782
4800	106.648	436.922	346.317	434.903	−398.408	723.633	−7.875
4900	106.705	439.121	348.188	445.571	−398.170	747.006	−7.963
5000	106.759	441.277	350.029	456.244	−397.957	770.375	−8.048
5100	106.810	443.392	351.839	466.923	−397.768	793.739	−8.130
5200	106.858	445.467	353.619	477.606	−397.603	817.101	−8.208
5300	106.903	447.502	355.372	488.294	−397.460	840.459	−8.283
5400	106.946	449.501	357.096	498.986	−397.339	863.815	−8.356
5500	106.986	451.464	358.794	509.683	−397.239	887.168	−8.426
5600	107.025	453.392	360.466	520.384	−397.158	910.521	−8.493
5700	107.061	455.287	362.113	531.088	−397.095	933.872	−8.558
5800	107.096	457.149	363.736	541.796	−397.050	957.222	−8.621
5900	107 129	458 980	365.335	552.507	−397.019	980.570	−8.681
6000	107.160	460 781	366.910	563.222	−397.003	1003.919	−8.740

PREVIOUS: June 1976 (1 atm) CURRENT June 1976 (1 bar)

$S°(298.15\ K) = 276.363 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 233.70 \pm 0.05\ K$

$\Delta_f H°(0\ K) = -1422.274 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1427.100 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 18.242 \pm 0.17\ kJ\ mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the dihydrate of sulfuric acid is derived from the enthalpy of solution data of Giauque *et al*.[1] We calculate $\Delta_f H°(298.15\ K)$ for the dihydrate using $\Delta_r H°(298.15\ K) = -9.907\ kcal\ mol^{-1}$ for the solution process $H_2SO_4(l) + 2\ H_2O(l) = H_2SO_4\ 2H_2O(l)$ and auxiliary data for H_2SO_4[2] and H_2O.[3]

Heat Capacity and Entropy

The heat capacity has been measured experimentally[4] in the range 15–300 K and has been summarized by Giauque *et al*.[1] Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda[5] based on experimental data (273–573 K). These temperature–dependent values are corrected to current atomic weights, converted from IPTS–48 to IPTS–68, and adjusted graphically in the region 290–310 K so as to provide smoothly varying heat capacity values. In the region above 310 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data); this linear dependence is used to obtain heat capacity data by extrapolation to 1000 K.

The entropy at 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and $S°(15\ K) = 0.363\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

The melting point and enthalpy of melting have been measured calorimetrically by Rubin and Giauque.[4] The melting point adopted in this table differs from that reported by Rubin and Giauque[4] by 0.02 K. This is due to the re analysis of the data by Giauque *et al*.[1] and a conversion of the resulting T_{fus} value from IPTS–48 to IPTS–68.

References

[1]W. F. Giauque, E. W. Horning, J. E. Kunzler, and T. R. Rubin, J. Amer. Chem. Soc. 82, 62 (1960).
[2]JANAF Thermochemical Tables: $H_2SO_4(l)$, 9–30–77.
[3]ICSU CODATA Task Group, J. Chem. Thermodyn. 4, 331 (1972).
[4]T. R. Rubin and W. F. Giauque, J. Amer. Chem. Soc. 74, 800 (1952).
[5]Om. P. Kharbanda, Ind. Chemist 31, 538 (1955).

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻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	−51.038	−1422.274	−1422.274	INFINITE
100	66.143	56.938	534.191	−47.725	−1437.362	−1359.594	710.179
200	113.413	117.668	311.144	−38.695	−1446.789	−1277.857	333.742
233.700	128.910	136.505	284.609	−34.612	CRYSTAL <--> LIQUID TRANSITION		
233.700	248.446	214.564	284.609	−16.370			
298.15	261.453	276.363	276.363	0.	−1427.100	−1199.560	210.158
300	262.055	277.982	276.368	0.484	−1426.981	−1198.148	208.616
400	294.604	357.829	287.036	28.317	−1421.376	−1122.886	146.634
500	327.155	427.065	308.254	59.405	−1412.161	−1049.281	109.618
600	359.707	489.589	333.342	93.748	−1399.668	−977.824	85.127
700	392.258	547.483	359.845	131.347	−1383.994	−908.713	67.809
800	424.810	601.987	386.737	172.200	−1365.221	−842.061	54.981
900	457.361	653.901	413.559	216.309	−1396.509	−776.864	45.088
1000	489.913	703.774	440.102	263.672	−1370.399	−709.387	37.055

