minum (Al)

ference State)   At. Wt. - 26.9815

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 1.094	.000	.000	.000
100	3.116	1.650	11.530	- .988	.000	.000	.000
200	5.156	4.572	7.302	- .546	.000	.000	.000
298	5.806	6.769	6.769	.000	.000	.000	.000
300	5.814	6.805	6.769	.011	.000	.000	.000
400	6.163	8.528	7.002	.610	.000	.000	.000
500	6.450	9.934	7.452	1.241	.000	.000	.000
600	6.717	11.134	7.968	1.900	.000	.000	.000
700	6.999	12.190	8.497	2.585	.000	.000	.000
800	7.370	13.147	9.019	3.302	.000	.000	.000
900	7.901	14.044	9.528	4.064	.000	.000	.000
1000	7.588	17.603	10.205	7.397	.000	.000	.000
1100	7.588	18.326	10.911	8.156	.000	.000	.000
1200	7.588	18.986	11.557	8.915	.000	.000	.000
1300	7.588	19.593	12.152	9.673	.000	.000	.000
1400	7.588	20.156	12.704	10.432	.000	.000	.000
1500	7.588	20.679	13.216	11.191	.000	.000	.000
1600	7.588	21.169	13.700	11.950	.000	.000	.000
1700	7.588	21.629	14.153	12.709	.000	.000	.000
1800	7.588	22.063	14.581	13.467	.000	.000	.000
1900	7.588	22.473	14.985	14.226	.000	.000	.000
2000	7.588	22.862	15.370	14.985	.000	.000	.000
2100	7.588	23.232	15.735	15.744	.000	.000	.000
2200	7.588	23.585	16.084	16.503	.000	.000	.000
2300	7.588	23.923	16.418	17.261	.000	.000	.000
2400	7.588	24.246	16.737	18.020	.000	.000	.000
2500	7.588	24.555	17.044	18.779	.000	.000	.000
2600	7.588	24.853	17.338	19.538	.000	.000	.000
2700	7.588	25.139	17.622	20.297	.000	.000	.000
2800	4.970	50.501	18.192	90.466	.000	.000	.000
2900	4.971	50.675	19.309	90.963	.000	.000	.000
3000	4.971	50.844	20.357	91.460	.000	.000	.000
3100	4.971	51.007	21.343	91.957	.000	.000	.000
3200	4.972	51.165	22.273	92.454	.000	.000	.000
3300	4.973	51.318	23.151	92.951	.000	.000	.000
3400	4.975	51.466	23.981	93.449	.000	.000	.000
3500	4.977	51.610	24.769	93.946	.000	.000	.000
3600	4.979	51.751	25.516	94.444	.000	.000	.000
3700	4.982	51.887	26.227	94.942	.000	.000	.000
3800	4.986	52.020	26.904	95.441	.000	.000	.000
3900	4.991	52.150	27.550	95.939	.000	.000	.000
4000	4.996	52.276	28.166	96.439	.000	.000	.000
4100	5.002	52.399	28.756	96.939	.000	.000	.000
4200	5.010	52.520	29.320	97.439	.000	.000	.000
4300	5.019	52.638	29.861	97.941	.000	.000	.000
4400	5.029	52.754	30.380	98.443	.000	.000	.000
4500	5.041	52.867	30.879	98.947	.000	.000	.000
4600	5.055	52.978	31.358	99.451	.000	.000	.000
4700	5.071	53.086	31.819	99.958	.000	.000	.000
4800	5.088	53.193	32.263	100.466	.000	.000	.000
4900	5.108	53.299	32.691	100.975	.000	.000	.000
5000	5.130	53.402	33.105	101.487	.000	.000	.000
5100	5.154	53.504	33.503	102.001	.000	.000	.000
5200	5.181	53.604	33.889	102.518	.000	.000	.000
5300	5.211	53.703	34.262	103.038	.000	.000	.000
5400	5.244	53.801	34.623	103.560	.000	.000	.000
5500	5.280	53.897	34.972	104.087	.000	.000	.000
5600	5.319	53.993	35.311	104.617	.000	.000	.000
5700	5.361	54.087	35.640	105.150	.000	.000	.000
5800	5.406	54.181	35.959	105.689	.000	.000	.000
5900	5.456	54.274	36.268	106.232	.000	.000	.000
6000	5.508	54.366	36.569	106.780	.000	.000	.000

Dec. 31, 1960; Dec. 31, 1965

ALUMINUM (Al) **(REFERENCE STATE)** AT. WT. = 26.9815

0 to 933°K.	Crystal
933 to 2766.8°K.	Liquid
2766.8 to 6000°K.	Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

Dialuminum Dioxide Unipositive Ion ($Al_2O_2^+$)

(Ideal Gas) GFW = 85.9612

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	13.099	64.387	64.387	.000	131.000	128.963	- 94.532
300	13.139	64.468	64.387	.024	130.998	128.949	- 93.939
400	15.011	68.519	64.927	1.437	130.999	128.271	- 70.084
500	16.319	72.018	66.003	3.007	131.073	127.581	- 55.765
600	17.205	75.077	67.266	4.686	131.176	126.872	- 46.213
700	17.814	77.778	68.579	6.439	131.277	126.146	- 39.385
800	18.244	80.186	69.882	8.243	131.346	125.408	- 34.260
900	18.556	82.354	71.149	10.084	131.346	124.665	- 30.273
1000	18.788	84.322	72.370	11.952	126.218	124.293	- 27.164
1100	18.965	86.121	73.539	13.840	126.246	124.099	- 24.656
1200	19.102	87.777	74.658	15.744	126.281	123.902	- 22.566
1300	19.211	89.311	75.727	17.659	126.319	123.702	- 20.796
1400	19.299	90.738	76.748	19.585	126.360	123.500	- 19.279
1500	19.370	92.072	77.726	21.519	126.402	123.292	- 17.964
1600	19.429	93.324	78.662	23.459	126.444	123.084	- 16.812
1700	19.479	94.503	79.560	25.404	126.486	122.873	- 15.796
1800	19.520	95.618	80.421	27.354	126.527	122.661	- 14.893
1900	19.555	96.674	81.249	29.308	126.565	122.445	- 14.084
2000	19.586	97.678	82.046	31.265	126.601	122.225	- 13.356
2100	19.612	98.634	82.813	33.225	126.635	122.004	- 12.697
2200	19.635	99.547	83.553	35.187	126.664	121.782	- 12.098
2300	19.654	100.420	84.267	37.152	126.693	121.563	- 11.551
2400	19.672	101.257	84.958	39.118	126.716	121.342	- 11.050
2500	19.687	102.061	85.626	41.086	126.735	121.111	- 10.588
2600	19.701	102.833	86.273	43.056	126.752	120.888	- 10.162
2700	19.713	103.577	86.900	45.026	126.763	120.662	- 9.767
2800	19.724	104.294	87.509	46.998	- 12.049	122.097	- 9.530
2900	19.734	104.986	88.100	48.971	- 11.522	126.877	- 9.562
3000	19.743	105.656	88.674	50.945	- 10.998	131.642	- 9.590
3100	19.751	106.303	89.232	52.920	- 10.477	136.388	- 9.615
3200	19.759	106.930	89.775	54.895	- 9.961	141.120	- 9.638
3300	19.765	107.538	90.305	56.871	- 9.448	145.833	- 9.658
3400	19.771	108.128	90.820	58.848	- 8.942	150.527	- 9.676
3500	19.777	108.702	91.323	60.826	- 8.435	155.209	- 9.692
3600	19.782	109.259	91.813	62.804	- 7.934	159.884	- 9.706
3700	19.787	109.801	92.292	64.782	- 7.437	164.532	- 9.718
3800	19.791	110.329	92.760	66.761	- 6.944	169.176	- 9.730
3900	19.795	110.843	93.217	68.740	- 6.452	173.807	- 9.740
4000	19.799	111.344	93.664	70.720	- 5.968	178.416	- 9.748
4100	19.803	111.833	94.101	72.700	- 5.486	183.016	- 9.756
4200	19.806	112.310	94.529	74.681	- 5.005	187.614	- 9.763
4300	19.809	112.776	94.948	76.661	- 4.532	192.197	- 9.768
4400	19.812	113.232	95.358	78.642	- 4.061	196.770	- 9.774
4500	19.814	113.677	95.761	80.624	- 3.596	201.325	- 9.778
4600	19.817	114.113	96.155	82.605	- 3.133	205.880	- 9.782
4700	19.819	114.539	96.541	84.587	- 2.678	210.407	- 9.784
4800	19.821	114.956	96.921	86.569	- 2.226	214.936	- 9.786
4900	19.823	115.365	97.293	88.551	- 1.778	219.464	- 9.789
5000	19.825	115.765	97.658	90.534	- 1.338	223.971	- 9.790
5100	19.827	116.158	98.017	92.516	- .904	228.475	- 9.791
5200	19.829	116.543	98.370	94.499	- .476	232.963	- 9.791
5300	19.830	116.921	98.716	96.482	- .055	237.451	- 9.791
5400	19.832	117.291	99.057	98.465	.360	241.928	- 9.791
5500	19.833	117.655	99.392	100.448	.765	246.395	- 9.791
5600	19.835	118.013	99.721	102.432	1.161	250.856	- 9.790

DIALUMINUM DIOXIDE UNIPOSITIVE ION ($Al_2O_2^+$) (IDEAL GAS) GFW = 85.9612

Point Group [D_{2h}]

ΔHf_0° = 132.3 ± 20 kcal/mol

$S_{298.15}^\circ$ = [64.4 ± 3] gibbs/mol

$\Delta Hf_{298.15}^\circ$ = 131 ± 20 kcal/mol

Ground State Quantum Weight [2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[180] (1)	[850] (1)
[550] (1)	[900] (1)
[850] (1)	[900] (1)

Bond Distance: Al-O = [1.66] Å

Bond Angle: O-Al-O = [90°] Al-O-Al = [90°] σ = [4]

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.777×10^{-114}] $g^3\ cm^6$

Heat of Formation

G. DeMaria, J. Drowart, and M. G. Inghram, J. Chem. Phys. 30, 318 (1959), have reported an ionization potential for Al_2O_2 of 9.9 ± 0.5eV(228 kcal). Using this value in conjunction with $\Delta Hf_{298}^\circ(Al_2O_2, g) = -97$ kcal/mol, we obtain $\Delta Hf_{298}^\circ(Al_2O_2^+, g) = 131 \pm 20$ kcal/mol.

Heat Capacity and Entropy

The molecular configuration is assumed to be the same as that used for Al_2O_2. The bond length is assumed to be longer than that in Al_2O_2 and is made equal to that reported for Al_2O. The bond angle is arbitrarily estimated to be the same as that in Al_2O_2. The vibrational frequencies are estimated to be slightly lower than those for Al_2O_2, since the $Al_2O_2^+$ molecule should be less rigidly bound. The ground state is assumed to be doublet, since there is an odd number of electrons.

The individual moments of inertia are $I_A = 7.32 \times 10^{-39}$ g cm^2, $I_B = 1.234 \times 10^{-38}$ g cm^2, and $I_C = 1.966 \times 10^{-38}$ g cm^2.

The enthalpy at 0°K is -3.010 kcal/mole.

uminum Oxide (alpha Al_2O_3)
rystal) Mol. Wt. - 101.960

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.394	- 397.494	- 397.494	INFINITE
100	3.069	1.024	24.184	- 2.316	- 398.697	- 392.241	857.201
200	12.223	5.946	13.711	- 1.553	- 399.838	- 385.329	421.047
298	18.889	12.174	12.174	.000	- 400.400	- 378.078	277.125
300	18.979	12.291	12.174	.035	- 400.406	- 377.940	275.316
400	22.986	18.339	12.972	2.147	- 400.555	- 370.418	202.378
500	25.345	23.752	14.598	4.577	- 400.475	- 362.891	158.612
600	26.889	28.517	16.529	7.193	- 400.304	- 355.389	129.444
700	27.969	32.749	18.549	9.940	- 400.098	- 347.920	108.620
800	28.758	36.537	20.565	12.778	- 399.889	- 340.481	93.011
900	29.354	39.961	22.533	15.685	- 399.697	- 333.066	80.875
1000	29.814	43.078	24.434	18.644	- 404.522	- 325.301	71.091
1100	30.176	45.938	26.261	21.644	- 404.181	- 317.396	63.058
1200	30.464	48.574	28.012	24.674	- 403.823	- 309.522	56.369
1300	30.995	51.032	29.689	27.745	- 403.437	- 301.680	50.715
1400	31.290	53.339	31.297	30.859	- 403.019	- 293.868	45.873
1500	31.620	55.509	32.839	34.004	- 402.581	- 286.086	41.681
1600	31.920	57.559	34.321	37.181	- 402.119	- 278.334	38.017
1700	32.220	59.503	35.745	40.388	- 401.635	- 270.612	34.788
1800	32.490	61.353	37.117	43.624	- 401.133	- 262.920	31.921
1900	32.760	63.116	38.439	46.886	- 400.613	- 255.254	29.359
2000	33.000	64.803	39.716	50.175	- 400.075	- 247.619	27.057
2100	33.220	66.419	40.949	53.486	- 399.521	- 240.011	24.977
2200	33.450	67.969	42.142	56.819	- 398.956	- 232.427	23.088
2300	33.670	69.461	43.298	60.175	- 398.374	- 224.872	21.367
2400	33.880	70.898	44.418	63.553	- 397.779	- 217.339	19.790
2500	34.100	72.286	45.505	66.952	- 397.172	- 209.834	18.343
2600	34.310	73.627	46.561	70.372	- 396.550	- 202.354	17.009
2700	34.520	74.926	47.588	73.814	- 395.915	- 194.898	15.775
2800	34.735	76.186	48.587	77.277	- 536.375	- 184.157	14.373
2900	34.940	77.408	49.560	80.760	- 535.307	- 171.598	12.931
3000	35.140	78.596	50.508	84.264	- 534.227	- 159.072	11.588
3100	35.340	79.751	51.433	87.788	- 533.132	- 146.584	10.334
3200	35.530	80.876	52.335	91.332	- 532.028	- 134.135	9.161
3300	35.720	81.973	53.217	94.894	- 530.908	- 121.718	8.061
3400	35.906	83.042	54.078	98.476	- 529.777	- 109.338	7.028
3500	36.095	84.085	54.921	102.076	- 528.634	- 96.992	6.056

Dec. 31, 1960; Sept. 30, 1961; Mar. 31, 1964

ALUMINUM OXIDE (ALPHA Al_2O_3) (CRYSTAL) MOL. WT. = 101.960

$S^\circ_{298.15}$ = 12.174 cal. deg.$^{-1}$ mole^{-1}

T_m = 2315°K.

$\Delta H^\circ_{f\ 0}$ = -397.5 ± 0.3 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -400.4 ± 0.3 kcal. mole^{-1}

ΔH_m = 28.30 ± 0.55 kcal. mole^{-1}

Heat of Formation.

The value of ΔH_f derived from the direct combustion of pure aluminum in oxygen was taken from A. D. Mah, J. Phys. Chem. 61, 1572 (1957). Other values for ΔH_f obtained in the same way are: -399.04 ± .24 kcal. mole^{-1} reported by P. E. Snyder and H. Seltz, J. Am. Chem. Soc. 67, 683 (1945); -400.4 ± .3 kcal. mole^{-1} reported by C. E. Holley, Jr., and E. J. Huber, Jr., J. Am. Chem. Soc. 73, 5577 (1951); and -402 ± 2 kcal. mole^{-1} reported by A. Schneider and G. Gattow, Z. anorg. u. allgem. Chem. 277, 41 (1954).

Heat Capacity and Entropy.

The heat capacity measurements reported by G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, (15° to 1200°K.), J. Research Natl. Bur. Standards 57, 67 (1956), were employed in this table. Low temperature measurements were also made by F. Simon and R. C. Swain (30-280°K.), Z. Physik. Chem. 28B, 189 (1935); E. C. Kerr, H. L. Johnston, and N. C. Hallett (20° to 295°K.), J. Am. Chem. Soc. 72, 4740 (1950); J. W. Edwards and G. L. Kingston (53-291°K.), Trans. Faraday Soc. 58, 1313-22 (1962); E. N. Rodigina and K. Z. Gomel'skii, (100-900°K.), Zhur. Fiz. Khim. 32, 1859-62 (1958); B. E. Walker, J. A. Grand, and R. R. Miller (300-900°K.), J. Phys. Chem. 60, 231-3 (1956); R. Dawson, E. B. Brackett, and T. E. Brackett (700-1400°K.), J. Phys. Chem. 67, 1669 (1963), and L. Terebesi (0-1300°K.), Helv. Chim. Acta. 17, 804 (1934). All of the above low temperature data are in good agreement with Furukawa's work.

The heat capacities above 1200°K. (1200-2500°K.) were taken from the enthalpy measurements of P. B. Kantor, L. S. Lazareva, V. V. Kandyba, and E. M. Fomichov, Ukr. Fiz. Zh. 7, 205-10 (1962). The heat capacity values above 2500°K. were extrapolated. High temperature measurements were also made by the following investigators: V. Ya. Chekhovskoi (500-2000°K.), Inzh. Fiz. Zh., Akad. Nauk. Belorussk SSR 5, 62-5 (1962); A. Ferrier and M. Olette (1100-2300°K.), Compt. Rend. 254, 4293-95 (1962); C. H. Shomate and B. F. Naylor (500-1800°K.), J. Am. Chem. Soc. 67, 72 (1945) and H. L Johnston and M. Hoch (1000-2000°K.), J. Phys. Chem. 65, 1184-5 (1961); and V. A. Kirillin, A. E. Sheidlin, and V. Ya. Chekhovskii (500-2000°K.), Doklady Akad. Nauk. SSSR 135, 125-8 (1960). Numerical values were not available from Kirillin, et al., but graphical values were in close agreement with an extrapolation of Furukawa's data. The entropy at 298.15 was reported by T. Furukawa, et al., loc. cit., using S°_{15} = 0.0105 cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

The melting data were obtained from the measurements of P. B. Kantor, L. S. Lazareva, V. V. Kandyba, and E. M. Fomichov, loc. cit. S. J. Schneider "Compilation of the Melting Points of the Metal Oxides," NBS Monograph 68, p. 6, Oct. 10, 1963, gives a review of the melting points that range from 2267 to 2345°K.

Aluminum Oxide, Gamma (γ - Al_2O_3)
(Crystal) Mol. Wt. = 101.9612

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	19.833	12.550	12.550	.000	- 396.000	- 373.790	273.982
300	19.928	12.673	12.550	.037	- 396.005	- 373.652	272.193
400	24.135	19.023	13.388	2.254	- 396.052	- 366.184	200.064
500	26.612	24.691	15.093	4.799	- 395.866	- 358.736	156.796
600	28.233	29.694	17.118	7.545	- 395.570	- 351.337	127.968
700	29.367	34.135	19.238	10.428	- 395.224	- 343.991	107.394
800	30.196	38.112	21.353	13.407	- 394.876	- 336.697	91.977
900	30.804	41.705	23.418	16.458	- 394.570	- 329.443	79.996
1000	31.305	44.977	25.413	19.565	- 399.370	- 321.853	70.338
1100	31.623	47.976	27.330	22.711	- 399.000	- 314.122	62.407
1200	31.987	50.743	29.167	25.891	- 398.610	- 306.423	55.805
1300	32.447	53.321	30.927	29.113	- 398.190	- 298.756	50.223
1400	32.855	55.741	32.614	32.378	- 397.738	- 291.123	45.444
1500	33.193	58.020	34.232	35.681	- 397.260	- 283.527	41.308
1600	33.516	60.172	35.787	39.016	- 396.758	- 275.960	37.693
1700	33.824	62.213	37.282	42.384	- 396.232	- 268.425	34.507
1800	34.115	64.155	38.721	45.781	- 395.684	- 260.921	31.679
1900	34.390	66.007	40.109	49.206	- 395.119	- 253.451	29.152
2000	34.650	67.778	41.449	52.658	- 394.535	- 246.013	26.882
2100	34.889	69.474	42.743	56.135	- 393.934	- 238.601	24.830
2200	35.123	71.102	43.995	59.636	- 393.319	- 231.219	22.968
2300	35.348	72.669	45.208	63.159	- 392.686	- 223.862	21.271
2400	35.574	74.178	46.384	66.706	- 392.040	- 216.533	19.717
2500	35.801	75.635	47.525	70.274	- 391.382	- 209.242	18.291
2600	36.026	77.043	48.633	73.866	- 390.706	- 201.965	16.976
2700	36.252	78.407	49.711	77.480	- 390.017	- 194.721	15.761
2800	36.472	79.730	50.760	81.116	- 528.134	- 185.841	14.505
2900	36.687	81.013	51.781	84.774	- 526.892	- 173.637	13.085
3000	36.897	82.260	52.776	88.453	- 525.636	- 161.473	11.763

ALUMINUM OXIDE, GAMMA (γ - Al_2O_3) (CRYSTAL) MOL. WT. = 101.9612

$\Delta H^\circ_{f\ 0}$ = Unknown

$S^\circ_{298.15}$ = [12.55] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-396.0 ± 0.5] kcal. mole^{-1}

T_m = 2323°K.

ΔH°_m = [20.9] kcal. mole^{-1}

Heat of Formation.

The enthalpy change (ΔH°_t) for the transition $Al_2O_3(\gamma, c) \rightarrow Al_2O_3(\alpha, c)$ has been determined by (1) V. Kostomaroff and M. Rey, Silicates Ind. 28, 9 (1963); and (2) T. Yokokawa and O. J. Kleppa, J. Phys. Chem. 68, 3246 (1964). The results obtained are presented in the table. The enthalpies of solution for $Al_2O_3(\gamma, c)$ and Al(c) in 2N KOH(aq.) have been measured by (3) K. K. Kelley, C. H. Shomate, F. E. Young, B. F. Naylor, A. E. Salo and E. H. Huffman, U. S. Bur. Mines Tech. Rept. 688 (1946). Based on their reported values, -16.13 ± 1.0 and -196.02 ± 0.25 kcal. mole^{-1}, respectively, the heat of formation ($\Delta H^\circ_{f\ 298.15}$) for $Al_2O_3(\gamma, c)$ was evaluated to be -384.84 ± 1.1 kcal. mole^{-1}. Hence, the enthalpy of transition ($\gamma \rightarrow \alpha$) was calculated as -15.6 ± 1.1 kcal. mole^{-1}, using $\Delta H^\circ_{f\ 298.15}$ (Al_2O_3, α, c) = -400.4 kcal. mole^{-1}.

Source	Method	Temperature, °K.	ΔH°_t, kcal. mole^{-1}	$\Delta H^\circ_{t\ 298.15}$, kcal. mole^{-1}
(2)	solution calorimetry	978	-5.3	-4.4
(1)	differential thermal analysis	1473	-11.0	-9.4
(3)	solution calorimetry	298.15	-15.6	-15.6

The heat of formation for $Al_2O_3(\gamma, c)$ was calculated from that for $Al_2O_3(\alpha, c)$ and the ΔH°_t value reported by Yokokawa and Kleppa, loc. cit., which was arbitrarily selected.

Heat Capacity and Entropy.

The heat capacities were assumed to be larger than those for $Al_2O_3(\alpha, c)$ by 5% at each temperature. The value of $S^\circ_{298.15}$ was estimated such that at T_m, $\Delta F^\circ_f (Al_2O_3, \gamma, c) > \Delta F^\circ_f (Al_2O_3, \alpha, c)$.

Melting Data.

T_m was reported by M. Plummer, J. Appl. Chem. 8, 35 (1958). The difference between ΔH°_f for Al_2O_3 (γ, c) and Al_2O_3 (l) at T_m is ΔH°_m.

Carbon Monoxide (CO)

(Ideal Gas) Mol. Wt. = 28.01055

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.072	-27.200	-27.200	INFINITE
100	6.956	39.613	53.401	-1.379	-26.876	-28.741	62.809
200	6.957	44.435	47.951	-.683	-26.599	-30.718	33.566
298	6.965	47.214	47.214	.000	-26.417	-32.783	24.029
300	6.965	47.257	47.214	.013	-26.414	-32.823	23.910
400	7.013	49.265	47.488	.711	-26.318	-34.975	19.109
500	7.121	50.841	48.006	1.417	-26.296	-37.144	16.235
600	7.276	52.152	48.591	2.137	-26.332	-39.311	14.318
700	7.450	53.287	49.182	2.873	-26.409	-41.468	12.946
800	7.624	54.293	49.759	3.627	-26.514	-43.612	11.914
900	7.786	55.200	50.314	4.397	-26.637	-45.744	11.108
1000	7.931	56.028	50.845	5.183	-26.771	-47.859	10.459
1100	8.057	56.790	51.351	5.983	-26.914	-49.962	9.926
1200	8.168	57.496	51.834	6.794	-27.062	-52.049	9.479
1300	8.263	58.154	52.295	7.616	-27.218	-54.126	9.099
1400	8.346	58.769	52.736	8.446	-27.376	-56.189	8.771
1500	8.417	59.348	53.158	9.285	-27.537	-58.241	8.485
1600	8.480	59.893	53.562	10.130	-27.700	-60.284	8.234
1700	8.535	60.409	53.950	10.980	-27.865	-62.315	8.011
1800	8.583	60.898	54.322	11.836	-28.032	-64.337	7.811
1900	8.626	61.363	54.681	12.697	-28.201	-66.349	7.631
2000	8.664	61.807	55.026	13.561	-28.372	-68.353	7.469
2100	8.698	62.230	55.359	14.430	-28.543	-70.346	7.321
2200	8.728	62.635	55.680	15.301	-28.719	-72.335	7.185
2300	8.756	63.024	55.991	16.175	-28.894	-74.311	7.061
2400	8.781	63.397	56.292	17.052	-29.074	-76.282	6.946
2500	8.804	63.756	56.584	17.931	-29.254	-78.247	6.840
2600	8.825	64.102	56.866	18.813	-29.438	-80.202	6.741
2700	8.844	64.435	57.140	19.696	-29.623	-82.153	6.649
2800	8.863	64.757	57.407	20.582	-29.810	-84.093	6.563
2900	8.879	65.069	57.666	21.469	-30.001	-86.028	6.483
3000	8.895	65.370	57.917	22.357	-30.194	-87.957	6.407
3100	8.910	65.662	58.163	23.248	-30.388	-89.878	6.336
3200	8.924	65.945	58.401	24.139	-30.586	-91.795	6.269
3300	8.937	66.220	58.634	25.032	-30.786	-93.707	6.206
3400	8.949	66.487	58.861	25.927	-30.988	-95.609	6.145
3500	8.961	66.746	59.083	26.822	-31.192	-97.509	6.088
3600	8.973	66.999	59.299	27.719	-31.399	-99.400	6.034
3700	8.984	67.245	59.511	28.617	-31.608	-101.286	5.982
3800	8.994	67.485	59.717	29.516	-31.818	-103.164	5.933
3900	9.004	67.718	59.919	30.416	-32.031	-105.039	5.886
4000	9.014	67.946	60.117	31.316	-32.247	-106.908	5.841
4100	9.024	68.169	60.311	32.218	-32.464	-108.774	5.798
4200	9.033	68.387	60.501	33.121	-32.684	-110.630	5.756
4300	9.042	68.599	60.687	34.025	-32.906	-112.483	5.717
4400	9.051	68.807	60.869	34.930	-33.130	-114.333	5.679
4500	9.059	69.011	61.047	35.835	-33.356	-116.177	5.642
4600	9.068	69.210	61.223	36.741	-33.584	-118.012	5.607
4700	9.076	69.405	61.395	37.649	-33.814	-119.845	5.573
4800	9.084	69.596	61.564	38.557	-34.046	-121.672	5.540
4900	9.092	69.784	61.729	39.465	-34.280	-123.497	5.508
5000	9.100	69.967	61.892	40.375	-34.516	-125.315	5.477
5100	9.107	70.148	62.052	41.285	-34.755	-127.132	5.448
5200	9.115	70.325	62.210	42.196	-34.995	-128.941	5.419
5300	9.123	70.498	62.365	43.108	-35.237	-130.741	5.391
5400	9.130	70.669	62.517	44.021	-35.480	-132.542	5.364
5500	9.138	70.836	62.667	44.934	-35.727	-134.336	5.338
5600	9.145	71.001	62.814	45.849	-35.974	-136.129	5.312
5700	9.153	71.163	62.959	46.763	-36.225	-137.919	5.288
5800	9.160	71.322	63.102	47.679	-36.476	-139.698	5.264
5900	9.167	71.479	63.242	48.595	-36.730	-141.473	5.240
6000	9.175	71.633	63.381	49.513	-36.985	-143.249	5.218

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

CARBON MONOXIDE (CO) (IDEAL GAS) MOL. WT. = 28.01055

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 47.21 ± 0.01 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = -27.20 ± 0.04 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -26.42 ± 0.04 kcal. mole^{-1}

ω_e = 2169.52 cm.$^{-1}$

B_e = 1.9302 cm.$^{-1}$

$\omega_e x_e$ = 13.453 cm.$^{-1}$

α_e = 0.01746 cm.$^{-1}$

σ = 1

r_e = 1.1281 Å

Heat of Formation.

The enthalpy change ($\Delta H^\circ_{r\ 298.15}$) for the reaction: $CO(g) + 1/2\ O_2(g) = CO_2(g)$ was reported to be -67.636 ± 0.029 kcal. mole^{-1}, based on molecular weight of CO_2 = 44.010, by F. D. Rossini, J. Research Nat. Bur. Standards 22, 407 (1939). It was recalculated to be -67.638 ± 0.03 kcal. mole^{-1}, using molecular weight of CO_2 = 44.011, for internal consistency. From the value of $\Delta H^\circ_{r\ 298.15}$, the heat of formation ($\Delta H^\circ_{f\ 298.15}$) for CO(g) was derived to be -26.417 ± 0.04 kcal. mole^{-1}, which yields D_0(CO) = 11.09 e.v.

The D_0(CO) value has been proposed to be 6.92 to 11.11 e.v. in the past few decades in order to explain data collected from spectroscopic, flame, shock-wave, detonation, and electron-impact studies. Recent evaluations by L. Brewer and A. Searcy, Ann. Rev. Phys. Chem. 7, 259 (1956); M. A. Fineman and A. W. Petrocelli, J. Chem. Phys. 36, 25 (1962); and C. F. Giese and W. B. Maier II, J. Chem. Phys. 39, 197 (1963) favored the value 11.11 e.v., reported by A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., 1953.

The heat of combustion of CO(g) was also determined by J. H. Awbery and E. Griffiths, Proc. Roy. Soc. (London) [A] 141, 1 (1933), R. W. Fenning and F. T. Cotton, ibid., [A] 141, 17 (1933), and W. A. Roth and H. Banse, Arch. Eisenhutten 6, 43 (1932-33).

Heat Capacity and Entropy.

The functions adopted here were obtained from J. Belzer, L. G. Savedoff and H. L. Johnston, Ohio State University, TR 316-6, May 1, 1953, assuming the thermodynamic functions for the naturally occurring isotopic mixture to be the same as those for $C^{12}O^{16}(g)$. The spectroscopic constants employed for calculation were reported by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950. The tabulated functions include the second order corrections to the rigid-rotator and harmonic-oscillator molecular model for vibrational anharmonicity, rotational stretching and rotational-vibrational interaction.

The spectroscopic constants listed above are for the naturally occurring isotopic composition given by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

Thermodynamic properties for CO from 70 to 300°K., with pressures to 300 atmospheres were reported by J. G. Hust and R. B. Stewart, NBS-TN-202, National Bureau of Standards, 1963. Calculations of the vapor pressure and heats of vaporization and sublimation of CO and CO_2 below one atmosphere were reported by J. C. Mullins, B. S. Kirk and W. T. Ziegler, U. S. Atomic Energy Commission NP-13862 (1963).

Carbon Dioxide (CO_2)

(Ideal Gas) Mol. Wt. = 44.00995

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.238	-93.965	-93.965	INFINITE
100	6.981	42.758	58.188	-1.543	-93.997	-94.100	205.645
200	7.734	47.769	51.849	-.816	-94.028	-94.191	102.922
298	8.874	51.072	51.072	.000	-94.054	-94.265	69.095
300	8.896	51.127	51.072	.016	-94.055	-94.267	68.670
400	9.877	53.830	51.434	.958	-94.070	-94.335	51.540
500	10.666	56.122	52.148	1.987	-94.091	-94.399	41.260
600	11.310	58.126	52.981	3.087	-94.124	-94.458	34.405
700	11.846	59.910	53.845	4.245	-94.169	-94.510	29.506
800	12.293	61.522	54.706	5.453	-94.218	-94.556	25.830
900	12.667	62.992	55.546	6.702	-94.270	-94.596	22.970
1000	12.980	64.344	56.355	7.984	-94.321	-94.628	20.680
1100	13.243	65.594	57.143	9.296	-94.371	-94.658	18.806
1200	13.466	66.756	57.896	10.632	-94.419	-94.681	17.243
1300	13.656	67.841	58.620	11.988	-94.469	-94.701	15.920
1400	13.815	68.859	59.315	13.362	-94.515	-94.716	14.785
1500	13.953	69.817	59.984	14.750	-94.562	-94.728	13.801
1600	14.074	70.722	60.627	16.152	-94.607	-94.739	12.940
1700	14.177	71.579	61.246	17.565	-94.650	-94.746	12.180
1800	14.269	72.391	61.843	18.987	-94.696	-94.750	11.504
1900	14.352	73.165	62.418	20.418	-94.742	-94.751	10.898
2000	14.424	73.903	62.974	21.857	-94.788	-94.752	10.353
2100	14.489	74.608	63.512	23.303	-94.834	-94.746	9.860
2200	14.547	75.284	64.031	24.755	-94.885	-94.744	9.411
2300	14.600	75.931	64.535	26.212	-94.936	-94.735	9.001
2400	14.649	76.554	65.023	27.674	-94.991	-94.724	8.625
2500	14.692	77.153	65.496	29.141	-95.048	-94.714	8.280
2600	14.734	77.730	65.956	30.613	-95.107	-94.698	7.960
2700	14.771	78.286	66.402	32.088	-95.170	-94.683	7.664
2800	14.807	78.824	66.836	33.567	-95.235	-94.662	7.388
2900	14.841	79.344	67.259	35.049	-95.305	-94.639	7.132
3000	14.873	79.848	67.670	36.535	-95.377	-94.615	6.892
3100	14.902	80.336	68.071	38.024	-95.451	-94.587	6.668
3200	14.930	80.810	68.461	39.515	-95.530	-94.560	6.458
3300	14.956	81.270	68.843	41.010	-95.611	-94.531	6.260
3400	14.982	81.717	69.215	42.507	-95.696	-94.495	6.074
3500	15.006	82.151	69.578	44.006	-95.784	-94.462	5.898
3600	15.030	82.574	69.933	45.508	-95.874	-94.421	5.732
3700	15.053	82.986	70.280	47.012	-95.968	-94.379	5.574
3800	15.075	83.388	70.620	48.518	-96.064	-94.331	5.425
3900	15.097	83.780	70.953	50.027	-96.162	-94.286	5.283
4000	15.119	84.162	71.278	51.538	-96.263	-94.237	5.149
4100	15.139	84.536	71.597	53.051	-96.367	-94.186	5.020
4200	15.159	84.901	71.909	54.566	-96.473	-94.130	4.898
4300	15.179	85.258	72.216	56.082	-96.583	-94.072	4.781
4400	15.197	85.607	72.516	57.601	-96.694	-94.015	4.670
4500	15.216	85.949	72.811	59.122	-96.807	-93.954	4.563
4600	15.234	86.284	73.100	60.644	-96.923	-93.885	4.460
4700	15.254	86.611	73.384	62.169	-97.040	-93.818	4.362
4800	15.272	86.933	73.663	63.695	-97.160	-93.746	4.268
4900	15.290	87.248	73.937	65.223	-97.281	-93.678	4.178
5000	15.306	87.557	74.206	66.753	-97.404	-93.603	4.091
5100	15.327	87.860	74.471	68.285	-97.530	-93.528	4.008
5200	15.349	88.158	74.731	69.819	-97.656	-93.450	3.927
5300	15.371	88.451	74.988	71.355	-97.783	-93.361	3.850
5400	15.393	88.738	75.239	72.893	-97.912	-93.280	3.775
5500	15.415	89.021	75.488	74.433	-98.042	-93.190	3.703
5600	15.437	89.299	75.732	75.976	-98.173	-93.104	3.633
5700	15.459	89.572	75.972	77.521	-98.305	-93.017	3.566
5800	15.481	89.841	76.209	79.068	-98.438	-92.918	3.501
5900	15.503	90.106	76.442	80.617	-98.572	-92.820	3.438
6000	15.525	90.367	76.672	82.168	-98.707	-92.724	3.377

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

CARBON DIOXIDE (CO_2) (IDEAL GAS) MOL. WT. = 44.00995

Point Group $D_{\infty h}$

$\Delta H^\circ_{f\ 0} = -93.965 \pm 0.011$ kcal. mole^{-1}

$S^\circ_{298.15} = 51.07 \pm 0.03$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -94.054 \pm 0.011$ kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
1342.86 (1)
667.30 (2)
2349.30 (1)

Bond Distance: C-O = 1.16 Å

Bond Angle: O-C-O = 180°

$\sigma = 2$

Rotational Constant: $B_o = 0.39038$ cm.$^{-1}$

Heat of Formation.

The enthalpy change ($\Delta H^\circ_{f\ 298.15}$) of the reaction C(c, graphite) + O_2(g) = CO_2(g) has been measured by F. H. Dewey and D. R. Harper, J. Res. Natl. Bur. Std. 21, 457 (1938), R. S. Jessup, ibid. 21, 491 (1938), and E. J. Prosen and F. D. Rossini, ibid., 33, 439 (1944). Based on these data, the heat of formation ($\Delta H^\circ_{f\ 298.15}$) for CO_2(g) was reported to be -94.0518 ± 0.0108 kcal. mole^{-1}, using molecular weight of CO_2 = 44.010, by E. J. Prosen, R. S. Jessup and F. D. Rossini, J. Research Natl. Bur. Standards 33, 447 (1944). This value was recalculated to be -94.054 ± 0.011 kcal. mole^{-1}, based on molecular weight of CO_2 = 44.011, for internal consistency.

Heat Capacity and Entropy.

The functions adopted here were obtained from H. W. Woolley, J. Research Nat. Bur. Standards 52, 289 (1954) who calculated the thermodynamic functions by means of a direct summation for the naturally occurring isotopic composition. The spectroscopic constants used are essentially those selected by T. Wentnik, Jr., J. Chem. Phys. 30, 105 (1959). Slightly different sets of spectroscopic constants were obtained by C. P. Courtoy, Mem. soc. roy. Liege 18, 496 (1957) and V. R. Stull, P. J. Wyatt and G. N. Plass, J. Chem. Phys. 37, 1442 (1962). The high-resolution infrared spectrum of O^{18} - enriched CO_2 was examined in the region 5400-1620 cm.$^{-1}$, using an Ebert grating Spectrometer with spectral slit widths ranging from 0.4 to 0.2 cm.$^{-1}$ by C. V. Berney, Ph. D. Thesis, University of Washington, 1962.

The molecular structure was reported by G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc. 1945. The rotational constant, B_o, was obtained from H. W. Woolley, loc. cit. The value of bond distance, r_e, was calculated from B_e which was derived from B_o, using $B_e - B_o = 0.0011$ cm.$^{-1}$ given in G. Herzberg, loc. cit. The principal moment of inertia is $I = 7.1495 \times 10^{-39}$ g. cm.^{2}

Heat capacities of CO_2(g) at high pressures were reported by M. P. Vukalovich, V. V. Altunin and A. N. Gureev, Teploenergetika, 12 (7), 58 (1965); K. Krueger, Ver. Deut. Ingr. Z., 106 (32) 1620 (1964), and M. P. Vukalovich and A. N. Gureev, Teploenergetika, 11 (8), 80 (1964).

Acetylene (C_2H_2)

(Ideal Gas) Mol. Wt. = 26.038

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	,000	,000	INFINITE	-2,393	54,325	54,325	INFINITE
100	7,014	39,002	55,982	-1,698	54,233	52,814	-115,418
200	8,505	44,213	48,903	-,938	54,234	51,383	-56,146
298	10,539	48,004	48,004	,000	54,190	49,993	-36,644
300	10,571	48,069	48,004	,020	54,189	49,966	-36,399
400	12,065	51,326	48,438	1,155	54,138	48,567	-26,534
500	13,114	54,139	49,303	2,418	54,064	47,181	-20,622
600	13,931	56,604	50,319	3,771	53,961	45,813	-16,687
700	14,615	58,805	51,377	5,199	53,837	44,466	-13,882
800	15,239	60,798	52,432	6,693	53,707	43,137	-11,784
900	15,801	62,625	53,464	8,245	53,573	41,821	-10,155
1000	16,318	64,317	54,466	9,852	53,450	40,522	-8,856
1100	16,789	65,895	55,434	11,507	53,333	39,234	-7,795
1200	17,221	67,375	56,368	13,208	53,228	37,960	-6,913
1300	17,613	68,769	57,269	14,950	53,128	36,690	-6,168
1400	17,968	70,087	58,138	16,729	53,041	35,432	-5,531
1500	18,291	71,338	58,977	18,543	52,961	34,177	-4,979
1600	18,582	72,528	59,787	20,387	52,887	32,923	-4,497
1700	18,845	73,663	60,570	22,258	52,823	31,679	-4,072
1800	19,085	74,747	61,327	24,155	52,765	30,436	-3,695
1900	19,302	75,785	62,061	26,074	52,714	29,199	-3,358
2000	19,504	76,780	62,772	28,015	52,670	27,962	-3,055
2100	19,684	77,736	63,462	29,974	52,631	26,730	-2,782
2200	19,853	78,656	64,132	31,951	52,594	25,493	-2,532
2300	20,004	79,541	64,783	33,944	52,564	24,266	-2,306
2400	20,151	80,396	65,416	35,952	52,535	23,037	-2,098
2500	20,282	81,221	66,032	37,974	52,510	21,804	-1,906
2600	20,404	82,019	66,631	40,008	52,486	20,579	-1,730
2700	20,519	82,791	67,216	42,055	52,466	19,349	-1,566
2800	20,625	83,540	67,785	44,112	52,448	18,124	-1,415
2900	20,726	84,265	68,341	46,179	52,429	16,901	-1,274
3000	20,820	84,969	68,884	48,257	52,413	15,674	-1,142
3100	20,910	85,654	69,414	50,343	52,399	14,451	-1,019
3200	20,996	86,319	69,932	52,439	52,385	13,227	-,903
3300	21,078	86,966	70,438	54,542	52,369	12,000	-,795
3400	21,154	87,596	70,934	56,654	52,356	10,779	-,693
3500	21,225	88,211	71,418	58,773	52,340	9,554	-,597
3600	21,297	88,810	71,893	60,899	52,325	8,331	-,506
3700	21,367	89,394	72,358	63,032	52,307	7,111	-,420
3800	21,431	89,965	72,814	65,172	52,291	5,894	-,339
3900	21,494	90,522	73,261	67,319	52,272	4,675	-,262
4000	21,557	91,067	73,699	69,471	52,252	3,455	-,189
4100	21,615	91,600	74,130	71,630	52,231	2,230	-,119
4200	21,670	92,122	74,552	73,794	52,206	1,017	-,053
4300	21,728	92,632	74,966	75,964	52,179	-,205	,010
4400	21,782	93,133	75,374	78,139	52,151	-1,425	,071
4500	21,835	93,623	75,774	80,320	52,120	-2,648	,129
4600	21,883	94,103	76,167	82,506	52,087	-3,858	,183
4700	21,935	94,574	76,554	84,697	52,052	-5,073	,236
4800	21,985	95,037	76,934	86,893	52,013	-6,286	,286
4900	22,036	95,490	77,308	89,094	51,973	-7,500	,335
5000	22,077	95,936	77,676	91,300	51,930	-8,715	,381
5100	22,129	96,374	78,038	93,510	51,881	-9,935	,426
5200	22,174	96,804	78,395	95,725	51,832	-11,144	,468
5300	22,219	97,227	78,746	97,945	51,780	-12,348	,509
5400	22,263	97,642	79,093	100,169	51,724	-13,559	,549
5500	22,309	98,051	79,434	102,397	51,663	-14,767	,587
5600	22,349	98,454	79,770	104,630	51,601	-15,977	,624
5700	22,393	98,850	80,101	106,867	51,534	-17,188	,659
5800	22,433	99,239	80,428	109,108	51,463	-18,394	,693
5900	22,474	99,623	80,750	111,354	51,390	-19,588	,726
6000	22,521	100,001	81,067	113,603	51,313	-20,802	,758

March 31, 1961

ACETYLENE (C_2H_2) (IDEAL GAS) MOL. WT. = 26.038

ΔH°_{f0} = 54.33 ± 0.19 kcal. mole^{-1}

Point Group $D_{\infty h}$

$\Delta H^\circ_{f\ 298.15}$ = 54.19 ± 0.19 kcal. mole^{-1}

$S^\circ_{298.15}$ = 48.004 cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
3373.7 (1)
1973.8 (1)
3281.9 (1)
611.6 (2)
729.3 (2)

Rotational Constant B_0 = 1.17684 ± 0.00016 cm.$^{-1}$ $\sigma = 2$

Ground State Multiplicity = 1

Spectroscopic constants used in calculating corrections to rigid rotator-harmonic oscillator approximation (cm.$^{-1}$):

X_{11} = -24.08
X_{12} = -16.94
X_{13} = -99.01
X_{14} = -16.46
X_{15} = -11.75
X_{22} = - 7.92
X_{23} = - 1.38
X_{24} = - 6.15
X_{25} = - 0.85
X_{33} = -25.69
X_{34} = - 9.06
X_{35} = - 5.73
X_{44} = 5.38
X_{45} = -12.65
X_{55} = - 2.27
D_0 = 2.19 X 10^{-6}
g_{44} = 1.1
g_{55} = 2.49

Values of α_i not available.

Heat of Formation

Taken from D. D. Wagman, J. E. Kilpatrick, K. S. Pitzer, and F. D. Rossini, J. Research Natl. Bureau Standards 35, 467 (1945).

Heat Capacity and Entropy

J. S. Gordon (private communication, February, 1961) has used the constants listed above to calculate C_p from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954). The constants are from E. E. Bell and H. H. Nielsen, J. Chem. Phys. 18, 1382 (1950) and H. C. Allen, E. D. Tidwell, and E. K. Plyler, J. Research Natl. Bureau Standards 57, 213 (1956). Heat capacities below 298.15°K have been calculated for a rigidly rotating harmonic oscillator.

Chlorine, Diatomic (Cl_2)

(Reference State - Ideal Gas) Mol. Wt. = 70.906

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.194	.000	.000	.000
100	7.001	45.150	60.130	-1.498	.000	.000	.000
200	7.576	50.156	54.016	-.772	.000	.000	.000
298	8.111	53.289	53.289	.000	.000	.000	.000
300	8.119	53.339	53.289	.015	.000	.000	.000
400	8.437	55.724	53.612	.845	.000	.000	.000
500	8.624	57.628	54.231	1.698	.000	.000	.000
600	8.741	59.212	54.933	2.567	.000	.000	.000
700	8.821	60.565	55.643	3.445	.000	.000	.000
800	8.878	61.747	56.334	4.331	.000	.000	.000
900	8.922	62.796	56.995	5.221	.000	.000	.000
1000	8.956	63.737	57.623	6.115	.000	.000	.000
1100	8.985	64.592	58.218	7.012	.000	.000	.000
1200	9.010	65.375	58.782	7.912	.000	.000	.000
1300	9.032	66.097	59.318	8.814	.000	.000	.000
1400	9.051	66.767	59.826	9.718	.000	.000	.000
1500	9.069	67.392	60.310	10.624	.000	.000	.000
1600	9.086	67.978	60.771	11.532	.000	.000	.000
1700	9.102	68.530	61.211	12.441	.000	.000	.000
1800	9.117	69.050	61.633	13.352	.000	.000	.000
1900	9.133	69.544	62.036	14.264	.000	.000	.000
2000	9.149	70.013	62.423	15.179	.000	.000	.000
2100	9.166	70.459	62.795	16.094	.000	.000	.000
2200	9.184	70.886	63.154	17.012	.000	.000	.000
2300	9.203	71.295	63.499	17.931	.000	.000	.000
2400	9.223	71.687	63.832	18.852	.000	.000	.000
2500	9.245	72.064	64.154	19.776	.000	.000	.000
2600	9.268	72.427	64.465	20.701	.000	.000	.000
2700	9.293	72.777	64.766	21.629	.000	.000	.000
2800	9.319	73.116	65.058	22.560	.000	.000	.000
2900	9.346	73.443	65.342	23.493	.000	.000	.000
3000	9.374	73.760	65.617	24.429	.000	.000	.000
3100	9.403	74.068	65.885	25.368	.000	.000	.000
3200	9.432	74.367	66.145	26.310	.000	.000	.000
3300	9.461	74.658	66.399	27.255	.000	.000	.000
3400	9.490	74.941	66.646	28.202	.000	.000	.000
3500	9.518	75.216	66.887	29.153	.000	.000	.000
3600	9.546	75.485	67.122	30.106	.000	.000	.000
3700	9.573	75.747	67.352	31.062	.000	.000	.000
3800	9.598	76.002	67.576	32.020	.000	.000	.000
3900	9.622	76.252	67.795	32.981	.000	.000	.000
4000	9.645	76.496	68.010	33.945	.000	.000	.000
4100	9.666	76.734	68.220	34.910	.000	.000	.000
4200	9.685	76.967	68.425	35.878	.000	.000	.000
4300	9.702	77.195	68.626	36.847	.000	.000	.000
4400	9.718	77.419	68.824	37.818	.000	.000	.000
4500	9.732	77.637	69.017	38.791	.000	.000	.000
4600	9.743	77.851	69.207	39.764	.000	.000	.000
4700	9.754	78.061	69.393	40.739	.000	.000	.000
4800	9.762	78.266	69.576	41.715	.000	.000	.000
4900	9.768	78.468	69.755	42.692	.000	.000	.000
5000	9.774	78.665	69.931	43.669	.000	.000	.000
5100	9.778	78.859	70.105	44.646	.000	.000	.000
5200	9.783	79.049	70.275	45.624	.000	.000	.000
5300	9.787	79.235	70.442	46.603	.000	.000	.000
5400	9.790	79.418	70.607	47.582	.000	.000	.000
5500	9.792	79.598	70.768	48.561	.000	.000	.000
5600	9.794	79.774	70.928	49.540	.000	.000	.000
5700	9.795	79.947	71.084	50.520	.000	.000	.000
5800	9.797	80.118	71.239	51.499	.000	.000	.000
5900	9.797	80.285	71.391	52.479	.000	.000	.000
6000	9.798	80.450	71.540	53.459	.000	.000	.000

CHLORINE, DIATOMIC (Cl_2) (IDEAL GAS - REFERENCE STATE) MOL. WT. = 70.906

Ground State Configuration $^1\Sigma^+$

$\Delta H_{f\ 0}^\circ = 0$

$S_{298.15}^\circ = 53.29 \pm 0.01$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298}^\circ = 0$

Electronic Levels and Multiplicities

State	ϵ cm.$^{-1}$	g_1
$^1\Sigma^+$	0	1
$^3\Pi_0^+$	18,147 ± 500	1
$^3\Pi_1$	17,841 ± 500	2
$^3\Pi_2$	17,560 ± 500	2

$\omega_e = 561.1$ cm.$^{-1}$

$\omega_e x_e = 4.0$ cm.$^{-1}$

$\sigma = 2$

$B_e = 0.2408$ cm.$^{-1}$

$\alpha_e = 0.0017$ cm.$^{-1}$

$r_e = 1.986$ Å

Heat of Formation.

The heat of formation (ΔH_f°) for $Cl_2(g)$ is zero at all temperatures, by definition.

Heat Capacity and Entropy.

The functions adopted here were calculated by R. L. Potter, J. Chem. Phys. 31, 1100 (1959) using a direct summation over the energy levels not including those of non-bonding states. The functions are for the naturally occurring isotopic composition.

The absorption spectrum of chlorine has been observed by A. Elliott, Proc. Roy. Soc. A 127, 638 (1930); C. F. Goodeve and B. A. Stephens, Trans. Faraday Soc. 32, 1517 (1936); H. Stammreich, R. Forneris and Y. Tavares, Spectrochim. Acta, 17, 775 (1961); Y. V. Rao and P. Venkateswarlu, J. Mol. Spectr. 9, 173 (1962); and A. E. Douglas, C. K. Moller and B. P. Stoicheff, Can. J. Phys. 41, 1174 (1963). There is disagreement over the vibrational assignments. The listed ground state spectroscopic constants for the naturally occurring isotopic composition are based upon the abundances given by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

The molecular structure of gaseous chlorine was determined by the sector-microphotometer method of electron diffraction by S. Shibata, J. Phys. Chem. 67, 2256 (1963). The value of r_e(Cl-Cl) was found to be 1.986 Å. The other r_e values, 1.983 - 1.989 Å, were reported by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., 1950; W. G. Richards and R. F. Barrow, Proc. Chem. Soc., 297 (1962), and L. S. Bartell and K. Kuchitsu, presented at the International Conference on Magnetism and Crystallography, 1961,quoted by S. Shibata, loc. cit.

Titanium Tetrachloride ($TiCl_4$)

(Liquid) GFW = 189.712

T, °K	$Cp°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200	34.584	46.498	63.496	- 3.400	- 193.496	- 181.719	198.573
298	34.704	60.326	60.326	.000	- 192.200	- 176.226	129.177
300	34.709	60.541	60.327	.065	- 192.177	- 176.127	128.308
400	34.936	70.557	61.691	3.547	- 190.972	- 170.961	93.408
500	35.153	78.376	64.274	7.051	- 189.820	- 166.091	72.598
600	35.370	84.805	67.176	10.577	- 188.698	- 161.452	58.809
700	35.586	90.273	70.095	14.125	- 187.592	- 156.999	49.017
800	35.803	95.039	72.921	17.694	- 186.505	- 152.704	41.717
900	36.020	99.269	75.618	21.285	- 185.430	- 148.542	36.071
1000	36.237	103.075	78.177	24.898	- 184.369	- 144.503	31.581

Sept. 30, 1961; Mar. 31, 1964; Dec. 31, 1967

TITANIUM TETRACHLORIDE ($TiCl_4$) (LIQUID) GFW = 189.712

$S°_{298.15}$ = 60.326 gibbs/mol

$\Delta Hf°_{298.15}$ = -192.2 ± 0.9 kcal/mol

Tm = 249.05°K

$\Delta Hm°$ = 2.382 kcal/mol

Tb = 409°K

$\Delta Hv°$ = 8.55 kcal/mol

Heat of Formation

The heat of formation, $\Delta Hf°_{298.15}$, of $TiCl_4(\ell)$ is calculated from that of $TiCl_4(g)$ and the value of $\Delta Hv°_{298.15}$. The value of $\Delta Hv°_{298}$ is determined from second and third law analyses of fugacity as follows.

	Source	Method	Range	No. Pts.	$\Delta Hv°_{298}$ 2nd Law	$\Delta Hv°_{298}$ 3rd Law	Drift, eu	$\Delta Hf°_{298}$
1.	Pike and Foster (1959)(1)	Manometric	363-415	18*	9.82±0.02	9.83	0.0±0.1	-192.2
2.	Seryakov et al. (1960)(2)	Manometric	358-412	8	9.79±0.03	9.84	0.1±0.1	-192.2
3.	Schafer et al. (1953) (3)	Isoteniscope	313-358	17*	9.86±0.02	9.82	-0.1±0.0	-192.2
4.	Schafer et al. (1953) (3)	Isoteniscope	313-357	16**	9.80±0.01	9.82	0.0±0.0	-192.2
5.	Schafer et al. (1953) (3)	Isoteniscope	313-357	16	9.91±0.02	9.83	-0.2±0.1	-192.2
6.	Schafer et al. (1953) (3)	Isoteniscope	312-359	17	9.90±0.02	9.83	-0.2±0.1	-192.2
7.	Weed (1957) (4)	Manometric	298-319	***	9.79±0.01	9.82	0.1±0.0	-192.2
8.	Weed (1957) (4)	Manometric	298-319	***	9.81±0.01	9.82	0.0±0.0	-192.2
9.	Weed (1957) (4)	Spectra	250-302	***	9.69±0.01	9.80	0.4±0.0	-192.2

* two points rejected due to failure of a statistical test

** three points rejected due to failure of a statistical test

*** selected points from extensive data

Third law analyses of the several vapor pressure sets result in drifts which are proportional to the mean temperatures. Conversion of these data to fugacity eliminates this temperature dependence and the drifts are then scattered randomly about a constant value. This constant value is made to be essentially zero by methods described on the $TiCl_4(g)$ table. The conversion to fugacity was made using Pitzer's method for normal fluids (5). The calculation was carried out using the value of 45.7 atm for the critical pressure, P_c, reported by Minzer (6) and estimated values of 643 ± 15°K for the critical temperature, T_c, and 0.23 ± 0.03 for the acentric constant, ω. Schafer et al. (7) reported a calorimetric determination of $\Delta Hv°_{298}$. Their value of 9.9 ± 0.2 kcal/mol was used to check the reliability of their equipment, assuming that the vapor pressure data (3) gave a more accurate determination of $\Delta Hv°_{298}$. The adopted value of $\Delta Hv°_{298}$ is 9.82 ± 0.02 kcal/mol.

Heat Capacity and Entropy

The entropy and heat capacity of $TiCl_4(\ell)$ has been measured by Furukawa (8). His reported values are adopted.

Melting Data

See $TiCl_4(c)$ table for details.

Vaporization Data

The boiling temperature, Tb, is taken as the temperature at which Kp = 1 for the reaction $TiCl_4(\ell) = TiCl_4(g)$. The vapor pressure data are discussed above.

References

1. F. P. Pike and C. T. Foster, Jr., J. Chem. Eng. Data 4, 305 (1959).
2. G. V. Seryakov, S. A. Vaks, L. S. Sidorina, Zhur. Obshch. Khim 30, 2130 (1960).
3. H. Schafer and F. Zeppenick, Z. Anorg. Chem. 272, 274 (1953).
4. H. C. Weed, Ph.D. Thesis, The Ohio State University, 1957.
5. G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1961.
6. W. Minzer, Naturwissenschaften 45, 126 (1958).
7. H Schafer, G. Breil and G. Pfeffer, Z. Anorg. Chem. 276, 325 (1954).
8. G. T. Furukawa, private communication, U. S. Natl. Bur. Std., 1964.

anium Tetrachloride ($TiCl_4$)

eal Gas) GFW = 189.712

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G^\circ-H^\circ_{298})/T$ (gibbs/mol)	$H^\circ-H^\circ_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 5.166	- 182.026	- 182.026	INFINITE
100	16.117	63.412	103.421	- 4.001	- 182.387	- 179.501	392.299
200	20.582	76.098	86.822	- 2.145	- 182.441	- 176.584	192.962
298	22.852	84.793	84.793	.000	- 182.400	- 173.721	127.341
300	22.881	84.935	84.794	.042	- 182.399	- 173.667	126.516
400	24.008	91.690	85.707	2.393	- 182.326	- 170.767	93.303
500	24.610	97.118	87.464	4.827	- 182.244	- 167.886	73.383
600	24.962	101.439	89.461	7.307	- 182.168	- 165.022	60.109
700	25.183	105.504	91.483	9.815	- 182.102	- 162.171	50.632
800	25.330	108.877	93.451	12.341	- 182.058	- 159.328	43.526
900	25.433	111.867	95.334	14.879	- 182.036	- 156.486	38.000
1000	25.507	114.551	97.124	17.427	- 182.040	- 153.650	33.580
1100	25.563	116.985	98.821	19.980	- 182.070	- 150.808	29.963
1200	25.605	119.211	100.428	22.539	- 183.063	- 147.927	26.941
1300	25.639	121.262	101.953	25.101	- 183.019	- 145.001	24.377
1400	25.665	123.163	103.401	27.666	- 182.991	- 142.076	22.179
1500	25.686	124.934	104.778	30.234	- 182.980	- 139.156	20.275
1600	25.704	126.592	106.090	32.803	- 182.990	- 136.233	18.609
1700	25.719	128.151	107.343	35.375	- 183.019	- 133.308	17.138
1800	25.731	129.622	108.540	37.947	- 183.074	- 130.385	15.831
1900	25.741	131.013	109.686	40.521	- 183.151	- 127.453	14.660
2000	25.750	132.334	110.786	43.095	- 187.705	- 124.366	13.590
2100	25.756	133.590	111.842	45.671	- 187.809	- 121.196	12.613
2200	25.765	134.789	112.856	48.247	- 187.919	- 118.024	11.725
2300	25.770	135.934	113.837	50.824	- 188.030	- 114.842	10.912
2400	25.776	137.031	114.781	53.401	- 188.145	- 111.657	10.160
2500	25.780	138.083	115.692	55.979	- 188.265	- 108.460	9.482
2600	25.784	139.094	116.573	58.557	- 188.387	- 105.274	8.849
2700	25.788	140.068	117.425	61.135	- 188.515	- 102.076	8.262
2800	25.791	141.006	118.250	63.714	- 188.648	- 98.870	7.717
2900	25.794	141.911	119.051	66.294	- 188.784	- 95.661	7.209
3000	25.796	142.785	119.827	68.873	- 188.927	- 92.450	6.735
3100	25.799	143.631	120.582	71.453	- 189.075	- 89.230	6.291
3200	25.801	144.450	121.315	74.033	- 189.229	- 86.010	5.874
3300	25.803	145.244	122.028	76.613	- 189.389	- 82.779	5.482
3400	25.804	146.014	122.722	79.193	- 189.553	- 79.543	5.113
3500	25.806	146.762	123.398	81.774	- 189.724	- 76.311	4.765
3600	25.807	147.489	124.058	84.355	- 291.525	- 72.802	4.420
3700	25.809	148.197	124.700	86.935	- 291.679	- 66.724	3.941
3800	25.810	148.885	125.328	89.516	- 291.849	- 60.648	3.488
3900	25.811	149.555	125.940	92.097	- 292.038	- 54.556	3.057
4000	25.812	150.209	126.539	94.679	- 292.245	- 48.464	2.648
4100	25.813	150.846	127.124	97.260	- 292.466	- 42.369	2.258
4200	25.814	151.468	127.696	99.841	- 292.709	- 36.270	1.887
4300	25.815	152.076	128.256	102.423	- 292.963	- 30.163	1.533
4400	25.816	152.669	128.804	105.004	- 293.233	- 24.041	1.194
4500	25.817	153.249	129.341	107.586	- 293.517	- 17.925	.871
4600	25.817	153.817	129.867	110.168	- 293.811	- 11.793	.560
4700	25.818	154.372	130.383	112.749	- 294.120	- 5.657	.263
4800	25.819	154.916	130.888	115.331	- 294.440	.480	- .022
4900	25.819	155.448	131.384	117.913	- 294.771	6.629	- .296
5000	25.820	155.969	131.870	120.495	- 295.110	12.783	- .559
5100	25.820	156.481	132.348	123.077	- 295.457	18.949	- .812
5200	25.821	156.982	132.817	125.659	- 295.814	25.119	- 1.056
5300	25.821	157.474	133.278	128.241	- 296.180	31.286	- 1.290
5400	25.822	157.957	133.730	130.823	- 296.553	37.472	- 1.517
5500	25.822	158.431	134.175	133.406	- 296.930	43.666	- 1.735
5600	25.823	158.896	134.612	135.988	- 297.315	49.853	- 1.946
5700	25.823	159.353	135.042	138.570	- 297.706	56.054	- 2.149
5800	25.823	159.802	135.465	141.152	- 298.101	62.271	- 2.346
5900	25.824	160.243	135.882	143.735	- 298.501	68.483	- 2.537
6000	25.824	160.677	136.291	146.317	- 298.906	74.706	- 2.721

Sept. 30, 1961; Mar. 31, 1964; Dec. 31, 1967

TITANIUM TETRACHLORIDE ($TiCl_4$) (IDEAL GAS) GFW = 189.712

Point Group T_d

ΔHf°_0 = -182.0 ± 0.9 kcal/mol

S°_{298} = 84.8 ± 0.7 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -182.4 ± 0.9 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
388 (1)	498.5 (3)
111 (2)	131 (3)

Bond Distance: Ti-Cl = 2.185 Å

Bond Angle: Cl-Ti-Cl = 109° 28'

σ = 12

Product of the Moments of Inertia: $I_AI_BI_C = 4.2092 \times 10^{-112}\ g^3\ cm^6$

Heat of Formation

The heat of formation, ΔHf°_{298}, of $TiCl_4(g)$ and $TiCl_4(\ell)$ has been measured by several investigators. The results of these measurements are as follows.

Investigators	Method	Reaction	ΔHf°_{298}, kcal/mol $TiCl_4(\ell)$	$TiCl_4(g)$
Johnson et al. (1959) (1)	Calorimetric	$Ti(c)+2Cl_2(g) = TiCl_4(g)$	(-192.2)	-182.4±0.7
Farber and Darnell (1955) (2)	Equilibrium	$TiO_2(c)+4HCl(g) = TiCl_4(g)+2H_2O(g)$	(-192.7)	-182.9±0.5
Skinner and Ruehrwein (1955) (3)	Calorimetric	$Ti(c)+xCl_2(g) = [TiCl_4+(x-2)Cl_2]$ soln	-190.3±3.0	(-180.5)
Gross et al.(1957) (4)	Calorimetric	$Ti(c)+xCl_2(\ell) = [TiCl_4+(x-2)Cl_2]$ soln	-191.5±0.3	(-181.7)
Krieve et al. (1956) (5)	Calorimetric	$Ti(c)+xCl_2(g) = [TiCl_4+(x-2)Cl_2]$ soln	-190.0±0.4	(-180.2)
Thomsen (1882) (6)		$TiCl_4(\ell)+2H_2O(\ell) = 4HCl_{(0.002\ m)}+TiO_2(c)$	-194.5	(-184.7)

The chosen value of ΔHf°_{298} is that reported by Johnson et al. (1). This investigation has the advantage of being independent of the heat of vaporization of chlorine and any heats of solution in deriving the value of the heat of formation.

Heat Capacity and Entropy

The adopted value for the interatomic distance is that reported by Kimura et al. (7). The tetrahedral structure was established by the Raman work of Bhagavantam (8). The vibrational frequencies determined from the infrared and Raman spectra of $TiCl_4$ by Hawkins and Carpenter (9) are adjusted downward 8 cm^{-1} for ν_2 and ν_4 so that the heats of vaporization determined by both second and third law methods are in agreement. See $TiCl_4(\ell)$ table for details. The principal moments of inertia are: $I_A = I_B = I_C = 74.943 \times 10^{-39}\ g\ cm^2$.

References

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Copper (Cu)

(Reference State) At. Wt. = 63.54

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P .
0	.000	.000	INFINITE	- 1.195	.000	.000	.000
100	3.826	2.392	12.749	- 1.036	.000	.000	.000
200	5.399	5.661	8.437	- .555	.000	.000	.000
298	5.843	7.913	7.913	.000	.000	.000	.000
300	5.846	7.949	7.913	.011	.000	.000	.000
400	6.077	9.665	8.146	.608	.000	.000	.000
500	6.250	11.040	8.591	1.224	.000	.000	.000
600	6.394	12.193	9.098	1.857	.000	.000	.000
700	6.516	13.188	9.613	2.502	.000	.000	.000
800	6.620	14.064	10.116	3.159	.000	.000	.000
900	6.725	14.850	10.599	3.826	.000	.000	.000
1000	6.822	15.564	11.060	4.504	.000	.000	.000
1100	6.910	16.218	11.500	5.190	.000	.000	.000
1200	6.998	16.823	11.918	5.886	.000	.000	.000
1300	7.086	17.387	12.318	6.590	.000	.000	.000
1400	7.500	20.263	12.772	10.488	.000	.000	.000
1500	7.500	20.780	13.288	11.238	.000	.000	.000
1600	7.500	21.264	13.772	11.988	.000	.000	.000
1700	7.500	21.719	14.226	12.738	.000	.000	.000
1800	7.500	22.148	14.654	13.488	.000	.000	.000
1900	7.500	22.553	15.060	14.238	.000	.000	.000
2000	7.500	22.938	15.444	14.988	.000	.000	.000
2100	7.500	23.304	15.810	15.738	.000	.000	.000
2200	7.500	23.653	16.158	16.488	.000	.000	.000
2300	7.500	23.986	16.491	17.238	.000	.000	.000
2400	7.500	24.305	16.810	17.988	.000	.000	.000
2500	7.500	24.612	17.116	18.738	.000	.000	.000
2600	7.500	24.906	17.410	19.488	.000	.000	.000
2700	7.500	25.189	17.693	20.238	.000	.000	.000
2800	7.500	25.462	17.966	20.988	.000	.000	.000
2900	5.892	51.236	18.686	94.396	.000	.000	.000
3000	6.010	51.438	19.774	94.991	.000	.000	.000
3100	6.131	51.637	20.799	95.598	.000	.000	.000
3200	6.253	51.834	21.766	96.217	.000	.000	.000
3300	6.375	52.028	22.680	96.849	.000	.000	.000
3400	6.496	52.220	23.546	97.492	.000	.000	.000
3500	6.616	52.410	24.368	98.148	.000	.000	.000
3600	6.732	52.598	25.149	98.815	.000	.000	.000
3700	6.846	52.784	25.894	99.494	.000	.000	.000
3800	6.954	52.968	26.604	100.184	.000	.000	.000
3900	7.059	53.150	27.282	100.885	.000	.000	.000
4000	7.158	53.330	27.931	101.596	.000	.000	.000
4100	7.251	53.508	28.553	102.316	.000	.000	.000
4200	7.339	53.684	29.149	103.046	.000	.000	.000
4300	7.421	53.858	29.722	103.784	.000	.000	.000
4400	7.498	54.029	30.272	104.530	.000	.000	.000
4500	7.568	54.198	30.802	105.283	.000	.000	.000
4600	7.633	54.365	31.312	106.043	.000	.000	.000
4700	7.693	54.530	31.805	106.810	.000	.000	.000
4800	7.747	54.693	32.280	107.582	.000	.000	.000
4900	7.797	54.853	32.739	108.359	.000	.000	.000
5000	7.842	55.011	33.183	109.141	.000	.000	.000
5100	7.884	55.167	33.612	109.927	.000	.000	.000
5200	7.921	55.320	34.028	110.718	.000	.000	.000
5300	7.955	55.471	34.431	111.512	.000	.000	.000
5400	7.987	55.620	34.822	112.309	.000	.000	.000
5500	8.016	55.767	35.202	113.109	.000	.000	.000
5600	8.043	55.912	35.570	113.912	.000	.000	.000
5700	8.069	56.054	35.929	114.717	.000	.000	.000
5800	8.094	56.195	36.277	115.526	.000	.000	.000
5900	8.118	56.334	36.616	116.336	.000	.000	.000
6000	8.142	56.470	36.945	117.149	.000	.000	.000

Dec. 31, 1965

COPPER (Cu) (REFERENCE STATE) AT. WT. = 63.54

0	to 1356.6°K.	Crystal
1356.6	to 2848°K.	Liquid
2848	to 6000°K.	Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

Copper (Cu)

(Crystal) At. Wt. = 63.54

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_P
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-1.195	.000	.000	INFINITE
100	3.826	2.392	12.749	-1.036	.000	.000	.001
200	5.399	5.661	8.437	-.555	.000	.000	.000
298	5.843	7.913	7.913	.000	.000	.000	.000
300	5.846	7.949	7.913	.011	.000	.000	.000
400	6.077	9.665	8.146	.608	.000	.000	.000
500	6.250	11.040	8.591	1.224	.000	.000	.000
600	6.394	12.193	9.098	1.857	.000	.000	.000
700	6.516	13.188	9.613	2.502	.000	.000	.000
800	6.620	14.064	10.116	3.159	.000	.000	.000
900	6.725	14.850	10.599	3.826	.000	.000	.000
1000	6.822	15.564	11.060	4.504	.000	.000	.000
1100	6.910	16.218	11.500	5.190	.000	.000	.000
1200	6.998	16.823	11.918	5.886	.000	.000	.000
1300	7.086	17.387	12.318	6.590	.000	.000	.000
1400	7.174	17.915	12.699	7.303	-3.185	.102	-.016
1500	7.262	18.413	13.063	8.025	-3.213	.337	-.049
1600	7.350	18.885	13.413	8.755	-3.233	.574	-.078
1700	7.438	19.333	13.748	9.495	-3.243	.813	-.105
1800	7.526	19.761	14.070	10.243	-3.245	1.052	-.128
1900	7.614	20.170	14.380	11.000	-3.238	1.290	-.148
2000	7.702	20.563	14.680	11.766	-3.222	1.528	-.167

Dec. 31, 1965

COPPER (Cu) (CRYSTAL) AT. WT. = 63.54

$S^\circ_{298.15}$ = 7.913 ± 0.04 cal. deg.$^{-1}$ mole^{-1}

T_m = 1356.6°K.