PREVIOUS. CURRENT September 1977

$S°(298.15\ K) = 345.373 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 236.78 \pm 0.05\ K$

$\Delta_f H°(0\ K) = -1716.249 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1720.402 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 23.999 \pm 0.21\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the trihydrate of sulfuric acid is derived from the enthalpy of solution data of Giauque *et al.*[1] We calculate $\Delta_f H°(298.15\ K)$ for the trihydrate using $\Delta_r H°(298.15\ K) = -11.693\ kcal \cdot mol^{-1}$ for the solution process $H_2SO_4(l) + 3\ H_2O(l) = H_2SO_4 \cdot 3H_2O(l)$ and auxiliary data for H_2SO_4[2] and H_2O.[3]

Heat Capacity and Entropy

The heat capacity has been measured experimentally[4,5] in the range 15–300 K and has been summarized by Giauque *et al.*[1] Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda[6] based on experimental data (273–573 K). These temperature–dependent values are corrected to current atomic weights and converted from IPTS 48 to IPTS 68. Of the five hydrates of sulfuric acid (mono–, di–, tri–, tetra–, and hemihexa–) only in the case of the trihydrate is there a serious discrepancy in the heat capacity values (at ambient temperature) between Giauque *et al.*[6] and Kharbanda.[7] Assuming that the data of Giauque *et al.*[1] are correct and that the linear dependence suggested by the nomograph of Kharbanda[6] is correct, we have shifted the data derived from the nomograph by 0.78 $cal \cdot K^{-1} \cdot mol^{-1}$ to obtain a smooth junction of the low temperature and high temperature heat capacity data. The data are extrapolated linearly to 1000 K.

The entropy at 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and $S°(15\ K) = 0.398\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

The melting point and enthalpy of melting have been measured calorimetrically by Hornung and Giauque.[5] The melting point adopted in this table differs from that reported by Hornung and Giauque[5] by 0 02 K. This is due to the re analysis of the data by Giauque *et al.*[1] and a conversion of the resulting T_{fus} value from IPTS–48 to IPTS–68.

References

[1]W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, J. Amer. Chem. Soc. 82, 62 (1960).
[2]JANAF Thermochemical Tables: $H_2SO_4(l)$, 9–30–77.
[3]ICSU CODATA Task Group, J. Chem. Thermodyn. 4, 331 (1972).
[4]J. E. Kunzler and W. F. Giauque, J. Amer. Chem. Soc. 74, 797 (1952).
[5]E. W. Hornung and W. F. Giauque, J. Amer. Chem. Soc. 77, 2983 (1955).
[6]Om. P. Kharbanda, Ind. Chemist 31, 538 (1955).

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
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	−64.520	−1716.249	−1716.249	INFINITE
100	82.711	68.614	673.238	−60.462	−1735.045	−1639.705	856.494
200	145.372	145.125	390.475	−49.070	−1746.258	−1539.587	402.099
236.780	169 .746	171.661	354.430	−43.276	___ CRYSTAL <--> LIQUID ___		
236.780	310 .829	273.019	354.430	−19.276	TRANSITION		
298 15	319.090	345.373	345.373	0.	−1720.402	−1443 893	252.964
300	319.320	347.348	345.379	0.591	−1720.258	−1442.178	251.106
400	347 779	442.970	358.216	33.902	−1713.566	−1350.672	176.380
500	376.606	523.671	383.430	70.121	−1703.672	−1261.054	131.741
600	405 434	594.883	412.845	109.223	−1690.930	−1173.680	102.178
700	434.262	659.546	443.535	151.208	−1675.434	−1088.659	81.237
800	463.089	719 415	474.321	196.075	−1657.267	−1006.044	65.688
900	491.917	775.624	504 706	243.825	−1689.591	−924.781	53.673
1000	520.745	828 944	534 486	294 459	−1664.947	−841.100	43.935

PREVIOUS: CURRENT September 1977

$S°(298.15\ K) = 414.529 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 244.90 \pm 0.05\ K$