$\Delta H^\circ_{f\ 0}$ = 0 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 0 kcal. mole^{-1}

ΔH°_m = 3.17 ± 0.15 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ = 81 ± 0.4 kcal. mole^{-1}

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The low temperature specific heat of copper has been measured by several workers and generally there is good agreement. The selected values lie close to the determinations of J. A. Kok and W. H. Keesom (1.2-20°K), Physica 3, 1035 (1936); D. L. Martin (20-300°K), Can. J. Phys. 38, 17 (1960); C. B. Satterthwaite, R. S. Craig and W. E. Wallace, J. Am. Chem. Soc. 76, 232 (1954), and S. M. Dockerty, Can. J. Research 9, 84 (1933) and 15A, 59 (1937). Several other workers have reported values of C_p slightly higher than the adopted values especially W. F. Giauque and P. F. Meads, J. Am. Chem. Soc. 63, 1897 (1941), however these measurements were not used for reasons discussed by Martin. The heat capacity above room temperature has been determined directly by several workers, the values of R. E. Pawel and E. E. Stansbury, J. Phys. Chem. Solids 26, 607 (1965) join well with the low temperature data and are adopted. These values lie within 1% of the values adpoted by R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley "Selected Values of Thermodynamic Properties of Metals and Alloys", John Wiley and Sons, Inc., New York,1963. Several determinations of the solid enthalpy are also in good agreement with selected heat capacity curve. For references to these determinations refer to Hultgren et al. loc. cit.

Melting Data.

The melting point of copper is well established and the recent determination of W. Heyne, Exptl. Tech. Physik. 12, 87 (1964) is adopted. The heat of fusion was obtained from the calculated enthalpy of the solid at the melting point and the liquid enthalpy measurements of F. Wust, A. Meuthen and R. Durrer, Forsch. Geb. Ingenieurw. VDI-Forsch. 204 (1918). The liquid enthalpies of I. B. Fieldhouse, J. C. Hedge, J. I. Lang and T. E. Waterman, ASTIA Doc. No. A. D. 150954 are somewhat higher than the adopted values.

Sublimation Data.

See Cu(g) for details.

Copper (Cu)

(Liquid) At. Wt. = 63.54

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	7.500	8.663	8.663	.000	2.224	2.000	-1.466
300	7.500	8.709	8.663	.014	2.227	1.999	-1.456
400	7.500	10.867	8.957	.764	2.380	1.899	-1.038
500	7.500	12.541	9.513	1.514	2.514	1.763	-.771
600	7.500	13.908	10.135	2.264	2.631	1.602	-.583
700	7.500	15.064	10.759	3.014	2.736	1.423	-.444
800	7.500	16.066	11.361	3.764	2.829	1.227	-.335
900	7.500	16.949	11.934	4.514	2.912	1.023	-.248
1000	7.500	17.739	12.475	5.264	2.984	.809	-.177
1100	7.500	18.454	12.987	6.014	3.048	.588	-.117
1200	7.500	19.107	13.470	6.764	3.102	.361	-.066
1300	7.500	19.707	13.927	7.514	3.148	.132	-.022
1400	7.500	20.263	14.360	8.264	.000	.000	.000
1500	7.500	20.780	14.771	9.014	.000	.000	.000
1600	7.500	21.264	15.162	9.764	.000	.000	.000
1700	7.500	21.719	15.534	10.514	.000	.000	.000
1800	7.500	22.148	15.890	11.264	.000	.000	.000
1900	7.500	22.553	16.230	12.014	.000	.000	.000
2000	7.500	22.938	16.556	12.764	.000	.000	.000
2100	7.500	23.304	16.869	13.514	.000	.000	.000
2200	7.500	23.653	17.169	14.264	.000	.000	.000
2300	7.500	23.986	17.458	15.014	.000	.000	.000
2400	7.500	24.305	17.737	15.764	.000	.000	.000
2500	7.500	24.611	18.006	16.514	.000	.000	.000
2600	7.500	24.906	18.266	17.264	.000	.000	.000
2700	7.500	25.189	18.517	18.014	.000	.000	.000
2800	7.500	25.461	18.760	18.764	.000	.000	.000
2900	7.500	25.725	18.996	19.514	-72.658	1.324	-.100
3000	7.500	25.979	19.224	20.264	-72.503	3.874	-.282
3100	7.500	26.225	19.446	21.014	-72.360	6.417	-.452
3200	7.500	26.463	19.662	21.764	-72.229	8.958	-.612
3300	7.500	26.694	19.871	22.514	-72.111	11.491	-.761
3400	7.500	26.918	20.075	23.264	-72.004	14.023	-.901
3500	7.500	27.135	20.274	24.014	-71.910	16.552	-1.034
3600	7.500	27.346	20.467	24.764	-71.827	19.080	-1.158
3700	7.500	27.552	20.656	25.514	-71.756	21.602	-1.276
3800	7.500	27.752	20.840	26.264	-71.696	24.125	-1.387
3900	7.500	27.947	21.020	27.014	-71.647	26.645	-1.493
4000	7.500	28.136	21.195	27.764	-71.608	29.168	-1.594

Dec. 31, 1965

COPPER (Cu) (LIQUID) AT. WT. = 63.54

$S^\circ_{298.15}$ = 8.663 cal. deg.$^{-1}$ mole^{-1}

T°_m = 1356.6°K.

T°_b = 2848°K.

$\Delta H^\circ_{f\ 298.15}$ = 2.224 kcal. mole^{-1}

ΔH°_m = 3.17 ± 0.15 kcal. mole^{-1}

ΔH°_v = 72.743 kcal. mole^{-1}

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding ΔH°_m and the difference between $H_{1356.6}-H_{298}$ for (c) and (l).

Heat Capacity and Entropy.

The heat capacity was calculated from the enthalpy data of F. Wust, A. Meuthen and R. Durrer, Forsch. Geb. Ingenieurw. VDI-Forsch. 204 (1918). The entropy was obtained in a manner analagous to the heat of formation.

Melting Data.

See crystal table for details.

Vaporization Data.

The boiling point and heat of vaporization were calculated from the adopted functions and heat of sublimation in order to maintain proper thermodynamic consistency.

Copper (Cu)

(Ideal Gas) At. Wt. = 63.54

T, °K.	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
0	.000	.000	INFINITE	- 1.481	80.714	80.714	INFINITE
100	4.968	34.317	44.161	- .984	81.052	77.859	- 170.153
200	4.968	37.760	40.198	- .488	81.067	74.648	- 81.567
298	4.968	39.744	39.744	.000	81.000	71.510	- 52.415
300	4.968	39.775	39.744	.009	80.998	71.450	- 52.049
400	4.968	41.204	39.939	.506	80.898	68.282	- 37.306
500	4.968	42.313	40.307	1.003	80.779	65.142	- 28.472
600	4.968	43.218	40.719	1.500	80.643	62.028	- 22.592
700	4.968	43.984	41.132	1.996	80.494	58.937	- 18.400
800	4.968	44.648	41.531	2.493	80.334	55.867	- 15.261
900	4.968	45.233	41.911	2.990	80.164	52.819	- 12.826
1000	4.968	45.756	42.269	3.487	79.983	49.791	- 10.881
1100	4.969	46.230	42.608	3.984	79.794	46.781	- 9.294
1200	4.970	46.662	42.928	4.481	79.595	43.788	- 7.974
1300	4.972	47.060	43.231	4.978	79.388	40.813	- 6.861
1400	4.977	47.429	43.518	5.475	75.987	37.955	- 5.925
1500	4.985	47.772	43.790	5.973	75.735	35.247	- 5.135
1600	4.997	48.094	44.049	6.472	75.484	32.556	- 4.447
1700	5.016	48.398	44.296	6.973	75.235	29.881	- 3.841
1800	5.041	48.685	44.532	7.476	74.988	27.221	- 3.305
1900	5.074	48.959	44.758	7.981	74.743	24.572	- 2.826
2000	5.116	49.220	44.975	8.491	74.503	21.939	- 2.397
2100	5.168	49.471	45.183	9.005	74.267	19.316	- 2.010
2200	5.229	49.713	45.383	9.525	74.037	16.705	- 1.659
2300	5.300	49.947	45.577	10.051	73.813	14.103	- 1.340
2400	5.380	50.174	45.763	10.585	73.597	11.511	- 1.048
2500	5.468	50.395	45.944	11.127	73.389	8.932	- .781
2600	5.565	50.612	46.120	11.679	73.191	6.355	- .534
2700	5.668	50.823	46.290	12.241	73.003	3.791	- .307
2800	5.778	51.032	46.456	12.813	72.825	1.229	- .096
2900	5.892	51.236	46.617	13.396	.000	.000	.000
3000	6.010	51.438	46.774	13.991	.000	.000	.000
3100	6.131	51.637	46.928	14.598	.000	.000	.000
3200	6.253	51.834	47.078	15.218	.000	.000	.000
3300	6.375	52.028	47.225	15.849	.000	.000	.000
3400	6.496	52.220	47.369	16.493	.000	.000	.000
3500	6.616	52.410	47.511	17.148	.000	.000	.000
3600	6.732	52.598	47.649	17.816	.000	.000	.000
3700	6.846	52.784	47.786	18.495	.000	.000	.000
3800	6.954	52.968	47.920	19.185	.000	.000	.000
3900	7.059	53.150	48.051	19.885	.000	.000	.000
4000	7.158	53.330	48.181	20.596	.000	.000	.000
4100	7.251	53.508	48.309	21.317	.000	.000	.000
4200	7.339	53.684	48.435	22.046	.000	.000	.000
4300	7.421	53.858	48.559	22.784	.000	.000	.000
4400	7.498	54.029	48.681	23.530	.000	.000	.000
4500	7.568	54.198	48.802	24.284	.000	.000	.000
4600	7.633	54.365	48.921	25.044	.000	.000	.000
4700	7.693	54.530	49.039	25.810	.000	.000	.000
4800	7.747	54.693	49.155	26.582	.000	.000	.000
4900	7.797	54.853	49.269	27.359	.000	.000	.000
5000	7.842	55.011	49.383	28.141	.000	.000	.000
5100	7.884	55.167	49.495	28.928	.000	.000	.000
5200	7.921	55.320	49.605	29.718	.000	.000	.000
5300	7.955	55.471	49.714	30.512	.000	.000	.000
5400	7.987	55.620	49.822	31.309	.000	.000	.000
5500	8.016	55.767	49.929	32.109	.000	.000	.000
5600	8.043	55.912	50.035	32.912	.000	.000	.000
5700	8.069	56.054	50.139	33.718	.000	.000	.000
5800	8.094	56.195	50.242	34.526	.000	.000	.000
5900	8.118	56.334	50.344	35.337	.000	.000	.000
6000	8.142	56.470	50.445	36.150	.000	.000	.000

Dec. 31, 1965

COPPER (Cu) (IDEAL GAS) AT. WT. = 63.54

Ground State Configuration $^2S_{1/2}$

$S^\circ_{298.15}$ = 39.744 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 80.714 ± 0.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 81.0 ± 0.5 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_1, cm.$^{-1}$	g_1	ϵ_1, cm.$^{-1}$	g_1	ϵ_1, cm.$^{-1}$	g_1	ϵ_1, cm.$^{-1}$	g_1
0.0	2	44406.3	6	54784.0	4	57948.7	4
11202.6	6	44544.2	4	55027.7	2	57893.1	4
13245.4	4	44915.6	2	55387.7	4	57895.1	6
30535.3	2	43726.2	6	55391.3	6	57905.2	6
30783.7	4	44963.2	8	55426.3	8	57908.7	8
39018.7	6	45821.0	2	55429.8	6	58568.9	2
40114.0	4	45879.3	4	56030.0	8	59249.5	4
40943.7	2	46172.8	4	58119.3	6	59250.7	6
40909.1	10	46598.4	6	56343.7	4	59275.3	4
41153.4	8	49383.0	4	58364.7	2	59323.2	2
41562.9	6	49383.3	2	56651.5	6	59647.9	2
42302.5	4	49935.2	4	58690.9	4	60070.0	16
43137.2	2	49942.1	6	56671.4	2	60595.0	16
43514.0	8	52848.8	2	57419.3	2	61150.0	26

Heat of Formation.

The heat of sublimation has been determined by second and third law analysis of the vapor pressure data of a large number of investigators. The results are summarized below:

Ref.	Range°K.	Method	Points	$\Delta H^\circ_{subl.\ 298.15}$ kcal. mole^{-1}		Drift
				2nd law	3rd law	cal. deg.$^{-1}$ mole^{-1}
1.	1242-1340	Knudsen	6	80.6 ± 0.2	81.39 ± 0.04	0.3 ± 0.2
1.	1370-1563	Knudsen	10*	83.0 ± 0.6	81.34 ± 0.2	-1.0 ± 0.5
2.	1367-1523	Langmuir	8	79.8 ± 1.6	80.20 ± 0.3	0.3 ± 1.2
3.	1605-1879	Transport	21*	79.7 ± 0.6	80.55 ± 0.25	0.5 ± 0.4
4.	1192-1360	Knudsen	13	80.6 ± 4.0	81.16 ± 1.2	0.4 ± 3.1
5.	1143-1292	Langmuir	5	81.3 ± 1.0	80.61 ± 0.2	-0.6 ± 0.8
6.	1475-1707	Knudsen	8	83.2 ± 1.3	81.05 ± 0.4	-1.4 ± 0.8
7.	987-1330	Knudsen	14	80.5 ± 2.3	82.14 ± 1.7	2.7 ± 2.0
8.	1356-1466	Langmuir	5	79.1 ± 2.3	79.96 ± 0.3	1.1 ± 1.6
8.	1268-1320	Langmuir	7*	92.5 ± 3.3	81.26 ± 0.5	-8.9 ± 2.6
9.	1429-1640	Knudsen	9	76.6 ± 1.0	80.30 ± 0.4	2.3 ± 0.6
10.	1419-1463	Knudsen	7	63.0 ± 11.7	81.84 ± 0.8	12.9 ± 8.2
11.	1083	Transport	1		79.2	
12.	2138-2643	Boiling	4	93.5 ± 4.3	77.25 ± 2.8	-6.3 ± 1.7
13.	2378-2573	Boiling	5	120.0 ± 8.0	76.1 ± 2.8	-18.0 ± 3.3
14.	2253-2583	Boiling	3	76.3 ± 13.8	75.0 ± 2.0	-0.9 ± 5.9
15.	1768-2116	Boiling	6	66.2 ± 2.5	73.5 ± 1.3	3.5 ± 1.3

*1 Point rejected due to failure of statistical test.

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The first eight references may be considered to have reasonable drifts and second and third law agreement. The three Langmuir values are grouped closely together at about 80.3 kcal. mole^{-1}. The Knudsen values all lie a little higher averaging 81.4 kcal. mole^{-1}, the single transport determination is at 80.55 kcal. mole^{-1}. If the evaporation coefficient is not unity in the Langmuir experiments then one would observe lower pressures and higher heats of sublimation, thus it appears that the coefficient must be unity and that all techniques are measuring valid heats of sublimation. A value of 81 ± 0.5 kcal. mole^{-1} was chosen weighted toward the more precise Knudsen work of Hersh.

Heat Capacity and Entropy.

The electronic ground state configuration and higher electronic levels were taken from C. E. Moore "Atomic Energy Levels", Natl. Bur. Stds. Circular 467, Washington 1952.

Copper Monoxide (CuO)

(Crystal) GFW = 79.5394

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-1.695	-36.713	-36.713	INFINITE
100	3.945	2.335	17.732	-1.540	-37.063	-34.988	76.466
200	8.321	6.460	11.058	-.920	-37.272	-32.810	35.853
298	10.066	10.183	10.183	.000	-37.250	-30.622	22.446
300	10.094	10.245	10.183	.019	-37.249	-30.581	22.278
400	11.244	13.323	10.595	1.091	-37.129	-28.374	15.503
500	11.960	15.914	11.406	2.254	-36.948	-26.204	11.454
600	12.500	18.145	12.348	3.478	-36.734	-24.076	8.770
700	12.980	20.108	13.319	4.752	-36.494	-21.984	6.864
800	13.430	21.871	14.280	6.073	-36.229	-19.930	5.445
900	13.870	23.478	15.214	7.438	-35.938	-17.909	4.349
1000	14.310	24.962	16.115	8.847	-35.621	-15.923	3.480
1100	14.750	26.347	16.983	10.300	-35.273	-13.970	2.776
1200	15.190	27.649	17.818	11.797	-34.896	-12.050	2.195
1300	15.630	28.882	18.622	13.338	-34.488	-10.161	1.708
1400	16.070	30.057	19.397	14.923	-37.233	-8.206	1.281
1500	16.510	31.180	20.146	16.552	-36.789	-6.147	.896
1600	16.950	32.260	20.869	18.225	-36.305	-4.121	.563
1700	17.390	33.301	21.570	19.942	-35.779	-2.125	.273
1800	17.830	34.307	22.250	21.703	-35.212	-.160	.019
1900	18.270	35.283	22.910	23.508	-34.605	1.770	-.204
2000	18.710	36.231	23.553	25.357	-33.956	3.668	-.401

June 30, 1966

COPPER MONOXIDE (CuO) (CRYSTAL) GFW = 79.5394

ΔHf°_0 = -36.71 kcal/mol

$S^\circ_{298.15}$ = 10.18 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -37.25 ± 0.5 kcal/mol

Td = 1395°K

Heat of Formation.

The more consistent data relative to the heat of formation are reviewed below. The selected value of -37.25 kcal/mol was derived from ΔHf°_{298} = -40.7 kcal/mol for $Cu_2O(c)$ and ΔHr°_{298} = 33.80 kcal/mol for $2CuO(c) = Cu_2O(c) + 0.5\ O_2$. Four different sets of oxygen dissociation pressure measurements yield heats of reaction in close agreement with each other and with the aqueous calorimetry of Thomsen. Thomsen's data may be reduced to the heat of reduction of CuO(c) with H_2 by combining heats of reaction for $CuO + H_2SO_4$, $Fe + H_2SO_4$, and $Fe + CuSO_4(aq)$. Direct calorimetric measurement of the heat of reduction by von Wartenberg and Werth yields ΔHf°_{298} = -38.04 ± 0.2 when corrected for incomplete condensation of water. Direct measurement is difficult and this value may correspond to incomplete reduction. The value of -33.02 reported by Wöhler and Jochum, Z. physik. Chem. 167A, 169 (1933), is unreasonable. Equilibrium constants derived from Balesdent and Chiche yield -37.6 kcal/mol by third law analysis, but a serious entropy error is present. This is no doubt due to uncertainties in the activity of Cu in Cu-Au alloys. Other data have been reviewed by Randall, Nielsen and West, Ind. Eng. Chem. 23, 388 (1931).

					ΔHr°_{298}(kcal/mol)			
Author	Method	Reaction**	Temp.	No. of Points	2nd Law	3rd Law	Drift (eu)	ΔHr°_{298}* (kcal/mol)
1. Thomsen (1883)	Aqueous Calorimetry	A	291	—	-31.15		—	-37.16
2. Wartenberg et al. (1932)	Calorimetry	A	295	—	-30.27±0.2		—	-38.04
3. Balesdent (1955)	Equilibrium Data	B	1011-1156	32	68.2 ±0.7	75.18	6.4±0.7	-37.59
4. Assayag (1955)	Kp	C	1047-1342	11	33.28±0.15	33.81	0.4±0.1	-37.25
5. Becker (1927)	Kp	C	1193-1293	6	33.84±0.27	33.80	0.0±0.2	-37.25
6. Roberts et al. (1921)	Kp	C	1189-1358	20	33.96±0.07	33.76	-0.1±0.1	-37.23
7. Foote et al. (1908)	Kp	C	1223-1323	7	33.19±0.17	33.74	0.4±0.1	-37.22
8. Combined 4,5,6,7	Kp	C	1047-1358	45	33.70±0.10	33.77	0.04±0.09	-37.24

*Based on third law where possible.

**Reaction A: $CuO(c) + H_2 = Cu(c) + H_2O(l)$ B: $2CuO(c) = 2Cu(c) + O_2$

C: $2CuO(c) = Cu_2O(c) + 0.5\ O_2$

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Heat Capacity and Entropy.

Low temperature values are based on data (15-297°K) from J. Hu and H. L. Johnston, J. Am. Chem. Soc. 75, 2471 (1953). Earlier data from R. W. Millar (71-302°K), J. Am. Chem. Soc. 51, 215 (1929), are in satisfactory agreement, while those of K. Clusius and P. Harteck (30-200°K), Z. physik. Chem. 134, 243 (1928), are higher by several percent. A small anomaly in the heat capacity is observed in the region 210-230°K. Magnetic measurements of M. O'Keefe and F. S. Stone, Phys. Chem. Solids 23, 261 (1962), and neutron diffraction studies of B. N. Brockhouse, Phys. Rev. 94, 781 (1954), suggest that this is a Néel point associated with antiferromagnetism. The entropy was obtained from the heat capacities based on S°_{15} = 0.016 eu.

High temperature values are based on specific heats (373-1273°K) obtained from a dynamic method by D. M. Chizhikov and A. S. Khirik, Tr. Inst. Met. im. A. A. Baikova, Akad. Nauk SSSR, No. 12, 79 (1963); cf. Chem. Abs. 59, 5800 b (1963). Enthalpy data (523-1253°K) of Wöhler and Jochum, loc. cit., lead to a value for S°_{1200} lower by about 0.25 eu, but this is inconsistent with the equilibrium data for $2CuO = Cu_2O + 0.5\ O_2$.

Temperature of Decomposition.

T_d is calculated as the temperature at which ΔF equals zero for $2CuO(c) = Cu_2O(c) + 0.5\ O_2(g)$.

Copper Monoxide (CuO)

(Ideal Gas) GFW = 79.5394

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.333	58.800	58.800	INFINITE
100	7.573	47.222	63.437	- 1.622	59.005	56.592	- 123.681
200	8.245	52.723	56.843	- .824	58.973	54.183	- 59.208
298	8.522	56.072	56.072	.000	58.900	51.847	- 38.005
300	8.526	56.124	56.072	.016	58.898	51.803	- 37.738
400	8.689	58.601	56.408	.877	58.807	49.451	- 27.019
500	8.791	60.552	57.049	1.752	58.700	47.125	- 20.598
600	8.862	62.161	57.771	2.634	58.572	44.821	- 16.326
700	8.921	63.532	58.498	3.524	58.428	42.541	- 13.282
800	8.982	64.727	59.204	4.419	58.267	40.281	- 11.004
900	9.049	65.789	59.878	5.320	58.094	38.043	- 9.238
1000	9.126	66.746	60.517	6.229	57.911	35.825	- 7.830
1100	9.211	67.620	61.124	7.146	57.723	33.626	- 6.681
1200	9.301	68.425	61.699	8.071	57.528	31.443	- 5.727
1300	9.394	69.174	62.246	9.006	57.331	29.278	- 4.922
1400	9.486	69.873	62.766	9.950	53.945	27.229	- 4.251
1500	9.575	70.531	63.262	10.903	53.712	25.328	- 3.690
1600	9.658	71.151	63.736	11.865	53.485	23.443	- 3.202
1700	9.735	71.739	64.189	12.835	53.264	21.573	- 2.773
1800	9.805	72.298	64.624	13.812	53.047	19.716	- 2.394
1900	9.867	72.829	65.042	14.795	52.833	17.869	- 2.055
2000	9.922	73.337	65.444	15.785	52.622	16.035	- 1.752
2100	9.969	73.822	65.832	16.779	52.414	14.211	- 1.479
2200	10.009	74.287	66.206	17.778	52.207	12.397	- 1.231
2300	10.043	74.733	66.567	18.781	52.002	10.590	- 1.006
2400	10.071	75.161	66.916	19.787	51.797	8.795	- .801
2500	10.094	75.572	67.254	20.795	51.591	7.008	- .613
2600	10.112	75.968	67.582	21.805	51.385	5.229	- .440
2700	10.127	76.350	67.899	22.817	51.178	3.458	- .280
2800	10.138	76.719	68.208	23.831	50.970	1.695	- .132
2900	10.147	77.075	68.508	24.845	- 21.898	1.262	- .095
3000	10.154	77.419	68.799	25.860	- 21.954	2.063	- .150
3100	10.159	77.752	69.082	26.876	- 22.024	2.865	- .202
3200	10.162	78.075	69.358	27.892	- 22.108	3.670	- .251
3300	10.165	78.387	69.627	28.908	- 22.206	4.475	- .296
3400	10.167	78.691	69.889	29.925	- 22.318	5.285	- .340
3500	10.169	78.986	70.145	30.941	- 22.445	6.098	- .381
3600	10.170	79.272	70.395	31.958	- 22.584	6.917	- .420
3700	10.172	79.551	70.638	32.976	- 22.736	7.738	- .457
3800	10.174	79.822	70.876	33.993	- 22.902	8.564	- .493
3900	10.176	80.086	71.109	35.010	- 23.079	9.393	- .526
4000	10.178	80.344	71.337	36.028	- 23.269	10.228	- .559
4100	10.182	80.595	71.560	37.046	- 23.468	11.069	- .590
4200	10.186	80.841	71.778	38.064	- 23.678	11.914	- .620
4300	10.190	81.080	71.991	39.083	- 23.897	12.767	- .649
4400	10.196	81.315	72.201	40.102	- 24.126	13.619	- .676
4500	10.202	81.544	72.406	41.122	- 24.361	14.479	- .703
4600	10.209	81.768	72.607	42.143	- 24.604	15.346	- .729
4700	10.217	81.988	72.804	43.164	- 24.855	16.217	- .754
4800	10.226	82.203	72.998	44.186	- 25.110	17.096	- .778
4900	10.235	82.414	73.188	45.209	- 25.371	17.975	- .802
5000	10.245	82.621	73.374	46.233	- 25.636	18.862	- .824
5100	10.256	82.824	73.558	47.258	- 25.906	19.758	- .847
5200	10.268	83.023	73.738	48.285	- 26.179	20.651	- .868
5300	10.281	83.219	73.915	49.312	- 26.455	21.555	- .889
5400	10.294	83.411	74.089	50.341	- 26.734	22.462	- .909
5500	10.307	83.600	74.260	51.371	- 27.015	23.378	- .929
5600	10.322	83.786	74.428	52.402	- 27.298	24.297	- .948
5700	10.337	83.969	74.594	53.435	- 27.582	25.218	- .967
5800	10.352	84.149	74.757	54.470	- 27.869	26.151	- .985
5900	10.368	84.326	74.918	55.506	- 28.156	27.086	- 1.003
6000	10.384	84.500	75.076	56.543	- 28.445	28.022	- 1.021

Sept. 30, 1966; June 30, 1970

COPPER MONOXIDE (CuO) (IDEAL GAS) GFW = 79.5394

Symmetry Number = 1 ΔHf°_0 = 58.8 ± 8 kcal/mol

$S^\circ_{298.15}$ = 56.07 ± 0.1 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 58.9 ± 8 kcal/mol

Electronic Levels and Molecular Constants

State	ϵ_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
$X^2\Pi$	0	2	1.726	0.4446	[0.0034]	632	[3.5]
	269	2					
$A^2\Pi$	4460	2		[0.4420]	[0.0040]	633	4.5
	4735	2					
$B^2\Sigma$	20953	2		[0.4426]	[0.0052]	637	6.5
$C^2\Pi$	23550	4		0.4213	[0.0046]	[610]	[5.0]

Heat of Formation

The heat of formation is calculated from that of the crystal, ΔHs°_{298} = 96.1 kcal/mol, which was obtained by 3rd law analysis of the sublimation pressure at 1273°K reported by Mack et al. (1). They employed a transpiration method and analysed for copper (in minute amounts) by its catalytic effect on the oxidation rate of sodium sulfite. The resulting pressure is only 100 times the predicted pressure of Cu(g) over CuO(c). Three pressures were reported but not used in the range 873-1173°K, since these yield a much smaller value for the heat of vaporization and imply a high dissociation energy.

Some estimates of D°_0 CuO obtained by different methods are given below. These estimates along with a correlation of D°_0 values for MnO, FeO, NiO and ZnO favor D°_0 = 82 ± 10, close to the value adopted.

Method	kcal/mol		
	ΔHs°_{298}	D°_0	ΔHf°_{298}
Mack et al. (1) Transpiration	96.1	80.8	58.9
Arithmetic mean of D°_0 for O_2 and Cu_2		82	57.7
Geometric mean of D°_0 for O_2 and Cu_2		73	66.7
Linear Birge Sponer extrapolation of $A^2\Pi$ state		76±12	63.7±12

Heat Capacity and Entropy

The visible spectrum of CuO has been extensively investigated, but only very recently has significant progress been made in its analysis. Antic-Jovanovic et al. (2) were able to obtain a vibrational analysis of the major band system by use of O^{18} isotope studies. Shirk and Bass (3) recently reported absorption and fluorescence spectra in inert-gas matrices which allows assignment of the ground state and the first two excited states. They have strong evidence for the lower state of the blue system being the ground state and also for the second system, which corresponds to the red-orange system, originating in the upper state of the blue system. Thus, it is probable that the B state is $^2\Sigma$ and the X and A states are both $^2\Pi$ with very similar molecular constants, which serves to confuse the analysis of the spectra. It also appears likely that the 4182Å band analysed by Lagerqvist and Uhler (4) is a $^2\Pi$-$^2\Pi$ transition terminating in the ground state; thus we adopt their rotational constants for the X and C states. The vibrational frequencies and anharmonicities for the A and B states were from Antic-Jovanovic (2), as well as the vibrational interval for the ground state. The anharmonicity for the ground state was chosen so as to provide a reasonable Birge-Sponer extrapolation of the dissociation energy. The values of the α_e were estimated from the Morse potential function relations. The rotational constants were assumed to be nearly constant. The values of the splitting in the electronic levels in the X and A states are from Antic-Jovanovic (2), and are roughly confirmed by Shirk and Bass (3).

The thermodynamic functions were calculated by summing over the individual partition functions for the separate states.

References

1. E. Mack, G. O. Osterhof and H. M. Kramer, J. Amer. Chem. Soc. 45, 617 (1923).
2. A. Antic-Jovanovic, D. S. Pesic and A. G. Gaydon, Proc. Roy. Soc. (London) 307A, 399 (1968).
3. J. S. Shirk and A. M. Bass, J. Chem. Phys. 52, 1894 (1970).
4. A. Lagerqvist and U. Uhler, Z. Naturforsch. 22B, 551 (1967).

Dicopper Monoxide (Cu_2O)

(Crystal) GFW = 143.0794

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.037	-40.309	-40.309	INFINITE
100	9.506	8.902	34.082	-2.518	-40.455	-38.798	84.792
200	12.893	16.598	23.537	-1.388	-40.635	-37.069	40.507
298	15.199	22.213	22.213	.000	-40.700	-35.299	25.875
300	15.230	22.307	22.213	.028	-40.700	-35.266	25.691
400	16.580	26.893	22.829	1.626	-40.652	-33.459	18.281
500	17.410	30.687	24.032	3.327	-40.548	-31.671	13.843
600	18.040	33.919	25.417	5.101	-40.418	-29.909	10.894
700	18.620	36.743	26.838	6.934	-40.264	-28.167	8.794
800	19.220	39.269	28.237	8.826	-40.085	-26.454	7.227
900	19.850	41.568	29.592	10.779	-39.873	-24.760	6.013
1000	20.520	43.694	30.897	12.797	-39.624	-23.094	5.047
1100	21.220	45.683	32.152	14.884	-39.329	-21.456	4.263
1200	21.920	47.559	33.358	17.041	-38.988	-19.846	3.614
1300	22.620	49.341	34.520	19.268	-38.597	-18.265	3.071
1400	23.320	51.043	35.640	21.565	-44.528	-16.514	2.578
1500	24.020	52.676	36.721	23.932	-44.097	-14.529	2.117
1600	24.720	54.249	37.768	26.369	-43.598	-12.574	1.718
1700	25.420	55.768	38.782	28.876	-43.032	-10.650	1.369
1800	26.120	57.241	39.767	31.453	-42.400	-8.762	1.064
1900	26.820	58.672	40.725	34.100	-41.700	-6.914	.795
2000	27.520	60.066	41.657	36.817	-40.933	-5.103	.558
2100	28.220	61.425	42.566	39.604	-40.099	-3.330	.347
2200	28.920	62.754	43.454	42.461	-39.198	-1.600	.159
2300	29.620	64.055	44.321	45.388	-38.229	.086	-.008
2400	30.320	65.331	45.170	48.385	-37.193	1.728	-.157
2500	31.020	66.582	46.002	51.452	-36.090	3.333	-.291

June 30, 1966

DICOPPER MONOXIDE (Cu_2O) (CRYSTAL) GFW = 143.0794

ΔHf°_0 = -40.31 kcal/mol

$S^\circ_{298.15}$ = 22.21 ± 0.08 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -40.7 ± 0.5 kcal/mol

Tm = 1509°K

ΔHm° = 13.58 ± 2 kcal/mol

Heat of Formation.

Summarized below are the more consistent results for the heat of formation. The selected value of -40.7 kcal/mol is based on data from Thomsen and from Ishakawa and Kimura. More recent equilibrium data yield essentially the same average for ΔHf but the separate values scatter by about ±0.7 kcal/mol and significant entropy errors are apparent.

Thomsen obtained values of -40.80, -40.87 and -41.51 from aqueous calorimetry using three different paths. He favored the first path which may be recalculated by combination of the heats of reaction of $Cu_2O + H_2SO_4$, $Fe + H_2SO_4$ and $Fe + CuSO_4(aq)$ to yield the heat of reduction of Cu_2O with H_2. Direct measurements of the heat of reduction reported by L. Wöhler and N. Jochum, Z. physik. Chem. 167A, 169 (1933), appear to be unreliable since they lead to -43.0 for the heat of formation. The cell data of Ishakawa and Kimura show very little drift and are in excellent agreement with Thomsen.

Author	Method	Reaction**	Temp. (°K)	No. of Points	ΔHr°_{298} (kcal/mol) 2nd Law	ΔHr°_{298} (kcal/mol) 3rd Law	Drift (eu)	ΔHf°_{298}* (kcal/mol)
1. Thomsen (1883)	Aqueous Calorimetry	A	291	—	-27.61		—	-40.70
2. Hill et al.(1958)	Fused salt Emf	B	987	1		-41.38	—	-41.38
3. Kiukkola et al.(1957)	Emf vs. Fe/Fe_xO	B	1073-1323	4	-43.03±0.56	-40.42	2.1±0.5	-40.42
	Emf vs. Fe_yO/Fe_3O_4	B	1073-1323	4	-44.14±0.10	-40.36	3.1±0.1	-40.36
4. Balesdent (1955)	Equilibrium data	C	1011-1156	28	36.03±1.1	41.20	4.7±1.0	-41.20
5. Makolkin (1942)	Aqueous Emf	D	288- 308	3	29.46±0.7	28.30	-4.0±2.5	-40.02
6. Maier (1929)	Aqueous Emf	D	298-318	7	29.94±0.4	28.07	-6.2±1.3	-40.24
7. Ishakawa et al.(1927)	Aqueous Emf	D	273-318	5	27.42±0.04	27.63	0.7±0.1	-40.69

*Based on 3rd law values wherever possible.

**Reaction A: $Cu_2O(c) + H_2 = 2Cu + H_2O(l)$, B: $2Cu + 0.5\ O_2 = Cu_2O(c)$

C: $Cu_2O(c) = 2Cu + 0.5\ O_2$, D: $2Cu + H_2O(l) = Cu_2O(c) + H_2$.

1. J. Thomsen, "Thermochemische Untersuchungen," vol. III, Barth, Leipzig, 1883.
2. D. G. Hill, B. Porter and A. S. Gillespie, Jr., J. Electrochem. Soc. 105, 408 (1958).
3. K. Kiukkola, C. Wagner, J. Electrochem. Soc. 104, 379 (1957).
4. D. Balesdent, Compt. rend. 240, 760 (1955); 1884 (1955).
5. I. A. Makolkin, J. Phys. Chem. (U.S.S.R.) 16, 13 (1942); cf. Chem. Abs. 37, 2641 (1943).
6. C. G. Maier, J. Am. Chem. Soc. 51, 194 (1929).
7. F. Ishakawa and G. Kimura, "Sexagint, Yikichi Osaka," pp. 255-69, Chem. Inst. Kyoto Imp. Univ., Kyoto, Japan, 1927; cf. Randall, Nielsen and West, Ind. Eng. Chem. 23, 388 (1931).

Heat Capacity and Entropy.

Low temperature values are based on data from L. V. Gregor (2.8-21°K), J. Phys. Chem. 66, 1645 (1962) and from J. Hu and H. L. Johnston (15-300°K), J. Am. Chem. Soc. 73, 4550 (1951). Earlier data by R. W. Millar (76-291°K), J. Am. Chem. Soc. 51, 215 (1929) are in satisfactory agreement. The entropy was obtained from the heat capacities based on $S^\circ_{2.8}$ = 0.0015 eu.

High temperature values were obtained from specific heats (373-1273°K) determined with a dynamic method by D. M. Chizhikov and A. S. Khirik, Tr. Inst. Met. im A. A. Baikova, Akad. Nauk SSSR, No. 12, 79 (1963); cf. Chem. Abs. 59, 79 (1963). Enthalpy data (543-1223°K) from Wöhler and Jochum, loc. cit., yield for S°_{1000} a value about 0.4 eu higher, but this is inconsistent with extensive equilibrium data for $2CuO(c) = Cu_2O(c) + 0.5\ O_2$ [see CuO(c)].

Melting Data.

For details see $Cu_2O(l)$.

Dicopper Monoxide (Cu_2O)

(Liquid) GFW = 143.0794

		gibbs/mol			kcal/mol		
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	24.000	22.901	22.901	.000	-32.029	-26.833	19.669
300	24.000	23.049	22.901	.044	-32.013	-26.801	19.525
400	24.000	29.954	23.843	2.444	-31.163	-25.194	13.765
500	24.000	35.309	25.620	4.844	-30.360	-23.794	10.400
600	24.000	39.685	27.611	7.244	-29.604	-22.554	8.215
700	24.000	43.385	29.607	9.644	-28.883	-21.435	6.692
800	24.000	46.589	31.534	12.044	-28.196	-20.420	5.578
900	24.000	49.416	33.367	14.444	-27.537	-19.487	4.732
1000	24.000	51.945	35.100	16.844	-26.906	-18.627	4.071
1100	24.000	54.232	36.737	19.244	-26.298	-17.828	3.542
1200	24.000	56.321	38.284	21.644	-25.714	-17.086	3.112
1300	24.000	58.242	39.746	24.044	-25.150	-16.389	2.755
1400	24.000	60.020	41.131	26.444	-30.978	-15.531	2.425
1500	24.000	61.676	42.446	28.844	-30.514	-14.446	2.105
1600	24.000	63.225	43.697	31.244	-30.052	-13.390	1.829
1700	24.000	64.680	44.889	33.644	-29.593	-12.361	1.589
1800	24.000	66.052	46.027	36.044	-29.138	-11.360	1.379
1900	24.000	67.349	47.115	38.444	-28.685	-10.385	1.195
2000	24.000	68.580	48.158	40.844	-28.235	-9.433	1.031
2100	24.000	69.751	49.159	43.244	-27.788	-8.503	.885
2200	24.000	70.868	50.120	45.644	-27.344	-7.596	.755
2300	24.000	71.935	51.046	48.044	-26.902	-6.711	.638
2400	24.000	72.956	51.938	50.444	-26.463	-5.842	.532
2500	24.000	73.936	52.798	52.844	-26.027	-4.989	.436
2600	24.000	74.877	53.629	55.244	-25.593	-4.156	.349
2700	24.000	75.783	54.433	57.644	-25.162	-3.340	.270
2800	24.000	76.656	55.211	60.044	-24.733	-2.539	.198
2900	24.000	77.498	55.965	62.444	-169.623	.894	-.067
3000	24.000	78.312	56.697	64.844	-168.890	6.762	-.493

June 30, 1966

DICOPPER MONOXIDE (Cu_2O) (LIQUID) GFW = 143.0794

$S°_{298.15}$ = 22.901 gibbs/mol $\Delta Hf°_{298.15}$ = -32.029 kcal/mol

Tm = 1509°K $\Delta Hm°$ = 13.58 ± 2 kcal/mol

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding ΔHm° and the difference between ($H°_{1509}-H°_{298}$) for the crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated on the basis of 8 gibbs per g atom, giving a value of 24 gibbs/mol which is essentially the same as that of the crystal at the melting point. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

Tm is the value recommended by S. J. Schneider, NBS Monograph 68, U. S. Govt. Printing Office, Washington, D.C., October, 1963, based on pressure-temperature-composition studies of H. S. Roberts and F. H. Smyth, J. Am. Chem. Soc. 43, 1061 (1921). The heat of melting was selected as 13.58 kcal/mol, corresponding to ΔSm° = 3 eu per g atom. A value of 13.4 kcal/mol has been derived from the Cu_2O-CuCl phase diagram by K. K. Kelley, USBM Bulletin 393, U. S. Govt. Printing Office, Washington, 1936. Another value may be obtained from oxygen dissociation pressures for the system $Cu_2O(l)$-CuO(c) determined by Roberts and Smyth, loc. cit. Equilibrium constants may be obtained for the reaction $2CuO(c) = Cu_2O(l) + 0.5\ O_2$ by assuming the activity of Cu_2O in the melt to be equal to its mole fraction. Based on the mole fractions given by Randall, Nielsen and West, Ind. Eng. Chem. 23, 388 (1931), the equilibrium data yield $\Delta H°_m = 15.8 \pm 0.8$ kcal/mol by second law analysis of all points or 12.9 ± 1.6 by omission of 4 points at high pressure and low mole fraction. These results appear to be consistent with the selected value within the approximations involved.

Hydrogen (H_2)

(Ideal Gas - Reference State)   Mol. Wt. - 2.016

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.024	.000	.000	.000
100	5.393	24.387	37.035	-1.265	.000	.000	.000
200	6.518	28.520	31.831	-.662	.000	.000	.000
298	6.892	31.208	31.208	.000	.000	.000	.000
300	6.894	31.251	31.208	.013	.000	.000	.000
400	6.975	33.247	31.480	.707	.000	.000	.000
500	6.993	34.806	31.995	1.406	.000	.000	.000
600	7.009	36.082	32.573	2.106	.000	.000	.000
700	7.036	37.165	33.153	2.808	.000	.000	.000
800	7.087	38.107	33.715	3.514	.000	.000	.000
900	7.148	38.946	34.250	4.226	.000	.000	.000
1000	7.219	39.702	34.758	4.944	.000	.000	.000
1100	7.300	40.394	35.240	5.670	.000	.000	.000
1200	7.390	41.033	35.696	6.404	.000	.000	.000
1300	7.490	41.628	36.130	7.148	.000	.000	.000
1400	7.600	42.187	36.543	7.902	.000	.000	.000
1500	7.720	42.716	36.937	8.668	.000	.000	.000
1600	7.823	43.217	37.314	9.446	.000	.000	.000
1700	7.921	43.695	37.675	10.233	.000	.000	.000
1800	8.016	44.150	38.022	11.030	.000	.000	.000
1900	8.108	44.586	38.356	11.836	.000	.000	.000
2000	8.195	45.004	38.678	12.651	.000	.000	.000
2100	8.279	45.406	38.989	13.475	.000	.000	.000
2200	8.358	45.793	39.290	14.307	.000	.000	.000
2300	8.434	46.166	39.581	15.146	.000	.000	.000
2400	8.506	46.527	39.863	15.993	.000	.000	.000
2500	8.575	46.875	40.136	16.848	.000	.000	.000
2600	8.639	47.213	40.402	17.708	.000	.000	.000
2700	8.700	47.540	40.660	18.575	.000	.000	.000
2800	8.757	47.857	40.912	19.448	.000	.000	.000
2900	8.810	48.166	41.157	20.326	.000	.000	.000
3000	8.859	48.465	41.395	21.210	.000	.000	.000
3100	8.911	48.756	41.628	22.098	.000	.000	.000
3200	8.962	49.040	41.855	22.992	.000	.000	.000
3300	9.012	49.317	42.077	23.891	.000	.000	.000
3400	9.061	49.586	42.294	24.794	.000	.000	.000
3500	9.110	49.850	42.506	25.703	.000	.000	.000
3600	9.158	50.107	42.714	26.616	.000	.000	.000
3700	9.205	50.359	42.917	27.535	.000	.000	.000
3800	9.252	50.605	43.116	28.457	.000	.000	.000
3900	9.297	50.846	43.311	29.385	.000	.000	.000
4000	9.342	51.082	43.502	30.317	.000	.000	.000
4100	9.386	51.313	43.690	31.253	.000	.000	.000
4200	9.429	51.540	43.874	32.194	.000	.000	.000
4300	9.472	51.762	44.055	33.139	.000	.000	.000
4400	9.514	51.980	44.233	34.088	.000	.000	.000
4500	9.555	52.194	44.407	35.042	.000	.000	.000
4600	9.595	52.405	44.579	35.999	.000	.000	.000
4700	9.634	52.612	44.748	36.961	.000	.000	.000
4800	9.673	52.815	44.914	37.926	.000	.000	.000
4900	9.711	53.015	45.077	38.895	.000	.000	.000
5000	9.748	53.211	45.238	39.868	.000	.000	.000
5100	9.785	53.405	45.396	40.845	.000	.000	.000
5200	9.822	53.595	45.552	41.825	.000	.000	.000
5300	9.859	53.783	45.705	42.809	.000	.000	.000
5400	9.895	53.967	45.857	43.797	.000	.000	.000
5500	9.930	54.149	46.006	44.788	.000	.000	.000
5600	9.965	54.328	46.153	45.783	.000	.000	.000
5700	10.000	54.505	46.298	46.781	.000	.000	.000
5800	10.034	54.679	46.441	47.783	.000	.000	.000
5900	10.067	54.851	46.582	48.788	.000	.000	.000
6000	10.100	55.020	46.721	49.796	.000	.000	.000

March 31, 1961

Hydrogen (H_2)   (Ideal Gas - Reference State)   Mol. Wt. = 2.016

D_0° = 103.266 ± 0.15 kcal. mole^{-1}

Ground State Configuration $^1\Sigma_g^+$

$\Delta H_f^\circ{}_{298.15}$ = 0

$S^\circ_{298.15}$ = 31.21 ± 0.01 cal. deg.$^{-1}$ mole^{-1}

ω_e = 4405.3 cm.$^{-1}$

$\omega_e x_e$ = 125.325 cm.$^{-1}$

D_e = 0.04644 cm.$^{-1}$

σ = 2

B_e = 60.848 cm.$^{-1}$

α_e = 3.0664 cm.$^{-1}$

r_e = 0.7417 Å

Heat Capacities and Entropy

H. W. Woolley, R. B. Scott and F. G. Brickwedde, J. Research Nat. Bur. Standards 41, 379 (1948), calculated the thermodynamic functions by a method of direct summation for normal H_2 (75% ortho and 25% para) using spectroscopic constants derived from an analysis of U. V. band spectra. These constants are more preferable for use in a summation method than those obtained by G. Herzberg, Can. J. Res. A28, 144 (1950) from the measured quadrupole transitions in the ground state which accurately describe the lower vibrational levels only. In any case the difference in the functions resulting from the two sets of data are less than 0.2%.

Since the entropies of Woolley et al. contain a contribution from nuclear spin, a correction of -Rln4 was applied. However, the entropy due to the mixing of ortho and para hydrogen which is a consequence of nuclear spin is included in the total entropy since this results in correct equilibrium constants based upon third law calculations. Differences in the values of R and c_2 were found to have a negligible effect upon the functions.

Similar calculations with a different method of estimating the higher rotational levels by H. L. Johnston, L. G. Savedoff, and J. Belzer, Technical Report No. 2, Project R.F-316, Ohio State Univ. (1949), result in functions that are 0.5% lower above 5000°K.

For details concerning the dissociation energy see the monatomic hydrogen sheet.

Water (H_2O)

(Ideal Gas) Mol. Wt. = 18.016

	cal. $mole^{-1} deg.^{-1}$			kcal. $mole^{-1}$			
T, °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
0	.000	.000	INFINITE	-2.367	-57.103	-57.103	INFINITE
100	7.961	36.396	52.202	-1.581	-57.433	-56.557	123.600
200	7.969	41.916	45.837	-.784	-57.579	-55.635	60.792
298	8.025	45.106	45.106	.000	-57.798	-54.636	40.048
300	8.027	45.155	45.106	.015	-57.803	-54.617	39.786
400	8.186	47.484	45.422	.825	-58.042	-53.519	29.240
500	8.415	49.334	46.026	1.654	-58.277	-52.361	22.886
600	8.676	50.891	46.710	2.509	-58.500	-51.156	18.633
700	8.954	52.249	47.406	3.390	-58.710	-49.915	15.583
800	9.246	53.464	48.089	4.300	-58.905	-48.646	13.289
900	9.547	54.570	48.749	5.240	-59.084	-47.352	11.498
1000	9.851	55.592	49.382	6.209	-59.246	-46.040	10.062
1100	10.152	56.545	49.991	7.210	-59.391	-44.712	8.883
1200	10.444	57.441	50.575	8.240	-59.519	-43.371	7.899
1300	10.723	58.288	51.136	9.298	-59.634	-42.022	7.064
1400	10.987	59.092	51.675	10.384	-59.734	-40.663	6.347
1500	11.233	59.859	52.196	11.495	-59.824	-39.297	5.725
1600	11.462	60.591	52.698	12.630	-59.906	-37.927	5.180
1700	11.674	61.293	53.183	13.787	-59.977	-36.549	4.699
1800	11.869	61.965	53.652	14.964	-60.041	-35.170	4.270
1900	12.046	62.612	54.107	16.160	-60.099	-33.786	3.886
2000	12.214	63.234	54.548	17.373	-60.150	-32.401	3.540
2100	12.366	63.834	54.976	18.602	-60.198	-31.012	3.227
2200	12.505	64.412	55.392	19.846	-60.242	-29.621	2.942
2300	12.634	64.971	55.796	21.103	-60.282	-28.229	2.682
2400	12.753	65.511	56.190	22.372	-60.321	-26.832	2.443
2500	12.863	66.034	56.573	23.653	-60.359	-25.439	2.224
2600	12.965	66.541	56.947	24.945	-60.393	-24.040	2.021
2700	13.059	67.032	57.311	26.246	-60.428	-22.641	1.833
2800	13.146	67.508	57.667	27.556	-60.462	-21.242	1.658
2900	13.226	67.971	58.014	28.875	-60.496	-19.838	1.495
3000	13.304	68.421	58.354	30.201	-60.530	-18.438	1.343
3100	13.374	68.856	58.685	31.535	-60.562	-17.034	1.201
3200	13.441	69.284	59.010	32.876	-60.596	-15.630	1.067
3300	13.503	69.698	59.326	34.223	-60.631	-14.223	.942
3400	13.562	70.102	59.639	35.577	-60.666	-12.818	.824
3500	13.617	70.496	59.943	36.936	-60.703	-11.409	.712
3600	13.669	70.881	60.242	38.300	-60.741	-10.000	.607
3700	13.716	71.256	60.534	39.669	-60.782	-8.589	.507
3800	13.764	71.622	60.821	41.043	-60.822	-7.177	.413
3900	13.808	71.980	61.103	42.422	-60.865	-5.766	.323
4000	13.850	72.331	61.379	43.805	-60.910	-4.353	.238
4100	13.890	72.673	61.651	45.192	-60.957	-2.938	.157
4200	13.927	73.006	61.917	46.583	-61.006	-1.522	.079
4300	13.963	73.336	62.179	47.977	-61.056	-.105	.005
4400	13.997	73.658	62.436	49.375	-61.109	1.311	-.065
4500	14.030	73.973	62.689	50.777	-61.164	2.729	-.133
4600	14.061	74.281	62.938	52.181	-61.220	4.154	-.197
4700	14.091	74.584	63.182	53.589	-61.279	5.576	-.259
4800	14.120	74.881	63.423	55.000	-61.339	6.998	-.319
4900	14.146	75.172	63.660	56.413	-61.401	8.422	-.376
5000	14.174	75.459	63.893	57.829	-61.465	9.844	-.430
5100	14.201	75.740	64.122	59.248	-61.532	11.275	-.483
5200	14.228	76.016	64.348	60.669	-61.600	12.700	-.534
5300	14.254	76.287	64.571	62.093	-61.669	14.135	-.583
5400	14.279	76.553	64.791	63.520	-61.741	15.560	-.630
5500	14.303	76.816	65.007	64.949	-61.813	16.995	-.675
5600	14.328	77.074	65.220	66.381	-61.889	18.426	-.719
5700	14.351	77.327	65.430	67.815	-61.965	19.862	-.762
5800	14.375	77.577	65.637	69.251	-62.043	21.299	-.803
5900	14.398	77.823	65.842	70.690	-62.122	22.736	-.842
6000	14.422	78.065	66.044	72.131	-62.203	24.174	-.880

March 31, 1961

WATER (H_2O) (IDEAL GAS) MOL. WT. = 18.016

$\Delta H^\circ_{f0} = -57.103$ kcal. $mole^{-1}$

Point Group C_{2v}

$\Delta H^\circ_{f\ 298.15} = -57.7979$ kcal. $mole^{-1}$

$S^\circ_{298.15} = 45.106$ cal. $deg.^{-1}$ $mole^{-1}$

Vibrational Levels and Multiplicities

ω, $cm.^{-1}$

3657.05 (1)
1594.59 (1)
3755.79 (1)

Bond Length and Angle O-H distance = 0.9584 Å H-O-H angle = 104.45° $\sigma = 2$

Product of Moments of Inertia $I_A I_B I_C = 5.7658 \times 10^{-120}$ $g.^3$ $cm.^6$

Heat of Formation

Taken from National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952.

Heat Capacity and Entropy

A. S. Friedman and L. Haar, J. Chem. Phys. 22, 2051 (1954), using the infra-red spectra analysis of W. S. Benedict, H. H. Claassen and J. H. Shaw, J. Research Natl. Bur. Standards 49, 91 (1952), have calculated the thermodynamic functions for water including the anharmonic corrections. Friedman and Haar in comparing their calculation to that of a direct summation by Glatt, Adams, and Johnston, Ohio State University Res. Foundation Tech. Report No. 316-8 (1953), found that the difference between the two calculations was less than the uncertainty in the direct summation.

C_p values from 100° to 5000°K. are from Friedman and Haar. C_p from 5000° to 6000°K was extrapolated linearly. Using the tabulated functions of Friedman and Haar C_p, S, and $H_T - H_0$ at T = 298.15°K. was calculated by the method of Lagrangian curvilinear interpolation, W. J. Taylor, J. Research Natl. Bur. Standards 35, 151 (1945).

The bond length and angle were obtained from a compilation by L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chem. Soc., Burlington House, London W1, 1958.

trogen, Diatomic (N_2)

eference State - Ideal Gas) Mol. Wt. = 28.0134

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.072	.000	.000	.000
100	6.956	38.170	51.957	- 1.379	.000	.000	.000
200	6.957	42.992	46.407	- .683	.000	.000	.000
298	6.961	45.770	45.770	.000	.000	.000	.000
300	6.961	45.813	45.770	.013	.000	.000	.000
400	6.990	47.818	46.043	.710	.000	.000	.000
500	7.069	49.386	46.561	1.413	.000	.000	.000
600	7.196	50.685	47.143	2.125	.000	.000	.000
700	7.350	51.806	47.731	2.853	.000	.000	.000
800	7.512	52.798	48.303	3.596	.000	.000	.000
900	7.670	53.692	48.853	4.355	.000	.000	.000
1000	7.815	54.507	49.378	5.129	.000	.000	.000
1100	7.945	55.258	49.879	5.917	.000	.000	.000
1200	8.061	55.955	50.357	6.718	.000	.000	.000
1300	8.162	56.604	50.813	7.529	.000	.000	.000
1400	8.252	57.212	51.248	8.350	.000	.000	.000
1500	8.330	57.784	51.665	9.179	.000	.000	.000
1600	8.398	58.324	52.065	10.015	.000	.000	.000
1700	8.458	58.835	52.448	10.858	.000	.000	.000
1800	8.512	59.320	52.816	11.707	.000	.000	.000
1900	8.559	59.782	53.171	12.560	.000	.000	.000
2000	8.601	60.222	53.513	13.418	.000	.000	.000
2100	8.638	60.642	53.842	14.280	.000	.000	.000
2200	8.672	61.045	54.160	15.146	.000	.000	.000
2300	8.703	61.431	54.468	16.015	.000	.000	.000
2400	8.731	61.802	54.766	16.886	.000	.000	.000
2500	8.756	62.159	55.055	17.761	.000	.000	.000
2600	8.779	62.503	55.335	18.638	.000	.000	.000
2700	8.800	62.835	55.606	19.517	.000	.000	.000
2800	8.820	63.155	55.870	20.398	.000	.000	.000
2900	8.838	63.465	56.127	21.280	.000	.000	.000
3000	8.855	63.765	56.376	22.165	.000	.000	.000
3100	8.871	64.055	56.619	23.051	.000	.000	.000
3200	8.886	64.337	56.856	23.939	.000	.000	.000
3300	8.900	64.611	57.087	24.829	.000	.000	.000
3400	8.914	64.877	57.312	25.719	.000	.000	.000
3500	8.927	65.135	57.532	26.611	.000	.000	.000
3600	8.939	65.387	57.747	27.505	.000	.000	.000
3700	8.950	65.632	57.957	28.399	.000	.000	.000
3800	8.962	65.871	58.162	29.295	.000	.000	.000
3900	8.972	66.104	58.362	30.191	.000	.000	.000
4000	8.983	66.331	58.559	31.089	.000	.000	.000
4100	8.993	66.553	58.751	31.988	.000	.000	.000
4200	9.002	66.770	58.940	32.888	.000	.000	.000
4300	9.012	66.982	59.124	33.788	.000	.000	.000
4400	9.021	67.189	59.305	34.690	.000	.000	.000
4500	9.030	67.392	59.482	35.593	.000	.000	.000
4600	9.039	67.591	59.657	36.496	.000	.000	.000
4700	9.048	67.785	59.827	37.400	.000	.000	.000
4800	9.057	67.976	59.995	38.306	.000	.000	.000
4900	9.066	68.162	60.160	39.212	.000	.000	.000
5000	9.074	68.346	60.322	40.119	.000	.000	.000
5100	9.083	68.525	60.481	41.027	.000	.000	.000
5200	9.091	68.702	60.637	41.935	.000	.000	.000
5300	9.100	68.875	60.791	42.845	.000	.000	.000
5400	9.109	69.045	60.942	43.755	.000	.000	.000
5500	9.118	69.213	61.091	44.667	.000	.000	.000
5600	9.127	69.377	61.238	45.579	.000	.000	.000
5700	9.136	69.539	61.382	46.492	.000	.000	.000
5800	9.145	69.698	61.524	47.406	.000	.000	.000
5900	9.155	69.854	61.664	48.321	.000	.000	.000
6000	9.165	70.008	61.802	49.237	.000	.000	.000

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

NITROGEN, DIATOMIC (N_2) (IDEAL GAS - REFERENCE STATE) MOL. WT. = 28.0134

Ground State Configuration $^1\Sigma_g^+$

$\Delta H_{f\ 0}^\circ = 0$

$S^\circ_{298.15} = 45.77 \pm 0.01$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ = 0$

$\omega_e = 2357.55$ cm.$^{-1}$

$\omega_e x_e = 14.059$ cm.$^{-1}$

$\sigma = 2$

$B_e = 1.99825$ cm.$^{-1}$

$\alpha_e = 0.01791 \pm 0.0001$ cm.$^{-1}$

$r_e = 1.08758 \pm 0.0001$ Å

Heat of Formation.

The heat of formation (ΔH_f°) for $N_2(g)$ is zero at all temperatures by definition.

Heat Capacity and Entropy.

The functions adopted here are based on the direct summation calculations of L. Glatt, J. Belzer and H. L. Johnston, Ohio State Univ. Res. Found. Proj. 316, Report No. 9, 1953. They calculated the functions for $N^{14}N^{14}$ by a direct summation using spectroscopic data given by G. Herzberg, "Diatomic Molecules", D. Van Nostrand Co., New York, 1950. The entropies were changed by -Rln9 to remove the effects of nuclear spin included by Glatt, Belzer, and Johnston, and by 0.012 for the difference in spectroscopic constants. J. A. Goff and S. Gratch, Trans. Am. Soc. Mech. Engrs., 72, 741 (1950), calculated a set of functions by a direct summation over the ground state levels only. Agreement with the functions of Glatt, Belzer, and Johnston is within 0.1%.

B. P. Stoicheff, Can. J. Phys. 32, 630 (1954), determined the spectroscopic constants of $N^{14}N^{14}$ by combining his measured rotational spectra with the results of band spectra given in the literature. The constants listed above have been corrected to apply to the naturally occurring isotopic composition listed by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys., 30, 585 (1958).

Oxygen, Diatomic (O_2)

(Reference State - Ideal Gas) Mol. Wt. = 31.9988

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.075	.000	.000	.000
100	6.958	41.395	55.205	- 1.381	.000	.000	.000
200	6.961	46.218	49.643	- .685	.000	.000	.000
298	7.020	49.004	49.004	.000	.000	.000	.000
300	7.023	49.047	49.004	.013	.000	.000	.000
400	7.196	51.091	49.282	.724	.000	.000	.000
500	7.431	52.722	49.812	1.455	.000	.000	.000
600	7.670	54.098	50.414	2.210	.000	.000	.000
700	7.883	55.297	51.028	2.988	.000	.000	.000
800	8.063	56.361	51.629	3.786	.000	.000	.000
900	8.212	57.320	52.209	4.600	.000	.000	.000
1000	8.336	58.192	52.765	5.427	.000	.000	.000
1100	8.439	58.991	53.295	6.266	.000	.000	.000
1200	8.527	59.729	53.801	7.114	.000	.000	.000
1300	8.604	60.415	54.283	7.971	.000	.000	.000
1400	8.674	61.055	54.744	8.835	.000	.000	.000
1500	8.738	61.656	55.185	9.706	.000	.000	.000
1600	8.800	62.222	55.608	10.583	.000	.000	.000
1700	8.858	62.757	56.013	11.465	.000	.000	.000
1800	8.916	63.265	56.401	12.354	.000	.000	.000
1900	8.973	63.749	56.776	13.249	.000	.000	.000
2000	9.029	64.210	57.136	14.149	.000	.000	.000
2100	9.084	64.652	57.483	15.054	.000	.000	.000
2200	9.139	65.076	57.819	15.966	.000	.000	.000
2300	9.194	65.483	58.143	16.882	.000	.000	.000
2400	9.248	65.876	58.457	17.804	.000	.000	.000
2500	9.301	66.254	58.762	18.732	.000	.000	.000
2600	9.354	66.620	59.057	19.664	.000	.000	.000
2700	9.405	66.974	59.344	20.602	.000	.000	.000
2800	9.455	67.317	59.622	21.545	.000	.000	.000
2900	9.503	67.650	59.893	22.493	.000	.000	.000
3000	9.551	67.973	60.157	23.446	.000	.000	.000
3100	9.596	68.287	60.415	24.403	.000	.000	.000
3200	9.640	68.592	60.665	25.365	.000	.000	.000
3300	9.682	68.889	60.910	26.331	.000	.000	.000
3400	9.723	69.179	61.149	27.302	.000	.000	.000
3500	9.762	69.461	61.383	28.276	.000	.000	.000
3600	9.799	69.737	61.611	29.254	.000	.000	.000
3700	9.835	70.006	61.834	30.236	.000	.000	.000
3800	9.869	70.269	62.053	31.221	.000	.000	.000
3900	9.901	70.525	62.267	32.209	.000	.000	.000
4000	9.932	70.776	62.476	33.201	.000	.000	.000
4100	9.961	71.022	62.682	34.196	.000	.000	.000
4200	9.988	71.262	62.883	35.193	.000	.000	.000
4300	10.015	71.498	63.081	36.193	.000	.000	.000
4400	10.039	71.728	63.275	37.196	.000	.000	.000
4500	10.062	71.954	63.465	38.201	.000	.000	.000
4600	10.084	72.176	63.652	39.208	.000	.000	.000
4700	10.104	72.393	63.836	40.218	.000	.000	.000
4800	10.123	72.606	64.016	41.229	.000	.000	.000
4900	10.140	72.814	64.194	42.242	.000	.000	.000
5000	10.156	73.019	64.368	43.257	.000	.000	.000
5100	10.172	73.221	64.540	44.274	.000	.000	.000
5200	10.187	73.418	64.708	45.292	.000	.000	.000
5300	10.200	73.613	64.875	46.311	.000	.000	.000
5400	10.213	73.803	65.038	47.332	.000	.000	.000
5500	10.225	73.991	65.199	48.353	.000	.000	.000
5600	10.237	74.175	65.358	49.377	.000	.000	.000
5700	10.247	74.356	65.514	50.401	.000	.000	.000
5800	10.258	74.535	65.668	51.426	.000	.000	.000
5900	10.267	74.710	65.820	52.452	.000	.000	.000
6000	10.276	74.883	65.970	53.479	.000	.000	.000

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

OXYGEN, DIATOMIC (O_2) (REFERENCE STATE - IDEAL GAS) MOL. WT. = 31.9988

Ground State Configuration $^3\Sigma_g^-$

$S^\circ_{298.15}$ = 49.00 ± 0.01 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0} = 0$

$\Delta H^\circ_{f\ 298.15} = 0$

ω_e = 1580.246 cm.$^{-1}$

$\omega_e x_e$ = 12.071 cm.$^{-1}$

$\sigma = 2$

B_e = 1.445 cm.$^{-1}$

α_e = 0.0158 cm.$^{-1}$

r_e = 1.2074 Å

Heat of Formation.

The heat of formation (ΔH_f°) for O_2(g) is zero at all temperatures, by definition.

Heat Capacity and Entropy.

The functions adopted here are based on those of H. W. Woolley, J. Research, Nat. Bur. Standards 40, 163 (1948), who used a direct summation to 5000°K. The spectroscopic constants used were the same as those listed by G. Herzberg, Spectra of Diatomic Molecules", D. Van Nostrand Co., 1950. Raman measurements of rotation-vibration levels by A. Weber and E. A. McGinnis, J. Molec. Spect. 4, 195 (1960), support the constants selected by Herzberg which were changed on this table to apply to the naturally occurring isotopic composition given by D. Strominger, J. M. Hollander, and T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

The entropies listed by Woolley were reduced by 0.0065 cal. deg.$^{-1}$ mole^{-1} which was added by Woolley to account for the contribution due to the presence of both odd and even rotational levels in O^{16}-O^{17} and O^{16}-O^{18} molecules. This correction is not necessary when isotope mixing entropy is neglected, cf. W. F. Giauque and R. Overstreet, J. Am. Chem. Soc. 54, 1731 (1932).