$\Delta_f H°(0\ K) = -2007.121 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -2011.199 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 30.644 \pm 0.25\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the tetrahydrate of sulfuric acid is derived from the enthalpy of solution data of Giauque *et al.*[1] We calculate $\Delta_f H°(298\ 15\ K)$ for the tetrahydrate using $\Delta_r H°(298.15\ K) = -12.880\ kcal \cdot mol^{-1}$ for the solution process $H_2SO_4(l) + 4H_2O(l) = H_2SO_4\ 4H_2O(l)$ and auxiliary data for H_2SO_4[2] and H_2O.[3]

Heat Capacity and Entropy

The heat capacity has been measured experimentally[4] in the range 15–300 K and has been summarized by Giauque *et al.*[1] Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda[5] based on experimental data (273–573 K). These temperature–dependent values are corrected to current atomic weights, converted from IPTS–48 to IPTS–68, and adjusted graphically in the region 300–330 K so as to provide smoothly varying heat capacity values. In the region above 350 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data), this linear dependence is used to obtain heat capacity data by extrapolation to 1000 K.

The entropy at 298 15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and $S°(15\ K) = 0.687\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

The melting point and enthalpy of melting have been measured calorimetrically by Hornung and Giauque.[4] The values adopted in this table for T_{fus} and $\Delta_{fus} H°$ differ from those reported by Hornung and Giauque[4] by 0.02 K and 2 $cal \cdot mol^{-1}$, respectively. This is due to the re–analysis of this data by Giauque *et al.*[1] and a conversion of the resulting T_{fus} value from IPTS–48 to IPTS–68.

References

[1]W F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, J. Amer Chem. Soc. 82, 62 (1960).
[2]JANAF Thermochemical Tables: $H_2SO_4(l)$, 9–30–77.
[3]ICSU–CODATA Task Group, J. Chem. Thermodyn. 4, 331 (1972).
[4]E. W. Hornung and W. F. Giauque, J. Amer. Chem. Soc. 77, 2983 (1955).
[5]Om. P. Kharbanda, Ind. Chemist 31, 538 (1955).

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

	J·K⁻¹mol⁻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	−77 404	−2007.121	−2007.121	INFINITE
100	98.358	88.906	811.941	−72.303	−2029.325	−1917.277	1001.483
200	166.040	177.734	473.245	−59.102	−2042.879	−1799.498	469.981
244.900	197.695	214.443	422.447	−50.940	CRYSTAL <--> LIQUID		
244.900	376.392	339.570	422.447	−20.297	TRANSITION		
298 15	386.382	414.529	414.529	0.	−2011.199	−1685.764	295.339
300	386.771	416.920	414.536	0.715	−2011.010	−1683.745	293.166
400	410.342	531.343	429.977	40.546	−2002.190	−1576.184	205.829
500	434.525	625.506	459.927	82 789	−1990.724	−1470.981	153.672
600	458 709	706.867	494.448	127.451	−1976.931	−1368.290	119.120
700	482.892	779.393	530.063	174.531	−1960.905	−1268.086	94.626
800	507.076	845.453	565.416	224.030	−1942.729	−1170.328	76.415
900	531.259	906.574	599.967	275.946	−1975.563	−1073.893	62.327
1000	555.443	963 799	633.518	330.281	−1951 951	−974.955	50.926

PREVIOUS: CURRENT September 1977

$S°(298.15\ K) = 587.819 \pm 0.63\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 220.30 \pm 0.05\ K$

$\Delta_f H°(0\ K) = -2727.58 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -2733.26 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 34.116 \pm 0.25\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the hemihexahydrate of sulfuric acid is derived from the enthalpy of solution data of Giauque *et al.*[1] We calculate $\Delta_f H°(298.15\ K)$ for the hemihexahydrate using $\Delta_r H°(298.15\ K) = -14\,669\ kcal \cdot mol^{-1}$ for the solution process $H_2SO_4(l) + 6.5H_2O(l) = H_2SO_4 \cdot 6.5H_2O(l)$ and auxiliary data for H_2SO_4[2] and H_2O.[3]

Heat Capacity and Entropy

The heat capacity has been measured experimentally[4] in the range 15–300 K and has been summarized by Giauque *et al.*[1] Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda[5] based on experimental data (273–573 K). These temperature dependent values are corrected to current atomic weights, converted from IPTS 48 to IPTS 68, and adjusted graphically in the region 300–320 K so as to provide smoothly varying heat capacity values. In the region above 350 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data); this linear dependence is used to obtain heat capacity data by extrapolation to 1000 K.