Lead Monoxide (PbO)

(Ideal Gas) Mol. Wt. = 223.21 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.142	12.017	12.017	INFINITE
100	6.964	49.455	63.918	-1.446	11.933	9.944	-21.731
200	7.272	54.349	58.041	-.739	11.697	8.045	-8.791
298	7.769	57.346	57.346	.000	11.477	6.301	-4.619
300	7.778	57.395	57.347	.014	11.473	6.269	-4.567
400	8.155	59.687	57.657	.812	11.263	4.566	-2.495
500	8.400	61.535	58.254	1.641	11.053	2.915	-1.274
600	8.560	63.082	58.933	2.489	10.834	1.309	-.477
700	8.670	64.410	59.623	3.351	9.437	-.070	.022
800	8.748	65.573	60.295	4.222	9.188	-1.412	.386
900	8.806	66.607	60.940	5.100	8.945	-2.722	.661
1000	8.850	67.537	61.554	5.983	8.709	-4.005	.875
1100	8.886	68.383	62.137	6.870	8.477	-5.266	1.046
1200	8.915	69.157	62.690	7.760	8.252	-6.504	1.184
1300	8.940	69.872	63.216	8.653	8.030	-7.725	1.299
1400	8.962	70.535	63.715	9.548	7.809	-8.929	1.394
1500	8.980	71.154	64.191	10.445	7.586	-10.115	1.474
1600	8.997	71.734	64.644	11.344	7.360	-11.289	1.542
1700	9.013	72.280	65.077	12.245	7.130	-12.447	1.600
1800	9.027	72.796	65.492	13.147	6.894	-13.593	1.650
1900	9.040	73.284	65.889	14.050	6.651	-14.725	1.694
2000	9.052	73.748	66.271	14.954	6.403	-15.843	1.731
2100	9.064	74.190	66.638	15.860	-36.302	-15.396	1.602
2200	9.075	74.612	66.990	16.767	-36.471	-14.398	1.430
2300	9.086	75.016	67.331	17.675	-36.662	-13.391	1.272
2400	9.096	75.402	67.659	18.584	-36.876	-12.373	1.127
2500	9.106	75.774	67.976	19.494	-37.115	-11.350	.992
2600	9.116	76.131	68.283	20.406	-37.375	-10.313	.867
2700	9.126	76.476	68.580	21.318	-37.658	-9.267	.750
2800	9.135	76.808	68.868	22.231	-37.965	-8.210	.641
2900	9.144	77.128	69.147	23.145	-38.291	-7.140	.538
3000	9.153	77.438	69.419	24.060	-38.636	-6.059	.441
3100	9.162	77.739	69.682	24.975	-38.999	-4.968	.350
3200	9.171	78.030	69.939	25.892	-39.380	-3.865	.264
3300	9.180	78.312	70.188	26.809	-39.773	-2.749	.182
3400	9.188	78.586	70.431	27.728	-40.180	-1.620	.104
3500	9.197	78.853	70.668	28.647	-40.598	-.482	.030
3600	9.205	79.112	70.899	29.567	-41.025	.672	-.041
3700	9.214	79.364	71.124	30.488	-41.460	1.836	-.108
3800	9.222	79.610	71.344	31.410	-41.900	3.014	-.173
3900	9.230	79.850	71.559	32.333	-42.345	4.200	-.235
4000	9.238	80.084	71.770	33.256	-42.794	5.396	-.295
4100	9.247	80.312	71.975	34.180	-43.245	6.608	-.352
4200	9.255	80.535	72.176	35.105	-43.696	7.831	-.407
4300	9.263	80.753	72.373	36.031	-44.148	9.062	-.461
4400	9.271	80.966	72.566	36.958	-44.599	10.306	-.512
4500	9.279	81.174	72.755	37.885	-45.048	11.557	-.561
4600	9.287	81.378	72.940	38.814	-45.495	12.823	-.609
4700	9.295	81.578	73.122	39.743	-45.939	14.092	-.655
4800	9.303	81.774	73.300	40.673	-46.380	15.379	-.700
4900	9.311	81.966	73.475	41.603	-46.817	16.665	-.743
5000	9.319	82.154	73.647	42.535	-47.249	17.964	-.785
5100	9.327	82.338	73.815	43.467	-47.679	19.275	-.826
5200	9.335	82.520	73.981	44.400	-48.103	20.592	-.865
5300	9.343	82.697	74.144	45.334	-48.522	21.920	-.904
5400	9.351	82.872	74.304	46.269	-48.938	23.251	-.941
5500	9.359	83.044	74.461	47.205	-49.349	24.591	-.977
5600	9.367	83.213	74.616	48.141	-49.756	25.939	-1.012
5700	9.375	83.378	74.768	49.078	-50.159	27.291	-1.046
5800	9.382	83.542	74.918	50.016	-50.557	28.659	-1.080
5900	9.390	83.702	75.066	50.954	-50.953	30.025	-1.112
6000	9.398	83.860	75.211	51.894	-51.344	31.400	-1.144

Lead Monoxide (PbO) (Ideal Gas)

Mol. Wt. = 223.21

$\Delta H^\circ_{f\ 298.15} = 11.48 \pm 0.27$ kcal. mole^{-1}

$S^\circ_{298.15} = 57.346$ cal. deg.$^{-1}$ mole^{-1}

Ground State Configuration $^1\Sigma^+$

Electronic Level and Multiplicity

ϵ cm.$^{-1}$	g_1
0	1

$\omega_e = 721.8$ cm.$^{-1}$

$\omega_e x_e = 3.70$ cm.$^{-1}$

$B_e = 0.3072$ cm.$^{-1}$

$\alpha_e = 0.0019$ cm.$^{-1}$

$\sigma = 1$

$r_e = 1.922$ Å

Heat of Formation. Calculated from $\Delta H^\circ_{f\ 298.15}$ for PbO (c, red) and $\Delta H^\circ_{s\ 298.15}$.

Heat Capacity and Entropy. The ground state configuration, molecular and spectroscopic constants are obtained from G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York (1950), modified for the natural isotopic abundances reported by J. R. Stehn and E. F. Clancy, "Chart of the Nuclides", General Electric Co., N. Y. (1956).

Lead Monoxide (PbO)

(Liquid) Mol. Wt. = 223.21

INTERIM TABLE

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	10.950	20.546	20.546	.000	- 46.712	- 40.916	29.991
300	10.970	20.614	20.546	.020	- 46.710	- 40.880	29.780
400	11.629	23.866	20.985	1.152	- 46.586	- 38.954	21.283
500	12.094	26.513	21.834	2.340	- 46.437	- 37.064	16.200
600	12.469	28.752	22.805	3.568	- 46.276	- 35.204	12.822
700	12.802	30.700	23.797	4.832	- 47.271	- 33.181	10.359
800	15.535	32.492	24.771	6.177	- 47.046	- 31.181	8.518
900	15.535	34.322	25.732	7.730	- 46.614	- 29.223	7.096
1000	15.535	35.958	26.674	9.284	- 46.180	- 27.314	5.969
1100	15.535	37.439	27.587	10.837	- 45.745	- 25.449	5.056
1200	15.535	38.791	28.465	12.391	- 45.308	- 23.622	4.302
1300	15.535	40.034	29.308	13.944	- 44.867	- 21.833	3.670
1400	15.535	41.185	30.116	15.498	- 44.431	- 20.079	3.134
1500	15.535	42.257	30.890	17.051	- 43.997	- 18.353	2.674
1600	15.535	43.260	31.632	18.605	- 43.569	- 16.658	2.275
1700	15.535	44.202	32.344	20.158	- 43.145	- 14.988	1.927
1800	15.535	45.090	33.027	21.712	- 42.730	- 13.345	1.620
1900	15.535	45.930	33.685	23.265	- 42.322	- 11.725	1.349
2000	15.535	46.726	34.317	24.819	- 41.922	- 10.124	1.106
2100	15.535	47.484	34.926	26.372	- 83.979	- 6.991	.728
2200	15.535	48.207	35.513	27.926	- 83.501	- 3.337	.332
2300	15.535	48.898	36.080	29.479	- 83.047	.296	- .028
2400	15.535	49.559	36.628	31.033	- 82.616	3.912	- .356
2500	15.535	50.193	37.158	32.586	- 82.212	7.506	- .656
2600	15.535	50.802	37.671	34.140	- 81.830	11.088	- .932
2700	15.535	51.388	38.169	35.693	- 81.472	14.655	- 1.186
2800	15.535	51.953	38.651	37.247	- 81.138	18.209	- 1.421
2900	15.535	52.499	39.119	38.800	- 80.824	21.753	- 1.639
3000	15.535	53.025	39.574	40.354	- 80.531	25.286	- 1.842

March 31, 1962

Lead Monoxide (PbO) (Liquid)

Mol. Wt. = 223.21

$\Delta H^\circ_{f\ 298.15}$ = [-46.712] kcal. mole^{-1}

$S^\circ_{298.15}$ = [20.566] cal. deg.$^{-1}$ mole^{-1}

T_m = 1170 ± 4°K.

ΔH°_m = 6.1 ± 0.1 kcal. mole^{-1}

T_b = 1789°K.

ΔH°_v = 49.53 ± 0.22 kcal. mole^{-1}

Heat of Formation. Calculated from that of the crystal.

Heat Capacity, Entropy, and Melting Data. C_p, T_m, and ΔH°_m are obtained from E. N. Rodigina, K. Z. Gomel'skii and V. F. Luginina, Zhur. Fiz. Khim., 35, 1799 (1961). The reported heat capacity is extrapolated to an assumed glass transition temperature of 780°K., below which the heat capacity is taken to be equal to that of the crystal, PbO (c, red).

Vaporization Phenomena. T_b and ΔH°_v calculated from $\Delta H^\circ_{s\ 298.15}$ for PbO (c, red) and functions for condensed and gaseous states.

Lead Monoxide, Red (PbO)

(Crystal) Mol. Wt. = 223.21

INTERIM TABLE

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			Log K_p
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	
0	.000	.000	INFINITE	-2.177	-51.903	-51.903	INFINITE
100	6.422	5.919	24.279	-1.836	-52.341	-49.977	109.218
200	9.674	11.479	16.554	-1.015	-52.463	-47.541	51.948
298	10.943	15.592	15.592	.000	-52.407	-45.134	33.082
300	10.960	15.660	15.592	.020	-52.405	-45.089	32.846
400	11.760	18.928	16.032	1.158	-52.275	-42.668	23.312
500	12.420	21.626	16.889	2.368	-52.103	-40.286	17.608
600	12.970	23.940	17.876	3.639	-51.900	-37.941	13.819
700	13.400	25.974	18.890	4.958	-52.840	-35.441	11.065
800	13.800	27.789	19.891	6.318	-52.600	-32.972	9.007
900	14.200	29.436	20.862	7.718	-52.321	-30.535	7.415
1000	14.600	30.954	21.796	9.158	-52.000	-28.131	6.148
1100	15.000	32.365	22.693	10.638	-51.639	-25.761	5.118
1200	15.400	33.687	23.555	12.158	-51.234	-23.425	4.266
1300	15.800	34.935	24.383	13.718	-50.788	-21.126	3.551
1400	16.200	36.121	25.179	15.318	-50.305	-18.863	2.945
1500	16.600	37.252	25.947	16.958	-49.785	-16.634	2.423
1600	17.000	38.336	26.687	18.638	-49.230	-14.442	1.973
1700	17.400	39.379	27.404	20.358	-48.640	-12.285	1.579
1800	17.800	40.385	28.097	22.118	-48.019	-10.165	1.234
1900	18.200	41.358	28.769	23.918	-47.364	-8.081	.929
2000	18.600	42.302	29.423	25.758	-46.677	-6.031	.659
2100	19.000	43.219	30.058	27.638	-88.408	-2.463	.256
2200	19.400	44.112	30.676	29.558	-87.564	1.609	-.160
2300	19.800	44.983	31.280	31.518	-86.703	5.643	-.536
2400	20.200	45.834	31.868	33.518	-85.826	9.641	-.878
2500	20.600	46.667	32.444	35.558	-84.935	13.598	-1.189

March 31, 1962

Lead Monoxide, Red (PbO) (Crystal)

Mol. Wt. = 223.21

$\Delta H^\circ_{f\ 298.15} = -52.41 \pm 0.16$ kcal. mole^{-1}

$S^\circ_{298.15} = 15.6 \pm 0.2$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{s\ 298.15} = 63.88 \pm 0.22$ kcal. mole^{-1}

$T_t = 762°K$

$\Delta H^\circ_t = 0.18 \pm 0.23$ kcal. mole^{-1}

Heat of Formation. Calculated from the cell reaction

$$H_2(g) \mid Ba(OH)_2\ (0.766 \sim 0.2242M) \mid PbO(c) + Pb(c)$$

reported by D. F. Smith and H. K. Woods, J. Am. Chem. Soc., 45, 2632 (1923), using $\Delta H^\circ_{f\ 298.15}$ for $H_2O(l)$, -68.317 kcal. mole^{-1}, given by Natl. Bur. Standards Circular 500 (1952). ΔH°_f values reported by other investigators were discussed by R. W. Millar, J. Am. Chem. Soc., 51, 207 (1929).

Heat Capacity and Entropy. Heat capacity values (51° to 298.15°K) were obtained from E. G. King, J. Am. Chem. Soc., 80, 2400 (1958). For the higher temperature range, heat capacity given by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960) was used and joined smoothly to data of King at 298.15°K by graphical extrapolation. King obtained entropies below 51°K by empirical extrapolation of the heat capacity curve which fits the measured heat capacities within 1.3%.

Transition Data. Heat of transition recalculated from the data given by E. G. King, loc. cit.

Heat of Sublimation. Calculated from free-energy functions and vapor pressure reported by A. N. Nesmeyanov, L. P. Firsova and E. P. Isakova, Zhur. Fiz. Khim. 34, 1699 (1960) and R. Hörbe and O. Knacke, Z. Erzbergbau u. Metallhuttenw. 12, 321 (1959).

Lead Monoxide, Yellow (PbO)

(Crystal) Mol. Wt. = 223.21

INTERIM TABLE

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2,209	-51,594	-51,594	INFINITE
100	6,581	6,352	24,842	-1,849	-52,013	-49,692	108,596
200	9,720	11,990	17,080	-1,018	-52,125	-47,305	51,690
298	10,958	16,114	16,114	,000	-52,066	-44,949	32,947
300	10,970	16,182	16,114	,020	-52,064	-44,905	32,711
400	11.631	19,433	16,553	1,152	-51,940	-42,535	23,239
500	12.094	22.080	17.402	2.339	-51.791	-40.202	17.571
600	12,469	24,319	18,373	3,568	-51,630	-37,898	13,804
700	12,803	26,267	19,364	4,832	-52,625	-35,432	11,062
800	13.115	27,997	20,337	6,128	-52,449	-32,988	9,011
900	13,415	29,557	21,276	7,453	-52,245	-30,567	7,422
1000	13,706	30,986	22,177	8,809	-52,009	-28,170	6,156
1100	13,992	32,306	23,038	10,194	-51,742	-25,800	5,126
1200	14.275	33,535	23.862	11.607	-51,444	-23.453	4,271
1300	14,555	34,689	24,651	13,049	-51,117	-21,134	3,553
1400	14,833	35,778	25,408	14,518	-50,764	-18,842	2,941
1500	15,110	36,811	26,134	16,015	-50,387	-16,573	2,415
1600	15,386	37,794	26,832	17,540	-49,987	-14,332	1,958
1700	15,660	38,735	27,505	19,092	-49,565	-12,116	1,558
1800	15,935	39,638	28,154	20,672	-49,124	-9,927	1,205
1900	16,209	40,507	28,781	22,279	-48,662	-7,762	,893
2000	16,483	41,346	29,389	23,914	-48,181	-5,622	,614
2100	16,756	42,156	29,977	25,576	-90,129	-1,953	,203
2200	17,029	42,942	30,549	27,265	-89,516	2,230	-,222
2300	17,302	43,705	31,104	28,982	-88,898	6,387	-,607
2400	17,575	44,447	31,645	30,726	-88,277	10,518	-,958
2500	17,847	45,170	32,172	32,497	-87,655	14,619	-1,278
2600	18,119	45,876	32,685	34,295	-87,029	18,698	-1,572
2700	18,391	46,564	33,187	36,120	-86,399	22,753	-1,842
2800	18,663	47,238	33,676	37,973	-85,765	26,784	-2,091
2900	18,936	47,898	34,155	39,853	-85,125	30,794	-2,321
3000	19,206	48,544	34,624	41,760	-84,479	34,781	-2,534

March 31, 1962

Lead Monoxide, Yellow (PbO) (Crystal)

Mol. Wt. = 223.21

$\Delta H^\circ_{f\ 298.15} = -52.07 \pm 0.28$ kcal. mole^{-1}

$S^\circ_{298.15} = 16.1 \pm 0.2$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{s\ 298.15} = 63.54 \pm 0.32$ kcal. mole^{-1}

$T_m = 1170 \pm 4$°K.

$\Delta H^\circ_m = 6.1 \pm 0.1$ kcal. mole^{-1}

Heat of Formation. Calculated from $\Delta H^\circ_{f\ 298.15}$ for PbO (c, red) and $\Delta H^\circ_{t\ 298.15}$ between PbO (c, red) and PbO (c, yellow).

Heat Capacity, Entropy, and Melting Data. C_p values (51° to 298.15°K.) obtained from E. G. King, J. Am. Chem. Soc., 80, 2400 (1958). For the higher temperature range, the heat capacity reported by E. N. Rodigina, K. Z. Gomel'skii and V. F. Luginina, Zhur. Fiz. Khim., 35, 1799 (1961) was used and joined smoothly to data of King at 298.15°K. by graphical extrapolation. T_m and ΔH°_m given by E. N. Rodigina, K. Z. Gomel'skii and V. F. Luginina, loc. cit.

Heat of Sublimation. Calculated from $\Delta H^\circ_{t\ 298.15}$ and $\Delta H^\circ_{s\ 299.15}$ for PbO (c, red).

Sulfur Dioxide (SO_2)

(Ideal Gas) Mol. Wt. = 64.066

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.522	- 70.341	- 70.341	INFINITE
100	8.013	49.932	67.182	- 1.725	- 70.421	- 70.966	155.088
200	8.693	55.670	60.135	- .893	- 70.662	- 71.425	78.046
298	9.530	59.298	59.298	.000	- 70.947	- 71.741	52.585
300	9.547	59.357	59.298	.018	- 70.952	- 71.746	52.264
400	10.395	62.222	59.683	1.016	- 71.764	- 71.947	39.308
500	11.132	64.623	60.437	2.093	- 72.356	- 71.923	31.436
600	11.723	66.707	61.312	3.237	- 72.824	- 71.790	26.148
700	12.180	68.550	62.217	4.433	- 73.206	- 71.562	22.342
800	12.532	70.200	63.114	5.669	- 86.593	- 72.574	19.825
900	12.806	71.693	63.985	6.937	- 86.577	- 70.822	17.197
1000	13.022	73.054	64.825	8.229	- 86.553	- 69.071	15.095
1100	13.194	74.303	65.631	9.540	- 86.524	- 67.326	13.376
1200	13.335	75.458	66.402	10.866	- 86.490	- 65.582	11.943
1300	13.451	76.530	67.141	12.206	- 86.452	- 63.840	10.732
1400	13.549	77.530	67.847	13.556	- 86.413	- 62.102	9.694
1500	13.632	78.468	68.524	14.915	- 86.373	- 60.369	8.795
1600	13.704	79.350	69.174	16.282	- 86.331	- 58.635	8.009
1700	13.767	80.183	69.797	17.656	- 86.288	- 56.905	7.315
1800	13.822	80.971	70.396	19.035	- 86.248	- 55.178	6.699
1900	13.872	81.720	70.973	20.420	- 86.208	- 53.452	6.148
2000	13.917	82.433	71.528	21.809	- 86.170	- 51.731	5.653
2100	13.958	83.113	72.064	23.203	- 86.133	- 50.010	5.204
2200	13.995	83.763	72.581	24.601	- 86.099	- 48.290	4.797
2300	14.030	84.386	73.080	26.002	- 86.067	- 46.573	4.425
2400	14.063	84.984	73.564	27.407	- 86.037	- 44.855	4.084
2500	14.093	85.558	74.032	28.815	- 86.010	- 43.141	3.771
2600	14.122	86.112	74.486	30.225	- 85.986	- 41.426	3.482
2700	14.149	86.645	74.927	31.639	- 85.964	- 39.713	3.214
2800	14.175	87.160	75.355	33.055	- 85.946	- 38.002	2.966
2900	14.200	87.658	75.770	34.474	- 85.930	- 36.288	2.735
3000	14.224	88.140	76.175	35.895	- 85.918	- 34.575	2.519
3100	14.247	88.607	76.568	37.319	- 85.906	- 32.864	2.317
3200	14.270	89.059	76.952	38.745	- 85.899	- 31.154	2.128
3300	14.291	89.499	77.325	40.173	- 85.893	- 29.446	1.950
3400	14.312	89.926	77.689	41.603	- 85.891	- 27.733	1.783
3500	14.333	90.341	78.045	43.035	- 85.891	- 26.026	1.625
3600	14.353	90.745	78.392	44.469	- 85.892	- 24.313	1.476
3700	14.373	91.136	78.731	45.906	- 85.896	- 22.602	1.335
3800	14.392	91.522	79.063	47.344	- 85.901	- 20.890	1.201
3900	14.411	91.896	79.387	48.784	- 85.908	- 19.183	1.075
4000	14.430	92.261	79.705	50.226	- 85.917	- 17.469	.954
4100	14.448	92.618	80.015	51.670	- 85.927	- 15.758	.840
4200	14.467	92.966	80.319	53.116	- 85.938	- 14.047	.731
4300	14.485	93.307	80.617	54.563	- 85.951	- 12.333	.627
4400	14.502	93.640	80.910	56.013	- 85.965	- 10.623	.528
4500	14.520	93.966	81.196	57.464	- 85.980	- 8.908	.433
4600	14.537	94.285	81.477	58.917	- 85.995	- 7.194	.342
4700	14.554	94.598	81.753	60.371	- 86.012	- 5.482	.255
4800	14.572	94.905	82.024	61.828	- 86.028	- 3.769	.172
4900	14.588	95.285	82.290	63.286	- 86.045	- 2.056	.092
5000	14.605	95.500	82.551	64.745	- 86.064	- .345	.015
5100	14.622	95.790	82.808	66.207	- 86.082	1.375	- .059
5200	14.639	96.074	83.060	67.670	- 86.100	3.087	- .130
5300	14.655	96.353	83.308	69.134	- 86.118	4.806	- .198
5400	14.672	96.627	83.553	70.601	- 86.136	6.518	- .264
5500	14.688	96.896	83.793	72.069	- 86.153	8.237	- .327
5600	14.704	97.161	84.029	73.538	- 86.173	9.952	- .388
5700	14.720	97.421	84.262	75.010	- 86.190	11.665	- .447
5800	14.736	97.677	84.491	76.482	- 86.208	13.387	- .504
5900	14.753	97.930	84.717	77.957	- 86.224	15.099	- .559
6000	14.769	98.178	84.939	79.433	- 86.241	16.823	- .613

June 30, 1961

SULFUR DIOXIDE (SO_2) (IDEAL GAS) MOL. WT. = 64.066

ΔH°_{f0} = -70.341 ± 0.05 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -70.947 ± 0.05 kcal. mole^{-1}

Point Group C_{2v}

$S_{298.15}$ = 59.30 ± 0.02 cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
1151.38 (1)
517.69 (1)
1361.76 (1)

Bond Lengths and Angles S-O = 1.432 ± 0.003 A. OSO = 119.53 ± 0.4°

Moments of Inertia

I_A = 1.38046 X 10^{-39} g. cm.^{2}

I_B = 8.13067 X 10^{-39} g. cm.^{2}

I_C = 9.53376 X 10^{-39} g. cm.^{2}

σ = 2

Heat of Formation

J. R. Eckman and F. D. Rossini, J. Research Nat. Bur. Standards 3, 597 (1929), measured the heat of combustion of rhombic sulfur to SO_2. Changes due to different atomic weights and electrical constants though negligible have been made.

Heat Capacities and Entropies

The functions were calculated by J. Gordon, private communication, Feb. 2, 1961, using the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954). Structural parameters are given by M. H. Sirvetz, J. Chem. Phys. 19, 938 (1951), obtained from microwave measurements. Frequencies were measured by R. D. Shelton, A. H. Nielsen, W. H. Fletcher, J. Chem. Phys. 21, 2178 (1953) and ibid., 22, 1791 (1954). A third law value of $S_{298.15}$ = 59.24 cal. deg.$^{-1}$ mole^{-1} was obtained by W. F. Giauque and C. C. Stevenson, J. Am. Chem. Soc. 60, 1389 (1938).

Cristobalite, High (SiO_2)
(Crystal) GFW = 60.0848

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	6.353	11.963	11.963	.000	-216.417	-204.032	149.560
300	6.490	12.003	11.963	.012	-216.427	-203.956	148.581
400	11.332	14.632	12.289	.937	-216.720	-199.743	109.134
500	13.589	17.429	13.039	2.195	-216.737	-195.492	85.449
600	14.830	20.026	13.991	3.621	-216.634	-191.252	69.663
700	15.590	22.373	15.023	5.145	-216.473	-187.033	58.394
800	16.094	24.490	16.077	6.731	-216.285	-182.842	49.950
900	16.449	26.407	17.120	8.359	-216.083	-178.672	43.387
1000	16.712	28.154	18.137	10.017	-215.876	-174.526	38.143
1100	16.915	29.757	19.122	11.699	-215.668	-170.402	33.856
1200	17.076	31.236	20.070	13.399	-215.461	-166.296	30.287
1300	17.208	32.608	20.983	15.113	-215.259	-162.207	27.269
1400	17.320	33.888	21.859	16.840	-215.061	-158.134	24.686
1500	17.416	35.086	22.701	18.577	-214.870	-154.074	22.449
1600	17.500	36.213	23.511	20.323	-214.686	-150.027	20.493
1700	17.575	37.276	24.290	22.076	-226.503	-145.985	18.755
1800	17.642	38.282	25.039	23.837	-226.281	-141.148	17.138
1900	17.704	39.238	25.762	25.605	-226.058	-136.426	15.693
2000	17.762	40.147	26.458	27.378	-225.835	-131.713	14.393
2100	17.816	41.015	27.131	29.157	-225.611	-127.012	13.218
2200	17.866	41.845	27.781	30.941	-225.389	-122.323	12.152
2300	17.914	42.641	28.410	32.730	-225.166	-117.646	11.179
2400	17.960	43.404	29.019	34.524	-224.944	-112.972	10.288
2500	18.005	44.138	29.609	36.322	-224.724	-108.314	9.469
2600	18.047	44.845	30.182	38.125	-224.503	-103.661	8.713
2700	18.089	45.527	30.738	39.931	-224.285	-99.018	8.015
2800	18.129	46.186	31.278	41.742	-224.067	-94.382	7.367
2900	18.168	46.822	31.803	43.557	-223.850	-89.751	6.764
3000	18.207	47.439	32.314	45.376	-223.634	-85.133	6.202

June 30, 1967

CRISTOBALITE, HIGH (SiO_2) (CRYSTAL) GFW = 60.0848

$S°_{298.15}$ = 11.963 gibbs/mol

Tt = 543 ± 3°K(low cristobalite → high cristobalite)

Tt = 1079 ± 250°K(high quartz → high cristobalite)

Tm = 1996 ± 5°K(high cristobalite → liquid)

$\Delta Hf°_{298.15}$ = -216.417 kcal/mol

ΔHt° = 0.321 ± 0.06 kcal/mol

ΔHt° = 0.48 ± 0.15 kcal/mol

ΔHm° = 2.29 ± 0.5 kcal/mol

Heat of Formation

The heat of formation is calculated from that of low cristobalite by addition of ΔHt° = 0.321 kcal/mol and the difference between $H°_{543} - H°_{298}$ for low and high forms.

Heat Capacity and Entropy

Cp° is derived from enthalpies of Mosesman (1) and White (2), whose data deviate from the adopted functions by -0.6 to + 0.5% and +0.9 to 0.0%, respectively. White's deviations for cristobalite have a magnitude and trend similar to his deviations for quartz and vitreous silica. Data of Wietzel (3) for his sample prepared at 1600°C deviate by +3% at 673°K and +1.6% at 1973°K. Cp° below 543°K is smoothly extrapolated to give the proper trend in the Gibbs energy, but the heat capacity at 298°K is not realistic. The entropy is calculated in a manner analogous to that of the heat of formation.

Transition Data

Literature on the polymorphism of SiO_2 is voluminous but is summarized in detail in recent books by Sosman (4) and Eitel (5). The known phases of SiO_2 include quartz, tridymite(?), cristobalite, vitreous silica and the more recently discovered high pressure phases. Muan (6) concisely reviewed the still controversial question of whether tridymite is stabilized only by the presence of foreign ions or whether it is a stable phase of SiO_2 intermediate between quartz and cristobalite. Transitions among the different phases are generally sluggish because of large energy barriers to the structural change and small differences in Gibbs free energies. As a result, the phases often persist far into metastable regions. In contrast, transitions within a particular phase are rapid and reversible (i.e., the low → high inversions of quartz or cristobalite).

High cristobalite is the stable phase near Tm. It becomes metastable with respect to quartz at lower temperatures but persists down to the high → low inversion at 543°K (see table for low cristobalite). The high form is cubic and the low form tetragonal (12, 13).

The adopted tables give 1079±250°K as the temperature at which ΔGr° = 0 for high quartz → high cristobalite; ΔHt° = 0.48±0.15 kcal/mol is the corresponding enthalpy difference. The uncertainty in Tt is derived from that in ΔHt° which, in turn, is taken from $\Delta Hr°_{970}$ = 0.45±0.15 kcal/mol obtained by Holm (7) from ΔHsoln measurements in an oxide melt. It is apparent that Tt is extremely sensitive to small changes in G or H. Holmquist (8) tentatively placed this inversion at 1298±25°K but did observe cristobalite formation at temperatures as low as 1171°K.

Melting Data

Melting point data were reviewed by Schneider (9) and adjusted to the 1948 International Temperature Scale. The adopted melting point for cristobalite is based on Greig (10). ΔHm° is calculated as the difference in ΔHf° for liquid and crystal at Tm. Mackenzie et al. (11) showed that cristobalite may be superheated by as much as 40° above Tm due to its slow rate of fusion.

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Cristobalite, Low (SiO_2)

(Crystal) GFW = 60.0848

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 1.682	- 215.938	- 215.938	INFINITE
100	3.524	2.688	17.868	- 1.518	- 216.532	- 212.570	464.571
200	7.586	6.663	11.268	- .921	- 216.912	- 208.443	227.776
298	10.744	10.372	10.372	.000	- 217.100	- 204.241	149.712
300	10.790	10.439	10.372	.020	- 217.102	- 204.161	148.731
400	12.702	13.826	10.821	1.202	- 217.138	- 199.839	109.187
500	14.023	16.808	11.726	2.541	- 217.074	- 195.519	85.461
600	15.050	19.461	12.799	3.998	- 216.940	- 191.220	69.652
700	15.700	21.833	13.923	5.537	- 216.764	- 186.946	58.367
800	16.150	23.960	15.047	7.130	- 216.569	- 182.702	49.912
900	16.500	25.882	16.146	8.763	- 216.362	- 178.478	43.340
1000	16.800	27.637	17.208	10.429	- 216.148	- 174.281	38.089

June 30, 1967

ΔHf°_0 = -215.9 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 10.372 ± 0.03 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -217.1 ± 0.5 kcal/mol

Tt = 543 ± 3°K(low cristobalite → high cristobalite)

ΔHt° = 0.321 ± 0.06 kcal/mol

Heat of Formation

The heat of formation is calculated from that of quartz using ΔHr°_{970} = 0.45 ± 0.15 kcal/mol for high quartz → high cristobalite, as determined by Holm(1) from ΔHsoln in an oxide melt. This value reduces to ΔHr°_{298} = 0.60 kcal/mol for low quartz → low cristobalite. Kracek(2) obtained essentially the same value, ΔHr°_{298} = 0.63 kcal/mol, from ΔHsoln in HF(aq, 74.7°C), while Hummel(3) found ΔHr°_{298} = 1.80 kcal/mol from ΔHsoln in HF(aq, 26.5°C). The larger ΔHr° corresponds to a less negative ΔHf° (i.e., less stable) and suggests that the sample of Hummel has disorder approaching that of vitreous silica. Presumably, this disagreement arises from different methods of preparation of cristobalite from quartz. Holm heated for 24 hours at 1743°K, while Hummel heated for 4 hours at 1973°K. Hummel's sample was then ground and treated with dilute HF to remove amorphous surface layers created by grinding; particles smaller than 2.5 microns were used in order to obtain adequate rates of dissolution. Neither author gave X-ray or DTA evidence to confirm that the samples were the more stable, ordered form of cristobalite(15).

The calorimetric data are summarized below along with equilibrium data which confirm the adopted values of ΔHf° for cristobalite and quartz. Data from Matoba(5) and Rein(6) were reduced to the standard state of Si(ℓ) using activity coefficients from the curves of (10).

Source	Method	Reaction	Range T, °K	No. of Points	ΔHr°_T kcal/mol	ΔHr°_{298} kcal/mol	Drift eu	ΔHf°_{298} kcal/mol
1. Holm (1967)	ΔHsoln in oxide melt	A	970	3	0.45±0.15	0.6	-	-217.10
2. Hummel (1959)	ΔHsoln in HF(aq, 26.5°C)	A	299.65	8	1.80±0.2	1.80	-	-215.90
3. Kracek (1953)	ΔHsoln in HF(aq, 74.7°C)	A	298-348	-	-	0.63±0.05	-	-217.07
4. Humphrey (1952)	ΔHsoln in HF(aq, 73.7°C)	A	298-347	6	-	0.93±0.1	-	-216.77
5. Matoba (1959)	Keq + γ(Si)	B	1843-1953	3	104.5±0.6*	112.48*	0.8	-217.17
6. Rein (1963)	Keq + γ(Si)	C	1773-1798	5	-	175.42*	31±37	-217.38
	Keq + γ(Si)	D	1823-1873	6	-	228.5*	10±6	-212.3
7. Kay (1960)	Kp	E	1703-1829	14	145.9±1.3*	146.92*	-2.3±0.7	-217.94
8. Baird (1958)	Kp	E	1673-1853	5	145.5±3.5*	147.43*	-1.9±1.9	-218.45

*Values at T are from second law analysis while those at 298.15°K are from third law.

A. SiO_2(quartz, low or high) = SiO_2(cristobalite, low or high)

B. SiO_2(high cristobalite) + $2H_2(g)$ = Si(ℓ) + $2H_2O(g)$

C. SiO_2(high cristobalite) + 2C(graph) = Si(ℓ) + 2CO(g)

D. SiO_2(high cristobalite) + 2SiC(β) = 3Si(ℓ) + 2CO(g)

E. SiO_2(high cristobalite) + 3C(graph) = SiC(β) + 2CO(g)

Heat Capacity and Entropy

Cp° below 300°K is based on data of Westrum(11). Earlier data of Anderson(12) are in satisfactory agreement. The entropy is obtained from Cp° using S°_5 = 0.0007 eu. Cp° above 300°K is derived from enthalpy data of Mosesman(13) and White(14). The former deviate from the adopted functions by -0.7 to 0.5% and the latter by +0.4%. Although the functions above 300°K appear to be reliable, it would be desirable to have new data for a well-characterized sample (see Transition Data).

Transition Data

Low cristobalite is metastable with respect to quartz but persists up to Tt. Tt is taken as the temperature at the peak in the heating curve for well-ordered cristobalite; however, see (15, 16) for detailed discussions of temperatures about 25° lower which were found from cooling curves. ΔHt° is derived from enthalpy data(13, 14) for high cristobalite using the adopted enthalpy for the low form. The enthalpy data of Mosesman(13) gave a lower Tt which suggests that the sample was less well-ordered than desirable. ΔHt° is confirmed, however, by other data which are summarized below. Additional polymorphism is discussed on the table for high cristobalite.

Source	Method	ΔHt°, kcal/mol
13. Mosesman (1941)	Enthalpy data	0.321
17. Berger (1965)	Microcalorimetric thermal analysis	0.318±0.018
18. Majumdar (1964)	ΔV and dT/DP	0.27
19. Sabatier (1957)	Differential thermal analysis	0.26±0.01

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Quartz (SiO_2)

(Crystal)   GFW = 60.0848

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 1.653	- 216.509	- 216.509	INFINITE
100	3.749	2.317	17.327	- 1.501	- 217.115	- 213.116	465.764
200	7.901	6.235	10.800	- .913	- 217.504	- 208.950	228.330
298	10.557	9.910	9.910	.000	- 217.700	- 204.703	150.051
300	10.700	9.976	9.910	.020	- 217.702	- 204.623	149.067
400	12.770	13.354	10.357	1.199	- 217.741	- 200.253	109.413
500	14.255	16.372	11.264	2.554	- 217.661	- 195.999	85.622
600	15.396	19.075	12.344	4.038	- 217.500	- 191.547	69.771
700	16.436	21.526	13.483	5.630	- 217.271	- 187.239	58.459
800	17.515	23.794	14.632	7.330	- 216.969	- 182.969	49.985
900	16.240	26.006	15.778	9.204	- 216.521	- 178.749	43.406
1000	16.480	27.729	16.889	10.840	- 216.336	- 174.561	38.150
1100	16.720	29.311	17.947	12.500	- 216.150	- 170.393	33.854
1200	16.960	30.776	18.956	14.184	- 215.959	- 166.241	30.277
1300	17.200	32.143	19.918	15.892	- 215.763	- 162.105	27.253
1400	17.440	33.427	20.838	17.624	- 215.560	- 157.987	24.663
1500	17.680	34.638	21.718	19.380	- 215.350	- 153.881	22.420
1600	17.920	35.787	22.561	21.160	- 215.132	- 149.791	20.460
1700	18.160	36.880	23.372	22.964	- 226.898	- 145.507	18.719
1800	18.400	37.925	24.151	24.792	- 226.609	- 140.833	17.099
1900	18.640	38.926	24.903	26.644	- 226.302	- 136.076	15.652
2000	18.880	39.889	25.628	28.520	- 225.976	- 131.339	14.352

Dec. 31, 1960; Dec. 31, 1962; June 30, 1967

QUARTZ (SiO_2)   (CRYSTAL)   GFW = 60.0848 O_2Si

ΔHf°_0 = -216.5 ± 0.4 kcal/mol

$S^\circ_{298.15}$ = 9.91 ± 0.03 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -217.7 ± 0.4 kcal/mol

Tt_1 = 847 ± 1.5°K(low quartz → high quartz) ΔHt°_1 = 0.174 ± 0.04 kcal/mol

Tt_2 = 1079 ± 250°K(high quartz → high cristobalite) ΔHt°_2 = 0.48 ± 0.15 kcal/mol

Tm = 1696 ± 50°K(high quartz → liquid)   ΔHm° = 1.84 ± 0.2 kcal/mol

Heat of Formation

The heat of formation is based on data of Wise (1) for combustion of SiO_2(low quartz) and Si(c) in F_2 to form SiF_4(g). Good (2) burned a mixture of Si(c) and vinylidene fluoride polymer in oxygen in the presence of HF(aq) to form H_2SiF_6(aq HF). Combining this result with a previous heat of solution of quartz (3), the authors derived ΔHf°_{298} = -217.5 ± 0.5 kcal/mol. Agreement with the adopted value is excellent, considering the complexity of the latter scheme. Both schemes are independent of ΔHf°(HF), although the polymer-Si scheme depends on the heat of dilution of HF(aq). Wise (1) has reviewed other data which confirm the adopted value rather than the oxygen combustion value (4) of -209.9 kcal/mol. Pertinent equilibrium data are analyzed on the table for SiO_2(low cristobalite), while the calorimetric results are summarized below.

Source	Reaction	ΔHr°_{298}, kcal/mol	ΔHf°_{298}, kcal/mol
1. Wise (1963)	SiO_2(low quartz) + $2F_2$(g) → SiF_4(g) + O_2(g)	-168.26 ± 0.28	-217.72 ± 0.34
2. Good (1964)	See text.	-	-217.5
3. Humphrey (1952)	Si(c) + $2O_2$(g) → SiO_2(low quartz)	-209.9	-209.9

Heat Capacity and Entropy

Heat capacities below 300°K are based on data of Jones (5) and Westrum (6). Earlier data of Anderson (7) are in good agreement. The entropy is obtained from Cp° using S°_2 = 0.00001 eu. Cp° from 300° to 847°K is derived from adiabatic calorimetric data of Moser (8) and Sinel'nikov (9). The adopted Cp° is discontinuous at 847°K and ΔCp° = -2.17 gibbs/mol. Values above the transition temperature are based on data of Moser and on data up to 1473°K obtained with a thermal analysis method by Leonidov (10). Cp° is extrapolated linearly to higher temperatures.

From a review of data available before 1953, Kelley (11) selected almost identical enthalpies below 847°K but a value higher by 96 cal/mol at 900°K. The higher value, due to use of a larger ΔHt°_1, was presumably based on Roth (12), Wietzel (13) and White 14) whose enthalpy data were given the most weight by Kelley. Near 900°K these three sets of data deviate from the adopted function by -150±30, +130±40 and +15±35 cal/mol, respectively; however, a recent enthalpy datum (15) obtained by transposed temperature drop calorimetry deviates by +75 cal/mol at 968°K.

Transition Data

Tt_1 is taken as 847 ± 1.5°K based on thermal analysis of many specimens by Kieth and Tuttle (16). Wide variations in Tt_1 for some specimens were attributed by the authors to small amounts of impurities. The discontinuity in the volume curve (17) during inversion from trigonal low quartz to hexagonal high quartz suggests that the transition should be treated as first order. Thus, the heat of transition is derived as (1011-854+17) = 174 cal/mol, where 1011 ± 6 is ($H^\circ_{873.15} - H^\circ_{823.15}$) measured by Moser (8), 854 is the corresponding increment calculated from the JANAF Cp°, and 17 is an endpoint correction for the difference between the observed and adopted curves below 823.15°K. Some of the more recent data which confirm the adopted ΔHt°_1 are summarized below.

Source	Method		ΔHt°_1, kcal/mol
8. Moser (1936)	H and Cp from adiabatic calorimetry		0.174
9. Sinel'nikov (1953)	Integration of Cp from adiabatic calorimetry		0.143
10. Leonidov (1964)	Thermal analysis		0.198
17. Berger (1964)	ΔV with dT/dP = 0.026°K/atm		0.12
18. Berger (1965)	Microcalorimetric thermal analysis	Single crystal	0.156, 0.165, 0.178 ± 0.010
		Various crushed samples	0.124 to 0.193

Additional polymorphism of SiO_2 is discussed on the table for high cristobalite. Quartz has been superheated through the cristobalite region to some 300° above its metastable melting point. This melting point is calculated from the adopted tables as 1696 ± 50°K, which agrees well with the range 1673 - 1723°K indicated by the data of Mackenzie (19). The adopted tables predict the inversion of high quartz to high cristobalite at 1079 ± 250°K. Holmquist (20) tentatively placed this inversion at 1298 ± 25°K. ΔHt°_2 and ΔHm° are calculated from the differences in heats of formation of the appropriate phases at Tt_2 and Tm.

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O_2Si

Silicon Dioxide (SiO_2)

(Liquid) GFW = 60.0848

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	1.098	INFINITE	-1.672	-214.568	-214.568	INFINITE
100	3.861	3.820	18.870	-1.505	-215.159	-211.310	461.817
200	7.824	7.792	12.337	-.909	-215.540	-207.297	226.524
298	10.560	11.455	11.455	.000	-215.740	-203.204	148.952
300	10.604	11.520	11.455	.020	-215.742	-203.126	147.977
400	12.552	14.856	11.897	1.184	-215.796	-198.909	108.679
500	13.882	17.808	12.790	2.509	-215.746	-194.690	85.099
600	14.829	20.427	13.849	3.947	-215.631	-190.490	69.386
700	15.529	22.768	14.959	5.467	-215.474	-186.311	58.169
800	16.063	24.878	16.069	7.047	-215.292	-182.159	49.763
900	16.481	26.795	17.156	8.675	-215.090	-178.028	43.231
1000	16.814	28.550	18.209	10.341	-214.875	-173.921	38.010
1100	17.083	30.165	19.223	12.036	-214.654	-169.837	33.743
1200	17.303	31.661	20.198	13.756	-214.427	-165.772	30.191
1300	17.485	33.054	21.134	15.495	-214.200	-161.728	27.189
1400	17.650	34.355	22.033	17.252	-213.972	-157.699	24.618
1500	17.800	35.576	22.895	19.022	-213.748	-153.687	22.392
1600	19.130	36.751	23.724	20.841	-213.489	-149.691	20.447
1700	20.490	37.968	24.527	22.850	-225.052	-145.611	18.720
1800	20.500	39.139	25.306	24.899	-224.542	-140.952	17.114
1900	20.500	40.247	26.064	26.949	-224.037	-136.321	15.681
2000	20.500	41.299	26.799	28.999	-223.537	-131.719	14.394
2100	20.500	42.299	27.514	31.049	-223.042	-127.139	13.232
2200	20.500	43.253	28.208	33.099	-222.554	-122.586	12.178
2300	20.500	44.164	28.882	35.149	-222.070	-118.052	11.218
2400	20.500	45.037	29.537	37.199	-221.592	-113.539	10.339
2500	20.500	45.873	30.174	39.249	-221.120	-109.047	9.533
2600	20.500	46.677	30.793	41.299	-220.652	-104.572	8.790
2700	20.500	47.451	31.396	43.349	-220.190	-100.118	8.104
2800	20.500	48.197	31.983	45.399	-219.733	-95.679	7.468
2900	20.500	48.916	32.554	47.449	-219.281	-91.254	6.877
3000	20.500	49.611	33.111	49.499	-218.834	-86.849	6.327
3100	20.500	50.283	33.654	51.549	-218.391	-82.456	5.813
3200	20.500	50.934	34.184	53.599	-217.953	-78.078	5.332
3300	20.500	51.565	34.701	55.649	-217.519	-73.715	4.882
3400	20.500	52.177	35.206	57.699	-217.090	-69.363	4.459
3500	20.500	52.771	35.700	59.749	-216.664	-65.026	4.060
3600	20.500	53.349	36.182	61.799	-308.203	-58.442	3.548
3700	20.500	53.910	36.654	63.849	-307.686	-51.509	3.042
3800	20.500	54.457	37.115	65.899	-307.172	-44.592	2.565
3900	20.500	54.989	37.567	67.949	-306.662	-37.690	2.112
4000	20.500	55.508	38.009	69.999	-306.156	-30.800	1.683
4100	20.500	56.015	38.442	72.049	-305.654	-23.925	1.275
4200	20.500	56.509	38.866	74.099	-305.153	-17.062	.888
4300	20.500	56.991	39.282	76.149	-304.655	-10.204	.519
4400	20.500	57.462	39.690	78.199	-304.161	-3.364	.167
4500	20.500	57.923	40.090	80.249	-303.668	3.471	-.169

Dec. 31, 1960; Dec. 31, 1962; June 30, 1967

$S^\circ_{298.15}$ = 11.455 ± 0.3 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -215.74 kcal/mol

Tm = 1996 ± 5°K(high cristobalite → liquid)

ΔHm° = 2.29 ± 0.5 kcal/mol

Heat of Formation

The heat of formation is calculated from that of quartz using ΔHr°_{970} = 1.45 ± 0.15 kcal/mol for high quartz → $SiO_2(\ell)$, as determined by Holm (1) from ΔHsoln in an oxide melt. This value reduces to ΔHr°_{298} = 1.96 kcal/mol for low quartz → $SiO_2(\ell)$ and is consistent within ±0.3 kcal/mol with other calorimetric data summarized below. Earlier results were reviewed by Hummel (4).

	Source	Method	Reaction	T, °K	ΔHr°_T kcal/mol	ΔHr°_{298} kcal/mol	ΔHf°_{298} kcal/mol
1.	Holm (1967)	ΔHsoln in oxide melt	A	970	1.45±0.15	1.96	-215.74
2.	Wise (1963)	ΔHc in fluorine	B	298	1.78±0.46	1.78	-215.92
3.	Kracek (1953)	ΔHsoln in HF(aq, 74.7°C)	A	298-348	-	2.18±0.05	-215.52
4.	Hummel (1959)	ΔHsoln in HF(aq, 26.5°C)	A	300	2.27±0.2	2.27	-215.43

A. SiO_2(quartz, low or high) → $SiO_2(\ell)$

B. $SiO_2(\ell) + 2F_2(g) \rightarrow SiF_4(g) + O_2(g)$

Heat Capacity and Entropy

Cp° below 300°K is based on data of Flubacher (5) and Westrum (6) for samples annealed at 1100 and 1070°C, respectively. Data of Turdakin (7) are higher by about 1 percent in the range 60-160°K and at 300°K but are in agreement elsewhere. The entropy is calculated from Cp° using $S^\circ_{2.34} - S^\circ_0$ = 0.0001 eu and S°_0 = 1.098 eu. Cp° data (6) for a different sample annealed at 1300°C yield an entropy larger by <0.04 eu. Earlier data were reviewed by Kelley (8). The residual entropy is calculated from $S^\circ_0 = S^\circ_{1996} - (S^\circ_{1996} - S^\circ_0)$ = 41.258 - 40.160 = 1.098 eu, where 40.160 is obtained from the adopted functions, while 41.258 is the sum of ΔSm° = 1.147 eu and S°_{1996} = 40.111 eu for high cristobalite. We estimate the uncertainty as ±0.3 eu, primarily from the uncertainty in ΔHm°.

Cp° above 300°K is based on adiabatic calorimetric data of Moser (9) up to 900°K. Enthalpy data of White (10) and Fischer (11) are in excellent agreement. Cp° from 900 to 1500°K is derived from enthalpy data of Southard (12) and White (10). Maximum deviation of the data from the adopted values in this range is 0.5 percent. Enthalpy data of Egan (13) and Kelley (14) deviate from the adopted values by less than 1 percent in the range 1000-1500°K, although large positive deviations appear at lower temperatures.

In the region 1500-1700°K, the adopted Cp° shows a rapid, sigmoidal rise which is suggested by the enthalpy data of Wietzel (15). This is presumed to be the glass transition region in which Cp° rises to that of the stable liquid. Cp° above 1700°K is estimated as 20.5 gibbs/mol or 6.83 gibbs/g-atom. This value is consistent with the enthalpy data (15) and with liquid heat capacities of Al_2O_3, $Na_2Si_2O_5$ and Na_2SiO_3.

Melting Data

The melting point of high cristobalite is 1996 ± 5°K, while the metastable melting point of high quartz is 1696 ± 50°K. ΔHm° is the difference between ΔHf° for liquid and high cristobalite at Tm. Values ranging from 1.8 to 3.6 kcal/mol have been derived from various interpretations of phase diagrams (1).

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Silicon Dioxide (SiO_2)

(Ideal Gas) GFW = 60.0848

T, °K	gibbs/mol Cp°	 S°	 −(G°−H°298)/T	kcal/mol H°−H°298	 ΔHf°	 ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.529	- 72.685	- 72.685	INFINITE
100	7.510	44.948	63.180	- 1.823	- 72.737	- 73.001	159.543
200	9.320	50.742	55.625	- .977	- 72.868	- 73.215	80.005
298	10.518	54.699	54.699	.000	- 73.000	- 73.357	53.772
300	10.537	54.765	54.700	.019	- 73.003	- 73.360	53.442
400	11.474	57.929	55.125	1.122	- 73.118	- 73.460	40.137
500	12.207	60.572	55.957	2.307	- 73.208	- 73.534	32.142
600	12.767	62.849	56.920	3.557	- 73.281	- 73.593	26.806
700	13.188	64.851	57.913	4.856	- 73.345	- 73.640	22.991
800	13.507	66.633	58.894	6.192	- 73.407	- 73.679	20.128
900	13.750	68.239	59.844	7.555	- 73.470	- 73.708	17.899
1000	13.938	69.698	60.758	8.940	- 73.536	- 73.730	16.114
1100	14.085	71.033	61.632	10.341	- 73.609	- 73.746	14.652
1200	14.203	72.264	62.468	11.756	- 73.687	- 73.755	13.433
1300	14.297	73.405	63.266	13.181	- 73.774	- 73.758	12.400
1400	14.374	74.467	64.028	14.615	- 73.869	- 73.753	11.513
1500	14.438	75.461	64.758	16.055	- 73.975	- 73.741	10.744
1600	14.491	76.395	65.456	17.502	- 74.090	- 73.722	10.070
1700	14.536	77.275	66.126	18.953	- 86.209	- 73.589	9.461
1800	14.573	78.107	66.768	20.409	- 86.292	- 72.844	8.845
1900	14.606	78.896	67.386	21.868	- 86.378	- 72.096	8.293
2000	14.634	79.645	67.980	23.330	- 86.466	- 71.340	7.796
2100	14.658	80.360	68.553	24.795	- 86.556	- 70.582	7.346
2200	14.679	81.042	69.105	26.261	- 86.652	- 69.819	6.936
2300	14.698	81.695	69.639	27.730	- 86.749	- 69.053	6.561
2400	14.714	82.321	70.154	29.201	- 86.850	- 68.279	6.218
2500	14.728	82.922	70.653	30.673	- 86.956	- 67.506	5.901
2600	14.741	83.500	71.136	32.146	- 87.065	- 66.725	5.609
2700	14.753	84.057	71.604	33.621	- 87.178	- 65.942	5.338
2800	14.763	84.593	72.059	35.097	- 87.295	- 65.150	5.085
2900	14.773	85.112	72.500	36.574	- 87.416	- 64.358	4.850
3000	14.781	85.613	72.929	38.052	- 87.541	- 63.562	4.631
3100	14.789	86.097	73.346	39.530	- 87.670	- 62.758	4.424
3200	14.796	86.567	73.752	41.009	- 87.803	- 61.953	4.231
3300	14.802	87.022	74.147	42.489	- 87.939	- 61.143	4.049
3400	14.808	87.464	74.532	43.970	- 88.079	- 60.329	3.878
3500	14.813	87.894	74.908	45.451	- 88.222	- 59.515	3.716
3600	14.818	88.311	75.274	46.932	- 180.330	- 56.432	3.426
3700	14.823	88.717	75.632	48.414	- 180.381	- 52.990	3.130
3800	14.827	89.112	75.982	49.897	- 180.434	- 49.543	2.849
3900	14.831	89.498	76.323	51.380	- 180.491	- 46.105	2.584
4000	14.834	89.873	76.657	52.863	- 180.552	- 42.656	2.331
4100	14.838	90.239	76.984	54.346	- 180.617	- 39.208	2.090
4200	14.841	90.597	77.304	55.830	- 180.682	- 35.761	1.861
4300	14.843	90.946	77.617	57.315	- 180.749	- 32.305	1.642
4400	14.846	91.288	77.924	58.799	- 180.821	- 28.858	1.433
4500	14.849	91.621	78.225	60.284	- 180.893	- 25.396	1.233
4600	14.851	91.948	78.520	61.769	- 180.967	- 21.941	1.042
4700	14.853	92.267	78.809	63.254	- 181.045	- 18.481	.859
4800	14.855	92.580	79.092	64.739	- 181.123	- 15.023	.684
4900	14.857	92.886	79.371	66.225	- 181.202	- 11.564	.516
5000	14.859	93.186	79.644	67.711	- 181.283	- 8.103	.354
5100	14.861	93.481	79.913	69.197	- 181.366	- 4.636	.199
5200	14.862	93.769	80.176	70.683	- 181.450	- 1.171	.049
5300	14.864	94.052	80.435	72.169	- 181.534	2.302	- .095
5400	14.865	94.330	80.690	73.656	- 181.620	5.765	- .233
5500	14.867	94.603	80.941	75.142	- 181.707	9.237	- .367
5600	14.868	94.871	81.187	76.629	- 181.796	12.709	- .496
5700	14.869	95.134	81.429	78.116	- 181.885	16.184	- .621
5800	14.870	95.393	81.668	79.603	- 181.976	19.661	- .741
5900	14.872	95.647	81.903	81.090	- 182.068	23.134	- .857
6000	14.873	95.897	82.134	82.577	- 182.161	26.615	- .969

Dec. 31, 1960; Dec. 31, 1962; Sept. 30, 1967

SILICON DIOXIDE (SiO_2) (IDEAL GAS) GFW = 60.0848

Point Group [$D_{\infty h}$]

$S^\circ_{298.15}$ = [54.7] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -72.7 ± 8 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -73 ± 8 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[980] (1)
[370] (2)
[1430] (1)

Bond Distance: Si-O = [1.55] Å
Bond Angle: O-Si-O = [180°]
Rotational Constant: B_0 = [0.2193] cm^{-1}

Heat of Formation

The adopted value is based on the data summarized below. Margrave (1) has reported a value of ΔHs°_{298} = 140.9±1 kcal/mol but details are not yet available. Assuming that this corresponds to reaction A below, we calculate ΔHf°_{298} = -75.5 kcal/mol. Firsova (2) reported two values of the sublimation pressure which were derived from Knudsen effusion data using auxiliary data for SiO(g). Porter (4) derived two pressures from a mass spectrometric study and also obtained a 2nd Law value for ΔHs° from ion intensities. The resulting range for ΔHs°_{298}, 136 to 141 kcal/mol, is consistent with the lower limit of 130 kcal/mol obtained by Bergman (3) from a method involving explosion in a spherical bomb. An alternative analysis of the mass spectrometric data (4) using the gas phase reaction B suggests an even higher ΔHs° of 148 kcal/mol. The adopted ΔHf° corresponds to ΔHs°_{298} = 143.4±8 kcal/mol and to $\Delta Hatom^\circ_0$ = 297.3±8 kcal/mol.

Source	Reaction	Method	Range, T°K	ΔHr°_{298}, kcal/mol 2nd Law	 3rd Law	Drift eu	ΔHf°_{298}, kcal/mol
Margrave (1967)	A	-	-	-	140.9±1	-	-75.5
Firsova (1960)	A	Knudsen, calculation	1600-1800	-	137.0±2	-	-79.4
Bergman (1959)	A	Explosion	-	-	>130	-	>-86
Porter (1955)	A	Knudsen mass spec.	1800-1900	128	139.6±0.3	6	-76.8
	A	Ion intensities	1750-1980	136±8	-	-	-80
	B	Knudsen mass spec.	1800-1900	-2	-44.8±1.2	-23	-68.8

A. SiO_2(high cristobalite) = SiO_2(g) B. $SiO(g)+1/2O_2(g) = SiO_2(g)$

Heat Capacity and Entropy

Point group, ground state quantum weight and the linear symmetrical configuration are estimated by analogy with the properties of CO_2. From the bond lengths in SiO, CO_2 and CO, the length in SiO_2 is estimated as 1.509 x 1.160/1.128. Bond lengths and atomization energies for these molecules are reasonably consistent with the existence of six-electron bonds in the monoxides and four-electron bonds in the dioxides (5). Vibrational frequencies are estimated from a valence bond calculation using force constants, $k = 9 \times 10^5$ and $k\delta/\ell^2 = 0.3 \times 10^5$ dyne/cm, which are obtained from those of SiO, CO_2 and CO. The moment of inertia is 12.76×10^{-39} g cm^2.

References

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Titanium Dioxide, Anatase (TiO_2)

(Crystal) GFW = 79.8988

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.062	-221.835	-221.835	INFINITE
100	4.585	2.302	21.322	-1.902	-222.503	-218.397	477.306
200	10.009	7.293	13.048	-1.151	-222.906	-214.107	233.965
298	13.257	11.931	11.931	.000	-223.000	-209.763	153.760
300	13.312	12.013	11.931	.025	-222.999	-209.681	152.752
400	15.244	16.144	12.481	1.465	-222.888	-205.253	112.145
50C	16.153	19.654	13.575	3.040	-222.690	-200.867	87.799
600	16.658	22.647	14.843	4.682	-222.469	-196.524	71.584
700	16.973	25.239	16.148	6.364	-222.251	-192.217	60.013
800	17.186	27.520	17.429	8.073	-222.050	-187.941	51.343
900	17.341	29.554	18.666	9.799	-221.874	-183.688	44.605
1000	17.459	31.387	19.848	11.540	-221.724	-179.452	39.219
1100	17.553	33.056	20.974	13.290	-221.602	-175.231	34.815
1200	17.630	34.586	22.045	15.050	-222.442	-170.982	31.140
1300	17.696	36.000	23.065	16.816	-222.247	-166.702	28.025
1400	17.754	37.314	24.036	18.588	-222.068	-162.437	25.358
1500	17.806	38.541	24.963	20.366	-221.906	-158.184	23.047
1600	17.853	39.691	25.848	22.149	-221.763	-153.939	21.027
1700.	17.896	40.775	26.694	23.937	-221.640	-149.705	19.246
1800	17.936	41.799	27.505	25.729	-221.542	-145.476	17.663
1900	17.974	42.770	28.283	27.524	-221.469	-141.253	16.248
2000	18.011	43.693	29.031	29.323	-225.868	-136.880	14.958
2100	18.046	44.572	29.750	31.126	-225.820	-132.429	13.782
2200	18.079	45.412	30.443	32.932	-225.776	-127.983	12.714
2300	18.112	46.217	31.112	34.742	-225.732	-123.541	11.739
2400	18.144	46.988	31.757	36.555	-225.691	-119.095	10.845
2500	18.175	47.730	32.381	38.371	-225.653	-114.658	10.023

Dec. 31, 1960; Mar. 31, 1967

TITANIUM DIOXIDE, ANATASE (TiO_2) (CRYSTAL) GFW = 79.8988

$\Delta Hf°_0$ = -221.8 ± 1 kcal/mol

$S°_{298.15}$ = 11.93 gibbs/mol

$\Delta Hf°_{298.15}$ = -223.0 ± 1 kcal/mol

Tt = 918 °K

$\Delta Ht°$ = [0.0] kcal/mol

Tm = Unknown

$\Delta Hm°$ = Unknown

$\Delta Hs°_{298.15}$ = 161 kcal/mol

Heat of Formation.

The value of $\Delta Hf°_{298}$ (anatase) is obtained from J. L. Margrave and B. D. Kybett, "Thermodynamic and Kinetic Studies of Borides and Other Refractory Materials at High Temperatures," Tech. Rept. AFML-TR-65-123, August 1965, Rice University, Houston, Texas. The authors measured the heat of fluorination of anatase, according to the reaction TiO_2 (anatase) + $2F_2(g)$ = $TiF_4(c)$ + $O_2(g)$, but no experimental data were given.

F. W. Vahldiek, J. Less-Common Metals 11, 99 (1966), studied the irreversible anatase-rutile phase transition at pressures of 3.8 to 24 kbars and temperatures 20 to 1000°C. Isothermal phase-transition studies were also carried out at 1 bar pressure and 880-950°C. From the slope, dT/dP, the enthalpy differences between rutile and anatase were calculated to be -2.79 and -2.89 kcal/mol at 1183 and 1223°K, respectively. Using these data and $\Delta Hf°_{298}$(rutile) = -225.8 kcal/mol, the value of $\Delta Hf°_{298}$(anatase) is derived as -223.23 kcal/mol, which is in excellent agreement with the adopted value.

Heat Capacity and Entropy.

Low temperature heat capacities, 52-296°K, were measured by C. H. Shomate, J. Am. Chem. Soc. 69, 218 (1947). Enthalpy data were determined in the range 416-1305°K by B. F. Naylor, J. Am. Chem. Soc. 68, 1077 (1946), and in the range 580 - 1000°K by J. Lietz, Hamburger Beitr. Angew. Mineral. Kristallphysik 1, 229 (1956). High temperature heat capacities are derived from the enthalpy data, subject to the constraint that there be a smooth joint at 298°K. The resulting enthalpies are higher by 1 to 3% than those measured by Lietz and lower by 1 to 4% than those measured by Naylor. Values above 1300°K are smoothly extrapolated. $S°_{298}$ is calculated from the low temperature Cp° using $S°_{50}$ = 0.45 eu.

In view of the discrepancies in the enthalpy data, a review of the anatase samples is pertinent. Those of Shomate and Lietz were prepared by precipitation of the hydrated oxide and conversion to the oxide at 550 - 565°C. Shomate's starting material was high purity Ti and the product analyzed as 99.3% TiO_2. Lietz' starting material was high purity $TiCl_4$. Naylor's sample, obtained from J. T. Baker Co., was dried at 1050°C; spectrographic analysis indicated 0.3% SiO_2 and 0.15% CaO. All three samples gave only the X-ray lines of anatase.

Transition Data.

Tm = 918°K and $\Delta Ht°$ = 0.040 kcal/mol have been reported by J. Lietz, loc. cit. A. Schröder, Z. Kryst. 66, 493 (1928), suggested a transition temperature at 915°K on the basis of a peak in the thermal expansion curve. Lietz reported $\Delta Ht°$ = 0.04 kcal/mol, but this value is not adopted since its magnitude is much less than the uncertainty in the selected enthalpies. Further study is desirable to confirm this transition.

Heat of Sublimation.

$\Delta Hs°_{298}$ is calculated as the difference between $\Delta Hf°_{298}$ for $TiO_2(g)$ and TiO_2(anatase).

Titanium Dioxide, Rutile (TiO_2)
(Crystal) GFW = 79.8988

	gibbs/mol			kcal/mol			
T, °K	$Cp°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0	.000	.000	INFINITE	- 2.065	- 224.638	- 224.638	INFINITE
100	4.430	2.438	21.438	- 1.900	- 225.301	- 221.208	483.450
200	10.053	7.375	13.149	- 1.155	- 225.710	- 216.927	237.047
298	13.153	12.031	12.031	.000	- 225.800	- 212.593	155.834
300	13.191	12.112	12.031	.024	- 225.800	- 212.511	154.814
400	14.621	16.126	12.569	1.423	- 225.730	- 208.089	113.694
500	15.429	19.481	13.625	2.928	- 225.602	- 203.692	89.034
600	15.991	22.346	14.846	4.500	- 225.451	- 199.325	72.604
700	16.438	24.845	16.099	6.122	- 225.293	- 194.983	60.876
800	16.524	27.066	17.334	7.785	- 225.138	- 190.665	52.087
900	17.173	29.068	18.528	9.485	- 224.988	- 186.364	45.255
1000	17.500	30.894	19.675	11.219	- 224.845	- 182.080	39.794
1100	17.513	32.577	20.772	12.985	- 224.707	- 177.810	35.328
1200	18.116	34.140	21.822	14.781	- 225.511	- 173.515	31.601
1300	18.412	35.601	22.826	16.608	- 225.255	- 169.191	28.444
1400	18.703	36.977	23.788	18.464	- 224.992	- 164.890	25.741
1500	18.990	38.277	24.711	20.348	- 224.724	- 160.606	23.400
1600	19.274	39.511	25.598	22.262	- 224.450	- 156.338	21.355
1700	19.556	40.688	26.451	24.203	- 224.174	- 152.091	19.553
1800	19.836	41.814	27.276	26.173	- 223.898	- 147.859	17.953
1900	20.115	42.894	28.068	28.170	- 223.623	- 143.642	16.523
2000	20.393	43.933	28.835	30.196	- 227.795	- 139.287	15.221
2100	20.670	44.934	29.578	32.249	- 227.497	- 134.866	14.036
2200	20.946	45.902	30.298	34.330	- 227.178	- 130.464	12.960
2300	21.221	46.840	30.997	36.439	- 226.836	- 126.078	11.980
2400	21.496	47.749	31.676	38.574	- 226.472	- 121.703	11.083
2500	21.771	48.632	32.337	40.737	- 226.087	- 117.347	10.258

Dec. 31, 1960; Mar. 31, 1967

TITANIUM DIOXIDE, RUTILE (TiO_2) (CRYSTAL) GFW = 79.8988

$\Delta Hf°_0$ = -224.6 ± 1 kcal/mol

$S°_{298.15}$ = 12.03 gibbs/mol

$\Delta Hf°_{298.15}$ = -225.8 ± 1 kcal/mol

Tm = 2143°K

$\Delta Hm°$ = [16] kcal/mol

$\Delta Hs°_{298.15}$ = 163.8 kcal/mol

Heat of Formation.

The heat of formation for rutile has been determined from combustion calorimetry by many investigators. Several of the more consistent $\Delta Hf°_{298}$ values are listed in the table below. Ariya et al.[3] reported that the composition of the rutile obtained from combustion of Ti(c) was between $TiO_{1.94}$ and $TiO_{1.95}$. Emf studies by R. N. Blumenthal and D. H. Whitmore, J. Electrochem. Soc. 110, 92 (1963), indicate that at 1200°K there is a two-phase region beginning at about $TiO_{1.99}$. If this region extends to 298°K, then the non-stoichiometric combustion products probably involve a mixture of two phases. Mah et al.[4] applied an approximate energy correction for incomplete combustion which corresponds to 0.7 - 1.5 kcal/mol in $\Delta Hf°_{298}$. Analogous corrections were applied by Ariya et al.[3] but were not mentioned by Neumann et al.[1] and Humphrey[2].

The $\Delta Hf°_{298}$ value reported by Margrave and Kybett[5] was obtained by fluorine bomb calorimetry, according to the reaction $TiO_2(rutile) + 2F_2(g) = TiF_4(c) + O_2(g)$. No experimental data were given.

Comparison of the fluorine result with the oxygen results indicates that the magnitude of the corrections for the oxygen data is reasonable, probably within ± 1 kcal/mol, provided that the fluorine data refer to stoichiometric TiO_2. Corresponding $\Delta Gf°$ corrections for TiO_{2-x} are of the same order of magnitude when estimated from the partial molar free energy values given by P. Kofstad, J. Phys. Chem. Solids 23, 1579 (1962), and J. B. Moser, R. N. Blumenthal and D. H. Whitmore, J. Am. Ceram. Soc. 48, 384 (1965).

The $\Delta Hf°_{298}$ value determined by Mah et al.[4] is adopted.

$\Delta Hf°_{298}$, kcal/mol	Source
-225.3 ± 0.3	1. B. Neumann, C. Kröger and H. Kunz, Z. Anorg. Allgem. Chem. 218, 379 (1934).
-225.5 ± 0.2	2. G. L. Humphrey, J. Am. Chem. Soc. 73, 1587 (1951).
-224.9 ± 0.4	3. S. Ariya, M. Morozova, and E. Volf, Z. Neorg. Khim 2, 13 (1957).
-225.8 ± 0.1	4. A. Mah, K. K. Kelley, N. Gellert, E. G. King, and C. O'Brien, U. S. Bur Mines RI5316 (1957).
-225 ± 1	5. J. L. Margrave and B. D. Kybett, "Thermodynamic and Kinetic Studies of Borides and Other Refractory Materials at High Temperatures," Tech. Rept. AFML-TR-65-123, Aug. 1965, Rice University, Houston, Texas.

Heat Capacity and Entropy.

The low temperature heat capacities, 10 - 297.7°K, have been measured by the following investigators: P. H. Keesom and N. Pearlman, Phys. Rev. 112, 800 (1958), 10 - 20°K; J. S. Dugdale, J. A. Morrison and D. Patterson, Proc. Roy. Soc. (London) A224, 228(1954), 20 - 50°K; H. Shomate, J. Am. Chem. Soc. 69, 218 (1947), 52.5 - 297.7°K; and H. J. McDonald and H. Seltz, J. Am. Chem. Soc. 61, 2405 (1939), 68.78 - 295.07°K. The first three sets of Cp data are joined smoothly and extrapolated to 298°K, yielding $S°_{298}$ = 12.03 eu, based on $S°_{10}$ = 0.0014 eu. The Cp values reported by McDonald and Seltz seem too high and are not used.

The high temperature enthalpies have been determined by B. F. Naylor, J. Am. Chem. Soc. 68, 1077 (1946), 393.5 - 1746°K; J. S. Arthur, J. Appl. Phys. 21, 732 (1950), 293.2 - 1073.2°K; and J. Lietz, Hamburger Beitrage Angew. Mineral u. Kristall Phys. 1, 229 (1956), 577.7 - 1283.0°K. The Cp values are derived from the data of Lietz and join smoothly at 298°K with the low temperature data. Deviations from the selected values are -1.6 to +1.0% for Lietz, -6.1 to + 4.0% for Arthur, and +8.6 to +0.8% for Naylor. The data point of Lietz at 947.95°K is omitted as a probable typographical error. The largest deviations in the case of Naylor and Arthur are near 400 and 500°K, respectively.

The mean specific enthalpies have also been measured by L. F. Nilson and O. Pettersson, Z. Physik, Chem. 1, 27 (1887), 373.2 - 717.2 °K.