The entropy at 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and $S°(15\ K) = 0\,721\ cal \cdot K^{-1}\ mol^{-1}$.

Fusion Data

The melting point and enthalpy of melting have been measured calorimetrically by Hornung *et al.* These data were reevaluated by Giauque *et al.*[1] We have adopted the revised values and have also corrected T_{fus} to the IPTS–68.

References

[1]W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, J. Amer. Chem. Soc. **82**, 62 (1960).
[2]JANAF Thermochemical Tables. $H_2SO_4(l)$, 9–30–77.
[3]ICSU CODATA Task Group, J. Chem. Thermodyn. **4**, 331 (1972).
[4]E. W. Hornung, T. E. Brackett, and W. F. Giauque, J Amer. Chem. Soc. **78**, 5747 (1956).
[5]Om. P. Kharbanda, Ind. Chemist **31**, 538 (1955).

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

	J·K⁻¹mol⁻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	−107.821	−2727.578	−2727.578	INFINITE
100	136.554	115.659	1125.761	−101.010	−2759.200	−2602.982	1359.658
200	239 876	242.053	652.984	−82.186	−2777.504	−2438.910	636.978
220.300	261.042	266.230	616.234	−77.106	CRYSTAL <--> LIQUID		
220.300	521.282	421.093	616.234	−42.990	TRANSITION		
298.15	570.279	587.819	587 819	0.	−2733.261	−2285.631	400.433
300	570.615	591.348	587 830	1.055	−2732.933	−2282.855	397.480
400	583.250	757.240	610.364	58.750	−2717.228	−2135.430	278.859
500	595.843	888.741	653.331	117.705	−2700.180	−1991.951	208.098
600	608.437	998.489	701.957	177.919	−2682.107	−1851.986	161.230
700	621.031	1093.226	751.237	239.393	−2663.102	−1715.123	127.984
800	633.625	1176.975	799.319	302 125	−2643.243	−1581.044	103.232
900	646.219	1252.333	845.536	366.118	−2675.696	−1448.421	84 064
1000	658.813	1321.071	889.701	431.369	−2653.004	−1313.267	68.598

PREVIOUS. CURRENT: September 1977

Continued from page 1269

[5]E. E. Ketchen and W E. Wallace, J. Amer Chem. Soc. 76, 4736 (1954).
[6]U S Nat. Bur Stand. Tech Note 270-3, (1968).
[7]F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, (1936).
[8]D R. Stull, D L. Hildenbrand, F. L. Oetting and G. C. Sinke, J. Chem. Eng Data 15, 52 (1970).
[9]W. D. Powers and G C. Blalock, Oak Ridge Natl. Lab., ONRL 1653, (January 1954).
[10]P. S. Seward and K. E. Martin, J. Amer. Chem. Soc 71, 3564 (1949).
[11]K K. Kelley, U S. Bur. Mines Bull. 393, (1936).
[12]N. A Reshetnikov and E. V. Baranskaya, Izv Vyssh. Ucheb Zaved., Khim. Khim. Tekhnol 10, 496 (1967); CA 67 94551.
[13]M. Maurice, Rev. Chim. Miner. 5, 89 (1968); CA 69 99905.

Continued from page 1272

References

[1]R. F. Porter and R. C. Schoonmaker, J Chem. Phys. 28, 168 (1958).
[2]R F Porter and R. C. Schoonmaker, J. Phys Chem. 62, 234 (1958).
[3]R. F. Porter and R. C. Schoonmaker, J. Phys. Chem. 62, 486 (1958).
[4]R. C. Schoonmaker and R. F. Porter, J Chem. Phys. 31, 830 (1959).
[5]A. V. Gusarov and L. N. Gorokhov, Russ. J. Phys. Chem. 42, 449 (1968).
[6]JANAF Thermochemical Tables: KOH(g), $K_2(OH)_2$(g), and KOH(l), 12-31-70.
[7]H. von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 162 (1921).
[8]J. Dubois and J. Millet, Compt. Rend. 269, 1336 (1969).
[9]H. Smith and T. M. Sugden, Proc Roy. Soc. A 219, 304 (1953).
[10]D. E. Jensen and P. J. Padley, Trans. Faraday Soc. 62, 2132 (1966).
[11]D. H. Cotton and D. R. Jenkins, Trans. Faraday Soc. 65, 1537 (1969).
[12]L. N. Gorokhov, A. V. Gusarov and I. G. Panchenkov, Russ. J Phys Chem. 44, 150 (1970).
[13]R. L. Kuczkowski, D. R. Lide, Jr., and L. C. Krisher, J. Chem. Phys. 44, 3131 (1966).
[14]a) D. R. Lide, Jr., and R. L. Kuczkowski, J. Chem. Phys. 46, 4768 (1967); b) C. Matsumura and D R. Lide, Jr., J. Chem. Phys. 50, 71 (1969).
[15]a) N. Acquista, S. Abramowitz and D. R. Lide, J. Chem Phys. 49, 780 (1968), b) N Acquista and S Abramowtiz, J. Chem. Phys. 51, 2911 (1969).
[16]L. H. Spinar and J. L. Margrave, Spectrochimia Acta 12, 244 (1958).
[17]D. E. Jensen, J. Phys. Chem. 74, 207 (1970).

Continued from page 1274

[9]I.B Fieldhouse, J.C. Hedge and J.I. Lang, Armour Research Foundation, PB 151583, (November 1958).
[10]C.E. Messer, E.B. Damon, P.C. Maybury, J. Mellor and R A Seales, J. Phys Chem. 62, 220 (1958).
[11]C.E. Messer and J. Mellor, J. Phys. Chem. 64, 503 (1960).
[12]C. E. Messer, Tufts University, Mass., NYO 8027, (May 5, 1960).
[13]C.E. Messer, J. Mellor, J. A. Krol and I. S Levy, J. Chem. Eng. Data 6, 328 (1961).
[14]J.W. Vogt, Thompson Ramo Wooldridge Inc., Cleveland, Ohio, NASA N63 22167, (June 1962).

Continued from page 1281

References

[1]H. Smith and T. M. Sugden, Proc. Roy. Soc. A219, 204 (1953).
[2]C. G. James and T. M. Sugden, Proc. Roy. Soc. A227, 312 (1955).
[3]D. E. Jensen and P. J. Padley, Trans. Faraday Soc. 62, 2132 (1966).
[4]D. H. Cotton and D R. Jenkins, Trans. Faraday Soc. 65, 1537 (1969).
[5]M. J. McEwan and L. F. Phillips, Combustion and Flame 9, 420 (1965).
[6]R. C. Schoonmaker and R. F Porter, J. Phys. Chem. 64, 457 (1960).
[7]J. Berkowitz, D J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).
[8]P. J Th. Zeegers and C. Th. J. Alkemade, Combustion and Flame 9, 247 (1965).

[9]M. J. McEwan and L. F Phillips, Combustion and Flame 11, 63 (1967).
[10]JANAF Thermochemical Tables NaOH(g), KOH(g), 12-31-70; CsOH(g), 6-30-71.
[11]S M Freund, P. D Godfrey and W Klemperer, Twenty-Fifth Symposium on Molecular Structure and Spectroscoy, The Ohio State University, Columbus, Ohio, (September 1970).
[12]N. Acquista and S Abramowitz, J Chem. Phys 51, 2911 (1969).

Continued from page 1296

[6]JANAF DATA, See recent review of the fluorides by J Chao, Thermochimica Acta 1, 71 (1970).
[7]H. von Wartenberg and P Albrecht, Z. Elektrochem. 27, 162 (1921).
[8]A. Buchler and J. B. Berkowitz Mattuck in "Advances in High Temperature Chemistry," Volume I, Ed. by L. Eyring, Academic Press, New York, (1967).
[9]N Acquista and S. Abramowitz, J. Chem. Phys 51, 2911 (1969).
[10]L. H. Spinar and J. L Margrave, Spectrochimia Acta 12, 244 (1958).