The samples used by Keesom and Pearlman, Dugdale et al., Shomate, Arthur and Lietz were of high purity, according to chemical and spectroscopic analysis. However, the sample employed by Naylor was black-colored and chemical analysis gave 97.9% TiO_2. The main impurities were: 0.55% ZrO_2, 0.50% SiO_2, 0.27% V_2O_5, 0.15% CaO, 0.15% Fe_2O_3 and 0.12% Al_2O_3. The sample of McDonald and Seltz was obtained commercially. Therefore the results reported by Naylor and McDonald et al. are given the least weight.

Melting Data.

See $TiO_2(l)$ table for details.

Heat of Sublimation.

The difference between $\Delta Hf°_{298}$ for $TiO_2(g)$ and $TiO_2(rutile)$ is $\Delta Hs°_{298}$.

Titanium Dioxide (TiO_2)

(Liquid) GFW = 79.8988

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	13.153	18.934	18.934	.000	-210.726	-199.577	146.294
300	13.191	19.015	18.934	.024	-210.726	-199.507	145.341
400	14.521	23.029	19.472	1.423	-210.656	-195.776	106.967
500	15.429	26.384	20.528	2.928	-210.528	-192.070	83.954
600	15.991	29.249	21.749	4.500	-210.377	-188.393	68.622
700	16.438	31.748	23.002	6.122	-210.219	-184.741	57.679
800	16.824	33.969	24.237	7.785	-210.064	-181.113	49.478
900	17.173	35.971	25.431	9.485	-209.914	-177.503	43.104
1000	17.500	37.797	26.578	11.219	-209.771	-173.909	38.008
1100	17.813	39.480	27.675	12.985	-209.633	-170.329	33.841
1200	18.116	41.043	28.725	14.781	-210.437	-166.724	30.365
1300	18.412	42.504	29.729	16.608	-210.181	-163.091	27.418
1400	21.000	43.880	30.691	18.464	-209.918	-159.481	24.896
1500	21.000	45.328	31.619	20.564	-209.434	-155.893	22.714
1600	21.000	46.684	32.519	22.664	-208.974	-152.339	20.809
1700	21.000	47.957	33.390	24.764	-208.539	-148.813	19.131
1800	21.000	49.157	34.233	26.864	-208.133	-145.312	17.643
1900	21.000	50.293	35.049	28.964	-207.755	-141.833	16.315
2000	21.000	51.370	35.838	31.064	-211.853	-139.219	15.104
2100	21.000	52.394	36.602	33.164	-211.508	-134.543	14.002
2200	21.000	53.371	37.342	35.264	-211.170	-130.888	13.003
2300	21.000	54.305	38.060	37.364	-210.836	-127.247	12.091
2400	21.000	55.198	38.755	39.464	-210.508	-123.616	11.257
2500	21.000	56.056	39.430	41.564	-210.186	-120.006	10.491
2600	21.000	56.879	40.086	43.664	-209.868	-116.404	9.785
2700	21.000	57.672	40.722	45.764	-209.556	-112.815	9.132
2800	21.000	58.436	41.341	47.864	-209.249	-109.239	8.526
2900	21.000	59.173	41.944	49.964	-208.947	-105.670	7.963
3000	21.000	59.884	42.530	52.064	-208.650	-102.111	7.439
3100	21.000	60.573	43.101	54.164	-208.357	-98.565	6.949
3200	21.000	61.240	43.657	56.264	-208.069	-95.033	6.490
3300	21.000	61.886	44.200	58.364	-207.785	-91.503	6.060
3400	21.000	62.513	44.729	60.464	-207.506	-87.983	5.655
3500	21.000	63.122	45.246	62.564	-207.230	-84.475	5.275
3600	21.000	63.713	45.751	64.664	-308.584	-80.704	4.899
3700	21.000	64.289	46.244	66.764	-308.288	-74.382	4.394
3800	21.000	64.849	46.727	68.864	-308.008	-68.065	3.915
3900	21.000	65.394	47.198	70.964	-307.744	-61.752	3.460
4000	21.000	65.926	47.660	73.064	-307.497	-55.449	3.030
4100	21.000	66.444	48.112	75.164	-307.266	-49.147	2.620
4200	21.000	66.950	48.554	77.264	-307.049	-42.857	2.230
4300	21.000	67.445	48.988	79.364	-306.847	-36.571	1.859
4400	21.000	67.927	49.413	81.464	-306.659	-30.287	1.504
4500	21.000	68.399	49.830	83.564	-306.484	-24.006	1.166
4600	21.000	68.861	50.238	85.664	-306.321	-17.727	.842
4700	21.000	69.312	50.639	87.764	-306.171	-11.453	.533
4800	21.000	69.755	51.033	89.864	-306.032	-5.188	.236
4900	21.000	70.188	51.419	91.964	-305.904	1.071	-.048
5000	21.000	70.612	51.799	94.064	-305.786	7.339	-.321

TITANIUM DIOXIDE (TiO_2) (LIQUID) GFW = 79.8988

$S^\circ_{298.15}$ = [18.934] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-210.726] kcal/mol

Tm = 2143°K ΔHm° = [16] kcal/mol

Heat of Formation.

The $\Delta Hf^\circ_{298}(l)$ is calculated from ΔHf°_{298}(rutile, c) by adding ΔHm° and the difference between $H^\circ_{2143} - H^\circ_{298.15}$ for TiO_2(rutile, c) and $TiO_2(l)$.

Heat Capacity and Entropy.

The heat capacity of $TiO_2(l)$ is estimated on the basis of 7.0 gibbs/g-atom. The value of S°_{298} is obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting point of TiO_2(rutile) has been measured by many investigators. Eleven pertinent Tm values were reviewed and corrected, according to the International Temperature Scale of 1948, by S. J. Schneider, Natl. Bur. Std. Monograph 68, October 10, 1963. The adopted melting point is obtained from G. Brauer and W. Littke, J. Inorg. Nucl. Chem. 16, 67 (1960). These authors found that TiO_2 loses oxygen on heating and the solid residue consists of a non-stoichiometric compound of the composition TiO_{2-x}. The value of the coefficient x depends on the temperature and on the oxygen pressure of the gaseous phase. Under oxygen pressures greater than or equal to 300 torr, the solid residue was $TiO_{2.000}$ within the sensitivity of chemical analysis; however, color of the residue was a more sensitive indicator of composition. At pressures of 600 torr or greater, the residue was bright yellow rather than blue-gray and the melting point was constant at the maximum value of 2143 ± 15°K. This value is adopted.

The heat of melting is calculated using an estimated entropy of melting, ΔSm° = 2.5 eu/g-atom.

Titanium Dioxide (TiO_2)
(Liquid) GFW = 79.8988

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	13.153	18.934	18.934	.000	-210.726	-199.577	146.294
300	13.191	19.015	18.934	.024	-210.726	-199.507	145.341
400	14.521	23.029	19.472	1.423	-210.656	-195.776	106.967
500	15.429	26.384	20.528	2.928	-210.528	-192.070	83.954
600	15.991	29.249	21.749	4.500	-210.377	-188.393	68.622
700	16.438	31.748	23.002	6.122	-210.219	-184.741	57.679
800	16.824	33.969	24.237	7.785	-210.064	-181.113	49.478
900	17.173	35.971	25.431	9.485	-209.914	-177.503	43.104
1000	17.500	37.797	26.578	11.219	-209.771	-173.909	38.008
1100	17.813	39.480	27.675	12.985	-209.633	-170.329	33.841
1200	18.116	41.043	28.725	14.781	-210.437	-166.724	30.365
1300	18.412	42.504	29.729	16.608	-210.181	-163.091	27.418
1400	21.000	43.880	30.691	18.464	-209.918	-159.481	24.896
1500	21.000	45.328	31.619	20.564	-209.434	-155.893	22.714
1600	21.000	46.684	32.519	22.664	-208.974	-152.339	20.809
1700	21.000	47.957	33.390	24.764	-208.539	-148.813	19.131
1800	21.000	49.157	34.233	26.864	-208.133	-145.312	17.643
1900	21.000	50.293	35.049	28.964	-207.755	-141.833	16.315
2000	21.000	51.370	35.838	31.064	-211.853	-138.219	15.104
2100	21.000	52.394	36.602	33.164	-211.508	-134.543	14.002
2200	21.000	53.371	37.342	35.264	-211.170	-130.888	13.003
2300	21.000	54.305	38.060	37.364	-210.836	-127.247	12.091
2400	21.000	55.198	38.755	39.464	-210.508	-123.616	11.257
2500	21.000	56.056	39.430	41.564	-210.186	-120.006	10.491
2600	21.000	56.879	40.086	43.664	-209.868	-116.404	9.785
2700	21.000	57.672	40.722	45.764	-209.556	-112.815	9.132
2800	21.000	58.436	41.341	47.864	-209.249	-109.239	8.526
2900	21.000	59.173	41.944	49.964	-208.947	-105.670	7.963
3000	21.000	59.884	42.530	52.064	-208.650	-102.111	7.439
3100	21.000	60.573	43.101	54.164	-208.357	-98.565	6.949
3200	21.000	61.240	43.657	56.264	-208.069	-95.033	6.490
3300	21.000	61.886	44.200	58.364	-207.785	-91.503	6.060
3400	21.000	62.513	44.729	60.464	-207.506	-87.983	5.655
3500	21.000	63.122	45.246	62.564	-207.230	-84.475	5.275
3600	21.000	63.713	45.751	64.664	-308.584	-80.704	4.899
3700	21.000	64.289	46.244	66.764	-308.288	-74.382	4.394
3800	21.000	64.849	46.727	68.864	-308.008	-68.065	3.915
3900	21.000	65.394	47.198	70.964	-307.744	-61.752	3.460
4000	21.000	65.926	47.660	73.064	-307.497	-55.449	3.030
4100	21.000	66.444	48.112	75.164	-307.266	-49.147	2.620
4200	21.000	66.950	48.554	77.264	-307.049	-42.857	2.230
4300	21.000	67.445	48.988	79.364	-306.847	-36.571	1.859
4400	21.000	67.927	49.413	81.464	-306.659	-30.287	1.504
4500	21.000	68.399	49.830	83.564	-306.484	-24.006	1.166
4600	21.000	68.861	50.238	85.664	-306.321	-17.727	.842
4700	21.000	69.312	50.639	87.764	-306.171	-11.453	.533
4800	21.000	69.755	51.033	89.864	-306.032	-5.188	.236
4900	21.000	70.188	51.419	91.964	-305.904	1.071	-.048
5000	21.000	70.612	51.799	94.064	-305.786	7.339	-.321

TITANIUM DIOXIDE (TiO_2) (LIQUID) GFW = 79.8988

$S^\circ_{298.15}$ = [18.934] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-210.726] kcal/mol

Tm = 2143°K ΔHm° = [16] kcal/mol

Heat of Formation.

The $\Delta Hf^\circ_{298}(l)$ is calculated from ΔHf°_{298}(rutile, c) by adding ΔHm° and the difference between $H^\circ_{2143} - H^\circ_{298.15}$ for TiO_2(rutile, c) and $TiO_2(l)$.

Heat Capacity and Entropy.

The heat capacity of $TiO_2(l)$ is estimated on the basis of 7.0 gibbs/g-atom. The value of S°_{298} is obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting point of TiO_2(rutile) has been measured by many investigators. Eleven pertinent Tm values were reviewed and corrected, according to the International Temperature Scale of 1948, by S. J. Schneider, Natl. Bur. Std. Monograph 68, October 10, 1963. The adopted melting point is obtained from G. Brauer and W. Littke, J. Inorg. Nucl. Chem. 16, 67 (1960). These authors found that TiO_2 loses oxygen on heating and the solid residue consists of a non-stoichiometric compound of the composition TiO_{2-x}. The value of the coefficient x depends on the temperature and on the oxygen pressure of the gaseous phase. Under oxygen pressures greater than or equal to 300 torr, the solid residue was $TiO_{2.000}$ within the sensitivity of chemical analysis; however, color of the residue was a more sensitive indicator of composition. At pressures of 600 torr or greater, the residue was bright yellow rather than blue-gray and the melting point was constant at the maximum value of 2143 ± 15°K. This value is adopted.

The heat of melting is calculated using an estimated entropy of melting, ΔSm° = 2.5 eu/g-atom.

rconium Dioxide (ZrO_2)

rystal) Mol. Wt. = 123.2188

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.091	- 260.999	- 260.999	INFINITE
100	4.524	2.268	21.604	- 1.934	- 261.767	- 257.504	562.748
200	10.224	7.301	13.173	- 1.174	- 262.210	- 253.034	276.490
298	13.430	12.036	12.036	- .000	- 262.300	- 248.502	182.148
300	13.447	12.119	12.036	.025	- 262.299	- 248.416	180.962
400	15.260	16.268	12.590	1.471	- 262.199	- 243.802	133.201
500	16.196	19.782	13.686	3.048	- 262.024	- 239.221	104.558
600	16.787	22.791	14.959	4.699	- 261.832	- 234.678	85.477
700	17.214	25.412	16.269	6.400	- 261.634	- 230.168	71.858
800	17.555	27.733	17.560	8.139	- 261.431	- 225.687	61.652
900	17.845	29.818	18.808	9.909	- 261.220	- 221.231	53.720
1000	18.104	31.712	20.005	11.707	- 261.003	- 216.798	47.379
1100	18.342	33.449	21.149	13.529	- 260.790	- 212.390	42.196
1200	18.567	35.054	22.242	15.375	- 261.530	- 207.950	37.871
1300	18.781	36.549	23.286	17.242	- 261.294	- 203.496	34.209
1400	18.989	37.948	24.284	19.131	- 261.051	- 199.059	31.073
1500	17.800	40.206	25.253	22.430	- 259.411	- 194.661	28.361
1600	17.800	41.355	26.224	24.210	- 259.303	- 190.347	25.999
1700	17.800	42.434	27.146	25.990	- 259.208	- 186.040	23.916
1800	17.800	43.451	28.024	27.770	- 259.126	- 181.737	22.065
1900	17.800	44.414	28.861	29.550	- 259.057	- 177.441	20.409
2000	17.800	45.327	29.662	31.330	- 259.001	- 173.149	18.920
2100	17.800	46.195	30.429	33.110	- 258.956	- 168.856	17.572
2200	17.800	47.023	31.164	34.890	- 263.828	- 164.402	16.331
2300	17.800	47.814	31.871	36.670	- 263.814	- 159.882	15.192
2400	17.800	48.572	32.551	38.450	- 263.806	- 155.362	14.147
2500	17.800	49.299	33.207	40.230	- 263.804	- 150.847	13.186
2600	17.800	49.997	33.839	42.010	- 263.806	- 146.328	12.299
2700	17.800	50.669	34.450	43.790	- 263.814	- 141.810	11.478
2800	17.800	51.316	35.041	45.570	- 263.827	- 137.290	10.715
2900	17.800	51.941	35.613	47.350	- 263.845	- 132.768	10.005
3000	17.800	52.544	36.167	49.130	- 263.868	- 128.247	9.342
3100	17.800	53.128	36.705	50.910	- 263.895	- 123.729	8.722
3200	17.800	53.693	37.227	52.690	- 263.927	- 119.207	8.141
3300	17.800	54.240	37.735	54.470	- 263.963	- 114.681	7.595
3400	17.800	54.772	38.228	56.250	- 264.004	- 110.158	7.081
3500	17.800	55.288	38.708	58.030	- 264.048	- 105.635	6.596
3600	17.800	55.789	39.176	59.810	- 264.096	- 101.106	6.138
3700	17.800	56.277	39.631	61.590	- 264.148	- 96.579	5.704
3800	17.800	56.752	40.075	63.370	- 264.203	- 92.048	5.294
3900	17.800	57.214	40.509	65.150	- 264.261	- 87.517	4.904
4000	17.800	57.665	40.932	66.930	- 264.323	- 82.987	4.534

ZICONIUM DIOXIDE (ZrO_2) (CRYSTAL) MOL. WT. = 123.2188

$\Delta H^\circ_{f\ 0}$ = -261.0 ± 0.4 kcal. mole^{-1}

$S^\circ_{298.15}$ = [12.036 ± 0.08] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -262.3 ± 0.4 kcal. mole^{-1}

T_t = 1478 ± 5°K.

ΔH°_t = 1.42 ± 0.1 kcal. mole^{-1}

T_m = 2950°K.

ΔH°_m = [20.8] kcal. mole^{-1}

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ = -262.3 ± 0.4 kcal. mole^{-1} is the average value of the $\Delta H^\circ_{f\ 298.15}$ = -261.5 ± 0.2 kcal. mole^{-1} and $\Delta H^\circ_{f\ 298.15}$ = -263.1 ± 0.5 kcal. mole^{-1} measured (by combustion calorimetry) by G. L. Humphrey, J. Am. Chem. Soc. 76, 978 (1954) and E. J. Huber, Jr., E. L. Head and C. E. Holley, Jr., J. Phys. Chem. 68, 3040 (1964) respectively. Also the heat of formation was measured calorimetrically by B. Neumann, C. Kröger and H. Kunz, Z. anorg. Chem. 218, 379 (1934), by W. A. Roth, E. Börger, and H. Siemonsen, ibid., 239, 321 (1938) and by A. Sieverts, A. Gotta and S. Halberstadt, ibid., 187, 155 (1930) and was found -258.2, -258.8 and -256.1 kcal. mole^{-1} respectively. However more weight was given to the Humphrey and Huber values.

Heat Capacity and Entropy.

The low temperature heat capacities, 54.3-295°K., were measured by K. K. Kelley, Ind. Eng. Chem. 36, 377 (1944). The heat capacities in the temperature range 298-1478°K. were calculated by using the J. P. Coughlin and E. G. King equation $C_p = 16.64 + 1.80 \times 10^{-3}T - 3.36 \times 10^5\ T^{-2}$ obtained from their measured enthalpy data in the range 396.8 - 1841°K., J. Am. Chem. Soc. 72, 2262 (1950). The values from the two sources join smoothly at 298°K. Above the transition 1478°K. the heat capacity was taken as constant at 17.80 cal. mole^{-1} deg.$^{-1}$, Coughlin and King, loc. cit. The entropy was calculated at 54.30° using the Debye and Einstein function $D(\frac{345}{T}) + E(\frac{513}{T}) + E(\frac{861}{T})$ given by Kelley, loc. cit. The value of $S^\circ_{54.3}$ = 0.5507 cal. deg.$^{-1}$ mole^{-1}.

Transition Data.

T_t and ΔH°_t were taken from Coughlin and King loc. cit.

Melting Data.

The T_m and ΔH°_m were taken from Natl. Bur. Standards Circ. 500 Washington (1952).

Sulfur Trioxide (SO_3)

(Ideal Gas) Mol. Wt. = 80.0622

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.796	-93.220	-93.220	INFINITE
100	8.145	50.733	70.715	-1.998	-93.656	-92.205	201.504
200	10.119	56.920	62.390	-1.094	-94.165	-90.555	98.949
298	12.108	61.344	61.344	.000	-94.590	-88.689	65.007
300	12.142	61.419	61.345	.022	-94.597	-88.652	64.580
400	13.784	65.146	61.842	1.322	-95.463	-86.597	47.312
500	15.082	68.367	62.832	2.768	-96.052	-84.310	36.850
600	16.075	71.209	63.996	4.328	-96.481	-81.919	29.837
700	16.824	73.746	65.211	5.975	-96.801	-79.441	24.801
800	17.391	76.031	66.423	7.687	-110.111	-78.213	21.366
900	17.823	78.105	67.607	9.448	-110.009	-74.230	18.025
1000	18.157	80.001	68.753	11.248	-109.891	-70.260	15.354
1100	18.419	81.745	69.856	13.077	-109.763	-66.306	13.173
1200	18.628	83.357	70.915	14.930	-109.626	-62.360	11.357
1300	18.796	84.855	71.930	16.802	-109.485	-58.426	9.822
1400	18.933	86.253	72.904	18.688	-109.341	-54.504	8.508
1500	19.046	87.563	73.838	20.587	-109.197	-50.593	7.371
1600	19.140	88.795	74.735	22.497	-109.051	-46.689	6.377
1700	19.219	89.958	75.596	24.415	-108.905	-42.796	5.502
1800	19.286	91.058	76.425	26.340	-108.763	-38.911	4.724
1900	19.344	92.103	77.223	28.272	-108.624	-35.034	4.030
2000	19.393	93.096	77.992	30.209	-108.488	-31.166	3.405
2100	19.436	94.044	78.734	32.150	-108.356	-27.304	2.841
2200	19.474	94.949	79.451	34.096	-108.230	-23.447	2.329
2300	19.507	95.815	80.143	36.045	-108.108	-19.596	1.862
2400	19.536	96.646	80.814	37.997	-107.992	-15.748	1.434
2500	19.562	97.444	81.463	39.952	-107.882	-11.910	1.041
2600	19.585	98.212	82.093	41.909	-107.777	-8.072	.678
2700	19.605	98.951	82.703	43.869	-107.678	-4.239	.343
2800	19.623	99.664	83.296	45.830	-107.586	-.409	.032
2900	19.640	100.353	83.873	47.793	-107.500	3.419	-.258
3000	19.655	101.019	84.433	49.758	-107.421	7.244	-.528
3100	19.669	101.664	84.979	51.724	-107.345	11.064	-.780
3200	19.681	102.289	85.510	53.692	-107.278	14.879	-1.016
3300	19.692	102.895	86.028	55.660	-107.214	18.693	-1.238
3400	19.702	103.483	86.532	57.630	-107.158	22.510	-1.447
3500	19.712	104.054	87.025	59.601	-107.106	26.319	-1.643
3600	19.721	104.609	87.506	61.573	-107.058	30.136	-1.829
3700	19.729	105.150	87.975	63.545	-107.018	33.945	-2.005
3800	19.736	105.676	88.434	65.518	-106.980	37.756	-2.171
3900	19.743	106.189	88.883	67.492	-106.947	41.559	-2.329
4000	19.749	106.689	89.322	69.467	-106.920	45.368	-2.479
4100	19.755	107.176	89.751	71.442	-106.896	49.179	-2.621
4200	19.761	107.652	90.172	73.418	-106.876	52.985	-2.757
4300	19.766	108.117	90.584	75.394	-106.859	56.794	-2.886
4400	19.770	108.572	90.988	77.371	-106.848	60.594	-3.010
4500	19.775	109.016	91.383	79.348	-106.839	64.404	-3.128
4600	19.779	109.451	91.771	81.326	-106.833	68.211	-3.241
4700	19.783	109.876	92.152	83.304	-106.831	72.016	-3.349
4800	19.787	110.293	92.526	85.283	-106.831	75.819	-3.452
4900	19.790	110.701	92.892	87.261	-106.834	79.621	-3.551
5000	19.793	111.101	93.253	89.241	-106.840	83.423	-3.646
5100	19.796	111.493	93.606	91.220	-106.849	87.234	-3.738
5200	19.799	111.877	93.954	93.200	-106.859	91.037	-3.826
5300	19.802	112.254	94.296	95.180	-106.871	94.850	-3.911
5400	19.805	112.625	94.632	97.160	-106.886	98.646	-3.992
5500	19.807	112.988	94.962	99.141	-106.901	102.460	-4.071
5600	19.809	113.345	95.287	101.122	-106.921	106.263	-4.147
5700	19.812	113.695	95.607	103.103	-106.941	110.070	-4.220
5800	19.814	114.040	95.922	105.084	-106.962	113.882	-4.291
5900	19.816	114.379	96.232	107.065	-106.985	117.682	-4.359
6000	19.817	114.712	96.537	109.047	-107.009	121.498	-4.425

Dec. 31, 1960; Sept. 30, 1965

SULFUR TRIOXIDE (SO_3) (IDEAL GAS) MOL. WT. = 80.0622

Point Group D_{3h}

$S^\circ_{298.15}$ = 61.344 cal. mole^{-1} deg.$^{-1}$

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -93.22 ± 0.17 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -94.59 ± 0.17 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
1068 (1)
495 (1)
1391 (2)
529 (2)

Bond Distance: S-O = 1.43 Å

Bond Angle: O-S-O = 120°

σ = 6

Product of the Moments of Inertia: $I_AI_BI_C$ = 1.0813 X 10^{-114} g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was calculated from the reaction $SO_2 + 1/2\ O_2 \rightarrow SO_3$ for which three sets of equilibrium constants are available. A summary of the second and third law treatment of the data is given below.

Ref.	Temp. Range	Points	2nd law ΔH°_{298} kcal. mole^{-1}	3rd law ΔH°_{298} kcal. mole^{-1}	Drift cal. mole^{-1} deg.$^{-1}$
1	933- 945°K	5	-27.67 ± 2.7	-23.608	3.7 ± 2.9
2	801-1170°K	8	-23.45 ± 0.1	-23.661	-0.8 ± 0.1
3	850-1001°K	11	-22.74 ± 0.6	-23.614	-1.5 ± 0.6
4	801-1170°K	23*	-23.40 ± 0.2	-23.638	-0.9 ± 0.2

References

1. G. B. Taylor and S. Lehner, Z. Physik. Chem. B30. (1931).
2. M. Bodenstein and W. Pohl, Z. Electrochem. 11, 373 (1905).
3. A. F. Kapustinsky and L. M. Shamovsky, Acta Physicochem. URSS 4, 791 (1936).
4. Combination of above references, with one point omitted due to failure of a statistical test.

The combined set was adopted though it appears that the three sets are not in excellent agreement, and the combination heavily favors Ref. 2. Although there is a definite trend in all the data it cannot be considered definitive enough for use in the modification of the SO_3 functions.

Heat Capacity and Entropy.

The bond length and angles were taken from the electron diffraction data of K. J. Palmer, J. Am. Chem. Soc. 60, 2360 (1938). The vibrational frequencies were taken from the infrared studies of R. W. Lovejoy, J. H. Colwell, D. F. Eggers and G. D. Halsey, J. Chem. Phys. 36, 612 (1962), which are in excellent accord with those of R. Bent and W. R. Ladner, Spectrochim. Acta 19, 931 (1963) using different techniques. These values differ from the assignment used by W. H. Stockmayer, G. M. Kavanagh and H. S. Mickley, J. Chem. Phys. 12, 408 (1944) in their analysis of the thermodynamic properties of SO_3.

The individual moments of inertia were $I_A = I_B$ = 8.148 X 10^{-39} g. cm.^{2} and I_C = 16.296 X 10^{-39} g. cm.^{2}

Ozone (O_3)

(Ideal Gas) Mol. Wt. = 48.000

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 2.474	34.739	34.739	INFINITE
100	7.957	47.969	47.981	- .002	36.141	37.573	- 82.112
200	8.379	53.564	57.909	- .869	34.254	37.411	- 40.879
298	9.378	57.080	57.080	.000	34.100	38.997	- 28.585
300	9.400	57.138	57.080	.017	34.098	39.028	- 28.430
400	10.455	59.992	57.462	1.012	34.026	40.684	- 22.227
500	11.296	62.419	58.217	2.101	34.019	42.351	- 18.511
600	11.916	64.536	59.097	3.263	34.048	44.015	- 16.032
700	12.369	66.409	60.011	4.479	34.097	45.672	- 14.259
800	12.704	68.083	60.917	5.733	34.154	47.321	- 12.927
900	12.956	69.595	61.799	7.017	34.217	48.963	- 11.889
1000	13.151	70.971	62.648	8.323	34.282	50.599	- 11.058
1100	13.303	72.232	63.463	9.646	34.347	52.227	- 10.376
1200	13.426	73.395	64.243	10.982	34.411	53.850	- 9.807
1300	13.526	74.473	64.989	12.330	34.474	55.468	- 9.324
1400	13.611	75.479	65.702	13.687	34.535	57.080	- 8.910
1500	13.682	76.420	66.386	15.052	34.593	58.688	- 8.550
1600	13.743	77.305	67.041	16.423	34.649	60.293	- 8.235
1700	13.796	78.140	67.670	17.800	34.703	61.895	- 7.957
1800	13.843	78.930	68.273	19.182	34.751	63.492	- 7.709
1900	13.885	79.680	68.854	20.569	34.795	65.088	- 7.486
2000	13.922	80.393	69.413	21.959	34.835	66.680	- 7.286
2100	13.957	81.073	69.953	23.353	34.872	68.272	- 7.105
2200	13.988	81.723	70.473	24.750	34.901	69.861	- 6.940
2300	14.017	82.345	70.976	26.150	34.927	71.449	- 6.789
2400	14.045	82.943	71.462	27.554	34.948	73.039	- 6.651
2500	14.070	83.516	71.933	28.959	34.961	74.623	- 6.523
2600	14.094	84.069	72.389	30.368	34.972	76.211	- 6.406
2700	14.117	84.601	72.831	31.778	34.975	77.797	- 6.297
2800	14.139	85.115	73.261	33.191	34.973	79.383	- 6.196
2900	14.160	85.611	73.678	34.606	34.966	80.971	- 6.102
3000	14.180	86.092	74.084	36.023	34.954	82.557	- 6.014
3100	14.199	86.557	74.479	37.442	34.937	84.145	- 5.932
3200	14.218	87.008	74.864	38.863	34.915	85.731	- 5.855
3300	14.236	87.446	75.238	40.285	34.889	87.318	- 5.783
3400	14.254	87.871	75.604	41.710	34.857	88.908	- 5.715
3500	14.272	88.285	75.960	43.136	34.822	90.496	- 5.651
3600	14.288	88.687	76.308	44.564	34.783	92.090	- 5.590
3700	14.305	89.079	76.648	45.994	34.740	93.682	- 5.533
3800	14.321	89.460	76.980	47.425	34.694	95.278	- 5.479
3900	14.337	89.833	77.305	48.858	34.645	96.869	- 5.428
4000	14.353	90.196	77.623	50.293	34.591	98.464	- 5.380
4100	14.369	90.550	77.934	51.729	34.535	100.064	- 5.334
4200	14.384	90.897	78.238	53.166	34.477	101.661	- 5.290
4300	14.399	91.235	78.536	54.605	34.416	103.266	- 5.248
4400	14.414	91.567	78.829	56.046	34.352	104.864	- 5.208
4500	14.429	91.891	79.116	57.488	34.287	106.468	- 5.171
4600	14.444	92.208	79.397	58.932	34.220	108.078	- 5.135
4700	14.456	92.519	79.673	60.377	34.150	109.682	- 5.100
4800	14.473	92.823	79.943	61.824	34.080	111.291	- 5.067
4900	14.487	93.122	80.209	63.272	34.009	112.894	- 5.035
5000	14.501	93.415	80.471	64.721	33.935	114.504	- 5.005
5100	14.515	93.702	80.727	66.172	33.861	116.121	- 4.976
5200	14.529	93.984	80.979	67.624	33.786	117.730	- 4.948
5300	14.543	94.261	81.227	69.078	33.711	119.352	- 4.921
5400	14.557	94.533	81.471	70.533	33.635	120.962	- 4.895
5500	14.571	94.800	81.711	71.989	33.559	122.585	- 4.871
5600	14.585	95.063	81.947	73.447	33.481	124.200	- 4.847
5700	14.598	95.321	82.180	74.906	33.404	125.818	- 4.824
5800	14.612	95.575	82.408	76.366	33.327	127.447	- 4.802
5900	14.625	95.825	82.634	77.828	33.250	129.067	- 4.781
6000	14.639	96.071	82.856	79.292	33.173	130.695	- 4.760

June 30, 1961

OZONE (O_3) (IDEAL GAS) MOL. WT. = 48.000

ΔH°_{f0} = 34.8 ± 0.4 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 34.2 ± 0.4 kcal. mole^{-1}

Point Group C_{2v}

$S^\circ_{298.15}$ = 57.080 cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
1110 (1)
705 (1)
1043 (1)

Ground state multiplicity = 1

No α_1 available $\sigma = 2$

Rotational constants: A_{000} = 3.55381 cm.$^{-1}$ B_{000} = 0.44530 cm.$^{-1}$ C_{000} = 0.39477 cm.$^{-1}$

X_{11} = -3.8 cm.$^{-1}$ X_{33} = -4.0 cm.$^{-1}$ X_{23} = -3.5 cm.$^{-1}$

X_{22} = -3.5 cm.$^{-1}$ X_{12} = -2.0 cm.$^{-1}$ X_{31} = -9.0 cm.$^{-1}$

Heat of Formation

P. Günther, E. Wassmuth, and L. A. Schryver, Z. phys. Chem. 158, 297 (1932), measured ΔE for the reaction $O_3(g) \rightarrow 3/2\ O_2(g)$ in a calorimeter calibrated my means of the reaction $CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g)$, and found the ratio of the ΔE values for these reactions to be 0.5077 ± 0.0024. The temperature of the experiments is not reported and is assumed to have been 18°C. From the above ratio, $\Delta H^\circ_{f\ 298.15}$ is calculated to be 33.89 ± 0.36 cal. mole^{-1}. A. Kailan and S. Jahn, Z. anorg. Chem. 68, 243 (1910), measured ΔH at an unspecified temperature for the reaction $O_3(g) \rightarrow 3/2\ O_2(g)$ in an electrically calibrated calorimeter. If the temperature of the experiments is assumed to have been 18°C and the modern joule-calorie conversion factor is used, $\Delta H^\circ_{f\ 298.15}$ is found to be 34.3 ± 0.6 kcal. mole^{-1}. Variability in the O_3 content of the feed gas is allowed for in the uncertainty. The value adopted here is 34.2 ± 0.4 kcal. mole^{-1}.

Heat Capacity and Entropy

J. S. Gordon, private communication, April, 1961, has calculated the thermodynamic functions from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes vibration-rotation interaction and anharmonicity into account. Gordon's data are from L. Pierce, J. Chem. Phys. 24, 139 (1956). The functions below 298.15°K have been calculated for a rigidly rotating harmonic oscillator.

Lead Metasilicate ($PbSiO_3$)

(Crystal) Mol. Wt. = 283.2742

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 3.876	- 272.011	- 272.011	INFINITE
100	10.680	8.883	42.363	- 3.348	- 273.039	- 266.727	582.904
200	17.343	18.523	28.116	- 1.919	- 273.514	- 260.197	284.316
298	21.520	26.273	26.273	.000	- 273.660	- 253.620	185.900
300	21.590	26.406	26.274	.040	- 273.661	- 253.496	184.663
400	24.580	33.046	27.159	2.355	- 273.572	- 246.782	134.829
500	26.760	38.776	28.922	4.927	- 273.320	- 240.112	104.948
600	28.380	43.806	30.992	7.688	- 272.954	- 233.503	85.049
700	29.500	48.269	33.148	10.585	- 273.684	- 226.770	70.797
800	30.250	52.260	35.292	13.574	- 273.215	- 220.101	60.126
900	30.780	55.855	37.380	16.627	- 272.711	- 213.491	51.840
1000	31.150	59.118	39.393	19.724	- 272.185	- 206.938	45.224
1100	31.440	62.101	41.324	22.854	- 271.645	- 200.441	39.822
1200	31.690	64.847	43.171	26.011	- 271.089	- 193.991	35.329
1300	31.890	67.392	44.938	29.190	- 270.523	- 187.589	31.535
1400	32.080	69.762	46.627	32.389	- 269.952	- 181.232	28.290
1500	32.270	71.982	48.244	35.607	- 269.373	- 174.914	25.484
1600	32.420	74.070	49.794	38.841	- 268.792	- 168.635	23.033
1700	32.550	76.039	51.280	42.090	- 280.312	- 162.283	20.862
1800	32.690	77.904	52.708	45.352	- 279.690	- 155.361	18.863
1900	32.780	79.674	54.081	48.626	- 279.070	- 148.472	17.077
2000	32.850	81.357	55.403	51.907	- 278.454	- 141.614	15.474

June 30, 1965

LEAD METASILICATE ($PbSiO_3$) (CRYSTAL) MOL. WT. = 283.2742

$\Delta H^\circ_{f\ 0}$ = -272.01 ± 1 kcal. mole^{-1}

$S^\circ_{298.15}$ = 26.273 ± 0.3 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -273.66 ± 1 kcal. mole^{-1}

T_m = 1037°K.