Continued from page 1301

References

[1]D H. Cotton and D R Jenkins, Trans Faraday Soc 64, 2988 (1968).
[2]V G. Ryabova and L. V. Gurvich, Teplofiz. Vys Temp. 3, 318 (1965).
[3]T. M. Sugden and K Schofield, Trans. Faraday Soc. 62, 566 (1966).
[4]L. V. Gurvich, V. G Ryabova, A N Khitrov, and E. M. Starovoitov, Teplofiz. Vys Temp. 9, 250 (1971).
[5]P J Kalff and C. Th J Alkemade, J Chem. Phys. 59, 2572 (1973).
[6]V. G Ryabova, A. N Khitrov and L. V Gurvich, Teplofiz. Vys. Temp. 10, 744 (1972).
[7]JANAF Thermochemical Tables: Sr(g), 12-31-70; H_2O(g), 3-31-61; H(g), 6-30-74; SrCl(g), SrF(g), 12-31-72; $Sr(OH)_2$, BaOH, $Ba(OH)_2$,12-31-75
[8]R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
[9]J. Berkowitz, D J Meschi, and W. A Chupka, J Chem. Phys. 33, 533 (1960).
[10]F E. Stafford and J Berkowitz, J Chem Phys. 40, 2963 (1964).
[11]D. D Jackson, Lawrence Livermore Laboratory, Univ of Calif., UCRL-51137, (December 8, 1971).
[12]A. D. Walsh, J Chem. Soc 1953, 2288 (1953).
[13]N Acquista, S Abramowitz and D R Lide, J. Chem. Phys. 49, 780 (1968).
[14]R. L. Kuczkowski and D. R Lide, J Chem. Phys. 44, 3131 (1966).
[15]N Acquista and S. Abramowitz, U. S Nat Bur. Stand Report 9905, (1968).
[16]C. G. James and T M. Sugden, Nature 175, 333 (1955).
[17]A. Lagerqvist and L. Huldt, Naturwissenschaften 42, 365 (1955).
[18]M. Charton and A. G. Gaydon, Proc Phys Soc (London) 69A, 520 (1952).
[19]V F Zhitkevich, A I. Lyutyi, N. A Nesterko, V. S Rossikhin, and I. L. Tsikora, Optika i Spektroskopiya 14, 35 (1963).
[20]J. Van der Hurk, Tj Hollander and C. Th. J. Alkemade, J. Quant. Spectrosc. Radiat. Transfer 13, 273 (1973).

Continued from page 1303

[7]M. E. Schwartz and L. J Schaad, J. Chem. Phys. 47, 5325 (1967).
[8]A J. Duben and J. P. Lowe, J Chem. Phys. 55, 4270 (1971).
[9]S. N. Foner and R. L. Hudson, J. Chem. Phys 36, 2681 (1962).
[10]K. McCulloh, to be published, refer to reference (1).
[11]T. T. Paukert and H. S. Johnston, J Chem. Phys 56, 2824 (1972).
[12]D. W. Smith and L. Andrews, J. Chem. Phys. 60, 81 (1974).
[13]D. E Milligan and M. E. Jacox, J. Chem. Phys 38, 2677 (1963).
[14]M. E Jacox and D. E. Milligan, J. Mol. Spectrosc. 42, 495 (1972).
[15]Y Beers and C. J. Howard, J. Chem. Phys 64, 1541 (1976).
[16]S. Saito, J. Mol. Spectrosc. 65, 229 (1977).
[17]C. E. Barnes, J. M. Brown, A. Carrington, J. Pinkstone, and T J. Sears, J. Mol. Spectrosc. 72, 86 (1978).
[18]P. A. Freedman and W. J. Jones, J. Chem. Soc., Faraday II 72, 2071 (1976).

Continued from page 1306

[5]V. H. Dibeler and S. K. Liston, J. Chem. Phys. 49, 482 (1968).
[6]V. H. Dibeler and H. M. Rosenstock, J. Chem. Phys. 39, 3106 (1963).
[7]H. Neuert and H. Clasen, Z. Naturforschung 79, 410 (1952).
[8]ISCU CODATA Task Group on Key Values for Thermodynamics Final Set of Key Values for Thermodynamics–Part I, (November 1971).
[9]S. Abramowitz *et al.*, U S. Nat. Bur Stand., Report 10904, 239, (1972).
[10]CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, (December 1973).
[11]IUPAC Commission on Atomic Weights, Pure Appl. Chem. 47, 75 (1976).
[12]B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, Oxford, (1970).
[13]L. Haar, A. S. Friedman, and C N. Beckett, U. S Nat. Bur Stand. Monograph 20, (1961).

Continued from page 1311

[7]G. Hunter and H O. Pritchard, J. Chem. Phys. 46, 2153 (1967).
[8]B. Jeziorski and W. Kolos, Chem. Phys. Lett. 3, 677 (1969).
[9]P. R. Bunker, J. Mol. Spectrosc. 46, 504 (1973).
[10]E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data 2, 663 (1973).
[11]R. W. Patch and B. J. McBride, NASA TN D-4523 (avail. NTIS), 73 pp (1968); J. Chem. Phys. 49, 961 (1968).
[12]V. S. Iorish and V. S. Yungman, Russ. J. Phys. Chem. 50, 1168 (1976).
[13]C. L. Beckel, B D. Hansen III, and J. M. Peek, J. Chem. Phys. 53, 3681 (1970).
[14]G. Herzberg, "The Spectra and Structure of Simple Free Radicals," Cornell University Press, Ithaca, (1971), pp. 59–60.
[15]T. Murai, J. Phys. Soc. Jap. 38, 514 (1975), M. Cohen *et al.*, Chem. Phys. Lett. 49, 374 (1977).

Continued from page 1315

References

[1]R. C. Schoonmaker and R. F. Porter, J. Phys. Chem. 64, 457 (1960).
[2]J. Berkowitz, D. J Meschi and W. A. Chupka, J. Chem Phys. 33, 533 (1960).
[3]J. B. Berkowitz-Mattuck and A. Buchler, J. Phys. Chem. 67, 1386 (1963).
[4]JANAF Thermochemical Tables. LiOH(g), 6–31–71; Li_2O(cr), 3–31–64; $Na_2(OH)_2$(g), 12–31–70; Li_2F_2(g), 12–31–68.
[5]J. Berkowitz, J. Chem. Phys. 32, 1519 (1960).
[6]a) A. Snelson, J. Chem. Phys. 46, 3652 (1967); b) A. Snelson, J. Phys Chem. 73, 1919 (1969).

Continued from page 1317

[8]G. C. Kennedy, Amer. J. Sci. 254, 567 (1956).
[9]G. M. Zhabrova and B. M. Kadenatsi, J. Gen. Chem. U.S.S.R. 24, 1129 (1954).
[10]L G. Berg and I. S. Rassonskaya, Dokl. Akad. Nauk S.S.S.R. 81, 855 (1951).
[11]E G King, M. J. Ferrante, and L. B Pankratz, U S. Bur. Mines RI 8041, 1975.
[12]P. N. Lashchenko and D. I. Kompanskii, Zh. Prikl. Khim. 8, 628 (1935).
[13]JANAF Thermochemical Tables MgO(cr), 12–31–74, H_2O(g), 3–31–61.
[14]U. S. Nat. Bur. Stand. Tech. Note 270 3, 1968· H_2O(l).
[15]M. Natarajan, T. S. Sarma, J. C. Ahluwalia, and C. N R. Rao, Trans. Faraday Soc. 65, 3088 (1969).

Continued from page 1343

[3]F. Haber, S. Tamaru, and Ch. Ponnaz, Z. Elektrochem. 21, 89 (1914).
[4]C. C. Stephenson and H. O. McMahan, J. Amer Chem. Soc 61, 437 (1939).
[5]F Haber and A. Maschke, Z. Electrochem. 21, 128 (1915).
[6]G. Schulz and H. Schaefer, Ber. Bunsenges. Physik. Chem. 70, 21 (1966).
[7]M. Berthelot, Compt. Rend. 89, 877 (1879); Ann. Chim Phys. [5] 20, 247 (1880).
[8]M. Berthelot, Ann. Chim. Phys. [5] 20, 244 (1880)
[9]J Thomsen, "Thermochemical Investigations," Vol. II, p. 68, Johann A Barth, Leipzig, (1882).
[10]G Becker and W. A. Rogh, Z. Elektrochem. 40, 836 (1934).
[11]F. Haber, S. Tamaru, and L. W. Oeholm. Z. Elektrochem. 21, 206 (1915).
[12]F. Haber and S. Tamaru, Z. Elektrochem. 21, 191 (1915).
[13]F. E. Wittig and W. Schmatz, Z. Elektrochem. 63, 475 (1959).
[14]W. H. Evans, Personal Communication, U. S Nat. Bur Stand, July 1972; evaluation of ICSU–CODATA Task Group on Key Values for Thermodynamics, (June 1972).
[15]L. Haar, J Res. Nat. Bur Stand. 72A, 207 (1968)
[16]S Abramowitz *et al.*, U. S. Nat. Bur. Stand., Rept. 10904, 239, (July 1972).
[17]CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, (December 1973).