Heat of Formation.

The heat of the reaction $PbO_{(red)} + SiO_2 \rightarrow PbSiO_3(c)$ was reported by K. K. Kelley, U. S. Bureau of Mines, Report Investigation 5901 (1962). This value for the heat of reaction of the oxides has been converted to the heat of formation using JANAF values for PbO(c) (March 31, 1962) and for SiO_2(c) (Dec. 31, 1962). The above $\Delta H^\circ_{r\ 298.15}$ = -3.75 ± 0.12 kcal. mole^{-1}.

Heat Capacity and Entropy.

In the low temperature region (53.25-298.15°K.) the C_p values are those determined by E. G. King, J. Am. Chem. Soc. 81, 799-800 (1959). Above 298.15 C_p values were estimated by summing the values for the constituent oxides and graphically smoothing these into the low temperature measurements. The entropy was calculated at 53.25°K. using the Debye and Einstein functions $D(\frac{140}{T}) + E(\frac{213}{T}) + 2E(\frac{596}{T}) + E(\frac{1440}{T})$ given by E. G. King, J. Am. Chem. Soc. 81, 799-800 (1959). The $S^\circ_{53.25}$ = 3.662 cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

T_m was taken from Geller, Creamer and Bunting, J. Research Natl. Bureau of Standards, 13, 237 (1934).

Lead (Pb)

(Reference State) At. Wt. = 207.21

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-1.644	.000	.000	.000
100	5.838	8.803	21.013	-1.221	.000	.000	.000
200	6.183	12.972	16.062	-.618	.000	.000	.000
298	6.414	15.484	15.484	.000	.000	.000	.000
300	6.418	15.524	15.484	.012	.000	.000	.000
400	6.626	17.399	15.738	.664	.000	.000	.000
500	6.823	18.898	16.225	1.337	.000	.000	.000
600	7.028	20.157	16.778	2.027	.000	.000	.000
700	7.250	23.180	17.613	3.897	.000	.000	.000
800	7.174	24.143	18.371	4.618	.000	.000	.000
900	7.098	24.984	19.060	5.332	.000	.000	.000
1000	7.026	25.728	19.690	6.038	.000	.000	.000
1100	6.953	26.394	20.270	6.737	.000	.000	.000
1200	6.880	26.996	20.806	7.428	.000	.000	.000
1300	6.848	27.545	21.303	8.114	.000	.000	.000
1400	6.841	28.052	21.767	8.799	.000	.000	.000
1500	6.853	28.525	22.202	9.483	.000	.000	.000
1600	6.880	28.968	22.612	10.170	.000	.000	.000
1700	6.914	29.386	22.998	10.859	.000	.000	.000
1800	6.957	29.782	23.364	11.553	.000	.000	.000
1900	7.002	30.159	23.712	12.251	.000	.000	.000
2000	7.050	30.520	24.043	12.954	.000	.000	.000
2100	6.094	51.819	25.099	56.112	.000	.000	.000
2200	6.301	52.107	26.320	56.732	.000	.000	.000
2300	6.516	52.392	27.447	57.373	.000	.000	.000
2400	6.734	52.674	28.493	58.035	.000	.000	.000
2500	6.951	52.953	29.465	58.720	.000	.000	.000
2600	7.165	53.230	30.374	59.426	.000	.000	.000
2700	7.372	53.504	31.226	60.152	.000	.000	.000
2800	7.569	53.776	32.026	60.900	.000	.000	.000
2900	7.754	54.045	32.781	61.666	.000	.000	.000
3000	7.926	54.311	33.494	62.450	.000	.000	.000
3100	8.082	54.573	34.170	63.250	.000	.000	.000
3200	8.221	54.832	34.812	64.066	.000	.000	.000
3300	8.345	55.087	35.422	64.894	.000	.000	.000
3400	8.451	55.338	36.004	65.734	.000	.000	.000
3500	8.542	55.584	36.560	66.584	.000	.000	.000
3600	8.616	55.826	37.092	67.442	.000	.000	.000
3700	8.675	56.063	37.601	68.307	.000	.000	.000
3800	8.720	56.295	38.090	69.176	.000	.000	.000
3900	8.752	56.522	38.560	70.050	.000	.000	.000
4000	8.772	56.743	39.012	70.926	.000	.000	.000
4100	8.781	56.960	39.447	71.804	.000	.000	.000
4200	8.780	57.172	39.866	72.682	.000	.000	.000
4300	8.770	57.378	40.271	73.560	.000	.000	.000
4400	8.753	57.580	40.662	74.436	.000	.000	.000
4500	8.730	57.776	41.041	75.310	.000	.000	.000
4600	8.701	57.968	41.406	76.182	.000	.000	.000
4700	8.667	58.154	41.761	77.050	.000	.000	.000
4800	8.630	58.337	42.104	77.915	.000	.000	.000
4900	8.590	58.514	42.437	78.776	.000	.000	.000
5000	8.549	58.687	42.761	79.633	.000	.000	.000
5100	8.506	58.856	43.075	80.486	.000	.000	.000
5200	8.462	59.021	43.380	81.334	.000	.000	.000
5300	8.419	59.182	43.676	82.178	.000	.000	.000
5400	8.377	59.339	43.965	83.018	.000	.000	.000
5500	8.335	59.492	44.246	83.854	.000	.000	.000
5600	8.296	59.642	44.519	84.685	.000	.000	.000
5700	8.258	59.788	44.786	85.513	.000	.000	.000
5800	8.223	59.932	45.046	86.337	.000	.000	.000
5900	8.191	60.072	45.299	87.158	.000	.000	.000
6000	8.163	60.209	45.547	87.975	.000	.000	.000

March 31, 1962

LEAD (Pb) **(REFERENCE STATE)** **AT. WT. = 207.21**

0° to 600.58°K	Crystal
600.58° to 2026°K	Liquid
2026° to 6000°K	Ideal Monatomic Gas

See crystal, liquid, and ideal monatomic gas for details.

(Crystal) At. Wt. = 207.21

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-1.644	.000	.000	INFINITE
100	5.838	8.803	21.013	-1.221	.000	.000	.000
200	6.183	12.972	16.062	-.618	.000	.000	.000
298	6.414	15.484	15.484	.000	.000	.000	.000
300	6.416	15.524	15.484	.012	.000	.000	.000
400	6.626	17.399	15.738	.664	.000	.000	.000
500	6.821	18.898	16.225	1.337	.000	.000	.000
600	7.028	20.157	16.778	2.027	.000	.000	.000
700	7.256	21.257	17.341	2.741	-1.156	.190	-.059
800	7.491	22.242	17.893	3.479	-1.139	.382	-.104
900	7.723	23.137	18.427	4.239	-1.093	.569	-.138
1000	7.956	23.963	18.940	5.023	-1.015	.750	-.164
1100	8.189	24.732	19.432	5.831	-.906	.921	-.183
1200	8.422	25.455	19.904	6.661	-.767	1.083	-.197
1300	8.654	26.130	20.357	7.515	-.599	1.230	-.207
1400	8.887	26.788	20.794	8.392	-.407	1.363	-.213
1500	9.120	27.409	21.214	9.292	-.191	1.483	-.216

March 31, 1962

LEAD (Pb) **(CRYSTAL)** **AT. WT. = 207.21**

$\Delta H^\circ_{f0} = 0$

$\Delta H^\circ_s\ 298.15 = 46.75 \pm 0.13$ kcal. mole^{-1}

$T_m = 600.58 \pm 0.00$°K

$\Delta H^\circ_f\ 298.15 = 0$

$S^\circ_{298.15} = 15.484$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_m = 1.141$ kcal. mole^{-1}

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Heat capacity measurements have been reported by M. Horowitz, A. A. Silvidi, S. F. Malaker and J. G. Daunt, (1° to 4°, 14° to 21°, and 64° to 77°K.), Phys. Rev. 88, 1182 (1952); P. F. Meads, W. R. Forsythe and W. F. Giauque, (15° to 300°K.), J. Am. Chem. Soc. 63, 1902 (1941); T. B. Douglas and J. L. Dever, (298.16° to 1200°K.), J. Am. Chem. Soc. 76, 4824 (1954), and many others whose work is listed by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960).

Heat capacities from 15° to 300° and 1° to 4°K. (in superconducting state) were taken from Meads, Forsythe, and Giauque, and Horowitz, Silvidi, Malaker, and Daunt, respectively. The missing data below the melting point were obtained by graphical extrapolation and joined smoothly to data of Douglas and Dever on approaching the melting point.

Melting.

The melting point of pure Pb(c) was found by E. H. McLaren and E. G. Murdock, Can. J. Phys. 38, 577 (1960) to be 327.426 ± 0.002°C. ΔH_m given by Douglas and Dever, loc. cit.

Heat of Sublimation.

$\Delta H^\circ_s\ 298.15$ was derived from third law analysis of the vapor pressure data of W. H. Rodebush and A. L. Dixon, J. Am. Chem. Soc. 47, 1036 (1925) and Phys. Rev. 26, 851 (1925); A. C. G. Egerton, Proc. Roy. Soc. (London) A103, 469 (1923); P. Harteck, Z. physik. Chem. 134, 1 (1928); A. T. Aldred and J. N. Pratt, Trans. Faraday Soc. 57, 611 (1961); E. Baur and R. Brunner, Helv. Chim. Acta. 17, 958 (1934), and J. Fischer, Z. anorg. Chem. 219, 1, 367 (1934), which are in good agreement. Most weight was given to the results of Rodebush and Dixon. Older vapor pressure data of lower accuracy have not been used.

Lead (Pb)

(Liquid) At. Wt. = 207.21

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}					
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$		ΔH_f°	ΔF_f°		Log K_p
0									
100									
200									
298	6.414	17.141	17.141	.000		1.025	.531	-	.389
300	6.418	17.181	17.141	.012		1.025	.528	-	.385
400	7.470	19.056	17.395	.664		1.025	.362	-	.198
500	7.396	20.715	17.900	1.407		1.095	.187	-	.082
600	7.322	22.056	18.484	2.143		1.141	.002	-	.001
700	7.250	23.179	19.077	2.871		.000	.000		.000
800	7.174	24.142	19.651	3.592		.000	.000		.000
900	7.098	24.982	20.198	4.306		.000	.000		.000
1000	7.026	25.726	20.714	5.012		.000	.000		.000
1100	6.953	26.393	21.201	5.711		.000	.000		.000
1200	6.880	26.994	21.659	6.403		.000	.000		.000
1300	6.848	27.544	22.091	7.089		.000	.000		.000
1400	6.841	28.051	22.498	7.773		.000	.000		.000
1500	6.853	28.523	22.885	8.458		.000	.000		.000
1600	6.880	28.966	23.251	9.144		.000	.000		.000
1700	6.914	29.384	23.599	9.834		.000	.000		.000
1800	6.957	29.780	23.932	10.527		.000	.000		.000
1900	7.002	30.158	24.250	11.225		.000	.000		.000
2000	7.050	30.518	24.554	11.928		.000	.000		.000
2100	7.100	30.863	24.847	12.635	-	42.452	1.555	-	.162
2200	7.151	31.195	25.128	13.348	-	42.359	3.648	-	.362
2300	7.202	31.514	25.398	14.066	-	42.282	5.737	-	.545
2400	7.253	31.821	25.660	14.788	-	42.222	7.824	-	.712
2500	7.303	32.119	25.912	15.516	-	42.179	9.907	-	.866
2600	7.352	32.406	26.156	16.249	-	42.152	11.991	-	1.008
2700	7.400	32.684	26.393	16.986	-	42.141	14.073	-	1.139
2800	7.450	32.954	26.623	17.729	-	42.146	16.155	-	1.261
2900	7.499	33.217	26.845	18.476	-	42.165	18.238	-	1.374
3000	7.548	33.472	27.062	19.229	-	42.196	20.322	-	1.480

March 31, 1962

LEAD (Pb) (LIQUID) AT. WT. = 207.21

ΔH_f° 298.15 = [1.025] kcal. mole^{-1}

T_m = 600.58 ± 0.00°K

T_b = 2026°K

$S_{298.15}^\circ$ = [17.141] cal. deg.$^{-1}$ mole^{-1}

ΔH_m° = 1.141 kcal. mole^{-1}

ΔH_v° = 42.53 ± 0.15 kcal. mole^{-1}

Heat of Formation.

Obtained from ΔH_m°.

Heat Capacity and Extrapolation.

Heat capacity from T_m to 1200°K taken from T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. 76, 4824 (1954). C_p values below T_m and above 1200°K were extrapolated, a glass transition being assumed at 400°K.

Entropy.

Calculated from that of crystal.

Vaporization Phenomena.

T_b and ΔH_v° calculated from ΔH_s° 298.15 and functions for condensed and gaseous states.

From the vapor pressure, the free energy functions of Pb(g) and Pb_2(g), and the dissociation energy of Pb_2(g), it appears that below the boiling point the amount of Pb_2(g) in the vapor is negligible.

ead (Pb)

Ideal Gas) At. Wt. = 207.21

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-1.481	46.910	46.910	INFINITE
100	4.968	36.463	46.307	-.984	46.984	44.218	-96.633
200	4.968	39.907	42.345	-.488	46.877	41.490	-45.337
298	4.968	41.890	41.890	.000	46.747	38.874	-28.494
300	4.968	41.921	41.890	.009	46.744	38.825	-28.283
400	4.968	43.350	42.085	.506	46.589	36.209	-19.782
500	4.968	44.459	42.453	1.003	46.413	33.632	-14.700
600	4.968	45.365	42.865	1.500	46.220	31.095	-11.326
700	4.968	46.130	43.278	1.996	44.846	28.781	-8.985
800	4.969	46.794	43.677	2.493	44.622	26.502	-7.240
900	4.972	47.379	44.057	2.990	44.405	24.250	-5.888
1000	4.978	47.903	44.416	3.488	44.197	22.021	-4.813
1100	4.992	48.379	44.755	3.986	43.996	19.813	-3.936
1200	5.017	48.814	45.075	4.487	43.806	17.624	-3.210
1300	5.056	49.217	45.378	4.990	43.623	15.450	-2.597
1400	5.113	49.594	45.666	5.499	43.447	13.288	-2.074
1500	5.191	49.949	45.940	6.014	43.278	11.142	-1.623
1600	5.290	50.287	46.201	6.537	43.114	9.004	-1.230
1700	5.411	50.611	46.451	7.072	42.960	6.877	-.884
1800	5.554	50.924	46.691	7.620	42.814	4.758	-.578
1900	5.716	51.229	46.922	8.184	42.680	2.647	-.304
2000	5.899	51.527	47.145	8.764	42.557	.544	-.059
2100	6.094	51.819	47.360	9.364	.000	.000	.000
2200	6.301	52.108	47.569	9.984	.000	.000	.000
2300	6.516	52.392	47.773	10.625	.000	.000	.000
2400	6.734	52.674	47.971	11.287	.000	.000	.000
2500	6.951	52.954	48.165	11.971	.000	.000	.000
2600	7.165	53.230	48.355	12.677	.000	.000	.000
2700	7.372	53.505	48.540	13.404	.000	.000	.000
2800	7.569	53.776	48.722	14.151	.000	.000	.000
2900	7.754	54.045	48.901	14.917	.000	.000	.000
3000	7.926	54.311	49.077	15.702	.000	.000	.000
3100	8.082	54.574	49.250	16.502	.000	.000	.000
3200	8.221	54.832	49.421	17.317	.000	.000	.000
3300	8.345	55.087	49.589	18.146	.000	.000	.000
3400	8.451	55.338	49.754	18.986	.000	.000	.000
3500	8.542	55.584	49.917	19.835	.000	.000	.000
3600	8.616	55.826	50.078	20.693	.000	.000	.000
3700	8.675	56.063	50.236	21.558	.000	.000	.000
3800	8.720	56.295	50.393	22.428	.000	.000	.000
3900	8.752	56.522	50.547	23.302	.000	.000	.000
4000	8.772	56.744	50.699	24.178	.000	.000	.000
4100	8.781	56.961	50.849	25.056	.000	.000	.000
4200	8.780	57.172	50.997	25.934	.000	.000	.000
4300	8.770	57.379	51.143	26.812	.000	.000	.000
4400	8.753	57.580	51.287	27.688	.000	.000	.000
4500	8.730	57.776	51.429	28.562	.000	.000	.000
4600	8.701	57.968	51.569	29.434	.000	.000	.000
4700	8.667	58.155	51.708	30.302	.000	.000	.000
4800	8.630	58.337	51.844	31.167	.000	.000	.000
4900	8.590	58.514	51.978	32.028	.000	.000	.000
5000	8.549	58.688	52.111	32.885	.000	.000	.000
5100	8.506	58.856	52.241	33.738	.000	.000	.000
5200	8.462	59.021	52.370	34.586	.000	.000	.000
5300	8.419	59.182	52.497	35.430	.000	.000	.000
5400	8.377	59.339	52.622	36.270	.000	.000	.000
5500	8.335	59.492	52.746	37.105	.000	.000	.000
5600	8.296	59.642	52.868	37.937	.000	.000	.000
5700	8.256	59.789	52.988	38.765	.000	.000	.000
5800	8.223	59.932	53.106	39.589	.000	.000	.000
5900	8.191	60.072	53.223	40.409	.000	.000	.000
6000	8.163	60.210	53.338	41.227	.000	.000	.000

March 31, 1962

LEAD (Pb) (IDEAL GAS) AT. WT. = 207.21

ΔH°_{f0} = 46.91 ± 0.13 kcal. mole⁻¹

Ground State Configuration $^3P_0$

$\Delta H^\circ_{f\ 298.15}$ = 46.75 ± 0.13 kcal. mole⁻¹

$S^\circ_{298.15}$ = 41.890 cal. deg.⁻¹ mole⁻¹

Electronic Levels and Multiplicities

ϵ_1, cm.⁻¹	g_1	ϵ_1, cm.⁻¹	g_1
0.00	1	46,152.76	15
7,819.35	3	48,760.32	12
10,650.47	5	51,741.79	12
21,457.90	5	52,505.53	48
29,466.81	1	53,493.33	4
34,959.90	1	54,895.15	4
35,287.24	3	55,343.74	60
42,918.68	3	56,716.24	52
44,400.92	1	57,520.36	68
44,675.00	3	58,403.73	139
44,809.41	5	59,321.54	51
45,443.26	5		

Heat of Formation.

The same as $\Delta H^\circ_{s\ 298.15}$

Heat Capacity and Entropy.

Electronic levels and multiplicities from C. E. Moore, Natl. Bur. Standards (U. S.) Circ. 467, Vol. III (1958).

ead, Diatomic (Pb_2)

Ideal Gas) Mol. Wt. = 414.42

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.391	80.397	80.397	INFINITE
100	7.712	58.087	74.840	- 1.675	80.267	76.219	- 166.568
200	8.545	63.744	68.016	- .854	79.882	72.322	- 79.026
298	8.825	67.216	67.216	.000	79.500	68.693	- 50.351
300	8.828	67.270	67.216	.016	79.492	68.626	- 49.991
400	8.964	69.830	67.564	.907	79.079	65.066	- 35.548
500	9.050	71.840	68.225	1.807	78.633	61.611	- 26.929
600	9.115	73.496	68.970	2.716	78.162	58.252	- 21.217
700	9.169	74.905	69.720	3.630	75.336	55.354	- 17.282
800	9.219	76.133	70.446	4.549	74.813	52.536	- 14.351
900	9.265	77.222	71.140	5.474	74.310	49.781	- 12.088
1000	9.309	78.200	71.798	6.402	73.826	47.082	- 10.289
1100	9.351	79.089	72.421	7.335	73.361	44.430	- 8.827
1200	9.393	79.905	73.011	8.273	72.917	41.821	- 7.616
1300	9.434	80.658	73.571	9.214	72.486	39.247	- 6.598
1400	9.475	81.359	74.102	10.159	72.061	36.705	- 5.730
1500	9.515	82.014	74.608	11.109	71.643	34.197	- 4.982
1600	9.555	82.629	75.090	12.063	71.223	31.713	- 4.332
1700	9.595	83.210	75.551	13.020	70.802	29.258	- 3.761
1800	9.635	83.759	75.992	13.982	70.376	26.824	- 3.257
1900	9.674	84.281	76.415	14.947	69.945	24.415	- 2.808
2000	9.714	84.779	76.820	15.916	69.508	22.031	- 2.407
2100	9.753	85.254	77.211	16.890	- 15.834	22.773	- 2.370
2200	9.793	85.708	77.587	17.867	- 16.097	24.616	- 2.445
2300	9,832	86.144	77.949	18.848	- 16.398	26.473	- 2.515
2400	9.871	86.564	78.300	19.834	- 16.736	28.346	- 2.581
2500	9.910	86.967	78.638	20.823	- 17.117	30.229	- 2.642
2600	9.949	87.357	78.966	21.816	- 17.536	32.132	- 2.701
2700	9.988	87.733	79.284	22.812	- 17.992	34.051	- 2.756
2800	10.027	88.097	79.592	23.813	- 18.487	35.987	- 2.809
2900	10.066	88.450	79.892	24.818	- 19.014	37.943	- 2.859
3000	10.105	88.792	80.183	25.827	- 19.573	39.918	- 2.908
3100	10.144	89.123	80.466	26.839	- 20.161	41.909	- 2.954
3200	10.183	89.446	80.741	27.855	- 20.777	43.920	- 2.999
3300	10.222	89.760	81.010	28.876	- 21.412	45.953	- 3.043
3400	10.261	90.066	81.272	29.900	- 22.068	48.006	- 3.086
3500	10.300	90.364	81.527	30.928	- 22.740	50.074	- 3.127
3600	10.339	90.655	81.777	31.960	- 23.424	52.167	- 3.167
3700	10.378	90.938	82.021	32.996	- 24.118	54.276	- 3.206
3800	10.417	91.216	82.259	34.036	- 24.816	56.406	- 3.244
3900	10.456	91.487	82.492	35.079	- 25.521	58.552	- 3.281
4000	10.495	91.752	82.720	36.127	- 26.225	60.711	- 3.317
4100	10.534	92.012	82.944	37.178	- 26.930	62.894	- 3.352
4200	10.573	92.266	83.163	38.234	- 27.630	65.097	- 3.387
4300	10.612	92.515	83.377	39.293	- 28.327	67.308	- 3.421
4400	10.651	92.760	83.588	40.356	- 29.016	69.546	- 3.454
4500	10.690	92.999	83.794	41.423	- 29.697	71.790	- 3.486
4600	10.728	93.235	83.997	42.494	- 30.370	74.055	- 3.518
4700	10.767	93.466	84.196	43.569	- 31.031	76.326	- 3.549
4800	10.806	93.693	84.391	44.647	- 31.683	78.626	- 3.580
4900	10.845	93.916	84.584	45.730	- 32.322	80.926	- 3.609
5000	10.884	94.136	84.772	46.816	- 32.950	83.242	- 3.638
5100	10.923	94.352	84.958	47.907	- 33.565	85.572	- 3.667
5200	10.962	94.564	85.141	49.001	- 34.167	87.918	- 3.695
5300	11.001	94.773	85.321	50.099	- 34.757	90.274	- 3.722
5400	11.040	94.979	85.498	51.201	- 35.335	92.638	- 3.749
5500	11.078	95.182	85.672	52.307	- 35.901	95.009	- 3.775
5600	11.117	95.382	85.843	53.417	- 36.453	97.397	- 3.801
5700	11.156	95.579	86.013	54.530	- 36.996	99.786	- 3.826
5800	11.195	95.774	86.179	55.648	- 37.526	102.198	- 3.851
5900	11.234	95.965	86.343	56.769	- 38.047	104.608	- 3.875
6000	11.273	96.154	86.505	57.895	- 38.555	107.026	- 3.898

Mar. 31, 1962; June 30, 1963; Sept. 30, 1963.

LEAD, DIATOMIC (Pb_2) **(IDEAL GAS)** **MOL. WT. = 414.42**

Ground State Configuration $[{}^3\Sigma_g^-]$

$S^\circ_{298.15}$ = [67.216] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 80.4 ± 4.6 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 79.5 ± 4.6 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_1, cm.$^{-1}$	g_1
0	[3]

ω_e = 256.5 cm.$^{-1}$

$\omega_e x_e$ = 2.96 cm.$^{-1}$

σ = 2

B_e = [0.01727] cm.$^{-1}$

α_e = [0.00020] cm.$^{-1}$

r_e = [3.08] Å

Heat of Formation.

Heat of formation was calculated from the dissociation energy of $Pb_2(g)$ reported by A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.

Heat Capacity and Entropy.

The values of ω_e and $\omega_e x_e$ were obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, 1950. Those for B_e and α_e were estimated according to the method suggested by G. Herzberg, loc..cit. The bond distance (r_e) was calculated from the moment of inertia, I = 1630 X 10^{-40} g. cm.^{2}, estimated by K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592, 1961. The ground state configuration was assumed to be ${}^5\Sigma$ by comparison to that for $Si_2(g)$ reported by A. E. Douglas, Can. J. Phys. 33, 801 (1955).

Sulfur (S)

(Reference State) At. Wt. = 32.064

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	$\log K_p$
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-1.053	.000	.000	.000
100	3.060	2.965	11.855	-.889	.000	.000	.000
200	4.639	5.622	8.104	-.496	.000	.000	.000
298	5.401	7.631	7.631	.000	.000	.000	.000
300	5.412	7.665	7.632	.010	.000	.000	.000
400	7.734	10.674	7.901	1.109	.000	.000	.000
500	9.081	12.768	8.673	2.047	.000	.000	.000
600	8.200	14.333	9.492	2.904	.000	.000	.000
700	7.799	15.601	10.309	3.704	.000	.000	.000
800	4.368	31.363	9.452	17.529	.000	.000	.000
900	4.396	31.879	11.916	17.967	.000	.000	.000
1000	4.418	32.344	13.936	18.408	.000	.000	.000
1100	4.435	32.765	15.628	18.851	.000	.000	.000
1200	4.450	33.152	17.073	19.295	.000	.000	.000
1300	4.461	33.509	18.324	19.740	.000	.000	.000
1400	4.471	33.840	19.420	20.187	.000	.000	.000
1500	4.480	34.148	20.392	20.635	.000	.000	.000
1600	4.488	34.438	21.261	21.083	.000	.000	.000
1700	4.495	34.710	22.044	21.532	.000	.000	.000
1800	4.501	34.967	22.755	21.982	.000	.000	.000
1900	4.507	35.211	23.404	22.432	.000	.000	.000
2000	4.513	35.442	24.000	22.883	.000	.000	.000
2100	4.518	35.662	24.550	23.335	.000	.000	.000
2200	4.523	35.873	25.060	23.787	.000	.000	.000
2300	4.528	36.074	25.535	24.240	.000	.000	.000
2400	4.532	36.267	25.978	24.693	.000	.000	.000
2500	4.537	36.452	26.393	25.146	.000	.000	.000
2600	4.541	36.630	26.784	25.600	.000	.000	.000
2700	4.545	36.801	27.151	26.054	.000	.000	.000
2800	4.549	36.966	27.499	26.509	.000	.000	.000
2900	4.553	37.126	27.828	26.964	.000	.000	.000
3000	4.557	37.281	28.141	27.420	.000	.000	.000
3100	4.561	37.430	28.438	27.875	.000	.000	.000
3200	4.565	37.575	28.721	28.332	.000	.000	.000
3300	4.568	37.715	28.992	28.788	.000	.000	.000
3400	4.572	37.852	29.250	29.245	.000	.000	.000
3500	4.575	37.984	29.498	29.703	.000	.000	.000
3600	4.579	38.113	29.735	30.160	.000	.000	.000
3700	4.583	38.239	29.964	30.619	.000	.000	.000
3800	4.586	38.361	30.183	31.077	.000	.000	.000
3900	4.590	38.480	30.394	31.536	.000	.000	.000
4000	4.593	38.597	30.598	31.995	.000	.000	.000
4100	4.596	38.710	30.794	32.454	.000	.000	.000
4200	4.600	38.821	30.984	32.914	.000	.000	.000
4300	4.603	38.929	31.168	33.374	.000	.000	.000
4400	4.607	39.035	31.345	33.835	.000	.000	.000
4500	4.610	39.139	31.517	34.296	.000	.000	.000
4600	4.613	39.240	31.684	34.757	.000	.000	.000
4700	4.617	39.339	31.846	35.218	.000	.000	.000
4800	4.620	39.436	32.003	35.680	.000	.000	.000
4900	4.624	39.532	32.156	36.142	.000	.000	.000
5000	4.627	39.625	32.304	36.605	.000	.000	.000
5100	4.630	39.717	32.449	37.068	.000	.000	.000
5200	4.633	39.807	32.589	37.531	.000	.000	.000
5300	4.637	39.895	32.726	37.994	.000	.000	.000
5400	4.640	39.982	32.860	38.458	.000	.000	.000
5500	4.643	40.067	32.990	38.922	.000	.000	.000
560C	4.647	40.151	33.117	39.387	.000	.000	.000
5700	4.650	40.233	33.241	39.852	.000	.000	.000
5800	4.653	40.314	33.363	40.317	.000	.000	.000
5900	4.656	40.393	33.481	40.782	.000	.000	.000
6000	4.660	40.472	33.597	41.248	.000	.000	.000

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1965

SULFUR (S) **(REFERENCE STATE)** **AT. WT. = 32.064**

0° to 368.54°K.	Crystal, Rhombic
368.54° to 388.36°K.	Crystal, Monoclinic
388.36° to 717.75°K.	Liquid
717.75° to 6000°K.	Ideal Gas, Diatomic

See crystal, liquid and diatomic gas for details.

ulfur (S)

Crystal) At. Wt. = 32.064

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-1.053	.000	.000	.000
100	3.060	2.965	11.855	-.889	.000	.000	.000
200	4.639	5.622	8.104	-.469	.000	.000	.000
298	5.401	7.631	7.631	.000	.000	.000	.000
300	5.412	7.665	7.632	.010	.000	.000	.000
400	6.133	9.571	7.871	.680	-.429	.012	-.007
500	6.819	11.013	8.358	1.327	-.720	.158	-.069
600	7.504	12.317	8.911	2.044	-.860	.349	-.127
700	8.190	13.525	9.485	2.828	-.876	.577	-.180
800	8.876	14.664	10.062	3.682	-13.847	-.488	.133
900	9.561	15.749	10.634	4.603	-13.364	1.154	-.280
1000	10.247	16.792	11.198	5.594	-12.814	2.738	-.598
1100	10.933	17.800	11.752	6.653	-12.198	4.263	-.847
1200	11.619	18.781	12.297	7.780	-11.515	5.731	-1.044
1300	12.304	19.738	12.833	8.977	-10.763	7.139	-1.200
1400	12.990	20.675	13.360	10.241	-9.946	8.485	-1.325
1500	13.676	21.595	13.878	11.575	-9.060	9.770	-1.423
1600	14.361	22.499	14.389	12.976	-8.107	10.996	-1.502
1700	15.047	23.390	14.892	14.447	-7.085	12.158	-1.563
1800	15.733	24.270	15.389	15.986	-5.996	13.259	-1.610
1900	16.418	25.139	15.879	17.593	-4.839	14.298	-1.645
2000	17.104	25.998	16.364	19.270	-3.613	15.274	-1.669

Dec. 31, 1960; Dec. 31, 1965

SULFUR (S) (CRYSTAL) AT. WT. = 32.064

$S_{298.15}^\circ$ = 7.63 ± 0.5 cal. deg.$^{-1}$ mole^{-1}

T_{t_1} = 368.54°K.

T_{t_2} = 374°K.

T_m = 388.36°K.

$\Delta H_{f\ 0}^\circ$ = 0 kcal. mole^{-1}

$\Delta H_{f\ 298.15}^\circ$ = 0 kcal. mole^{-1}

ΔH_{t_1} = 96.01 ± 0.5 cal. mole^{-1}

ΔH_{t_2} = 0.38 ± 0.2 cal. mole^{-1}

ΔH_m = 410.52 ± 0.5 cal. mole^{-1}

$\Delta H_{s\ 298.15}^\circ$ = 66.68 ± 0.3 kcal. mole^{-1}

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

E. D. Eastman and W. C. McGavock, J. Am. Chem. Soc. 59, 145 (1937), have measured the low temperature heat capacities of sulfur from 15° to 375°K. E. D. West, J. Am. Chem. Soc. 81, 29 (1959), has measured the high temperature heat capacities from 298° to 678°K. These two sets of data were joined smoothly at 298.15 K. by a graphical method.

The values of entropy at 110°C and above in E. D. West's paper (table VIII) have been lowered by 0.5841 joule. deg.$^{-1}$ mole^{-1} because of a calculational error which was pointed out by J. P. McCullough and D. W. Scott, private communication, Sept. 27, 1960.

The entropy of rhombic sulfur at 298.15°K. was taken from E. D. Eastman and W. C. McGavock, loc. cit., based on an extrapolation of S_{15}° = 0.12 cal. deg.$^{-1}$ mole^{-1}.

Transition Data.

The enthalpies of transition at 368.54°K. and 374°K. were obtained from E. D. West, loc. cit. The first transition at 368.54°K. was the known rhombic-monoclinic transition, but the second one near 374°K. was a previously unreported transition.

Melting Data.

The heat of melting and the temperature were obtained from E. D. West, loc. cit.

Heat of Sublimation.

The heat of sublimation of sulfur (c) is the heat of formation of monatomic sulfur (g). See S(g) table for details. Since S_8 and lower polymers are major vapor species at room temperature, the heat of sublimation to the equilibrium gas is much smaller. See S_8(g) table for details.

lfur (S)

iquid) At. Wt. = 32.064

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	7.579	8.444	8.444	.000	.336	.093	-.068
300	7.579	8.491	8.444	.014	.340	.092	-.067
400	7.734	10.674	8.741	.773	.000	.000	.000
500	9.081	12.768	9.346	1.711	.000	.000	.000
600	8.200	14.333	10.053	2.568	.000	.000	.000
700	7.799	15.601	10.790	3.368	-.000	-.000	.000
800	7.694	16.634	11.457	4.142	-13.051	-1.269	.347
900	7.694	17.540	12.084	4.910	-12.721	.185	-.045
1000	7.694	18.350	12.671	5.680	-12.393	1.601	-.350
1100	7.694	19.084	13.221	6.449	-12.066	2.983	-.593
1200	7.694	19.753	13.738	7.218	-11.741	4.338	-.790
1300	7.694	20.369	14.224	7.988	-11.416	5.666	-.952
1400	7.694	20.939	14.684	8.757	-11.094	6.967	-1.088
1500	7.694	21.470	15.119	9.527	-10.773	8.245	-1.201
1600	7.694	21.966	15.531	10.296	-10.451	9.503	-1.298
1700	7.694	22.433	15.924	11.065	-10.131	10.740	-1.381
1800	7.694	22.873	16.298	11.835	-9.811	11.959	-1.452
1900	7.694	23.289	16.655	12.604	-9.492	13.161	-1.514
2000	7.694	23.683	16.996	13.374	-9.174	14.344	-1.567

Dec. 31, 1960; Dec. 31, 1965

SULFUR (S) (LIQUID) AT. WT. = 32.064

$S_{298.15}^\circ$ = 8.44 ± 0.5 cal. deg.$^{-1}$ mole^{-1}

T_m = 388.36°K.

T_b = 717.75°K.

$\Delta H_{f\ 298.15}^\circ$ = 0.34 ± 0.01 kcal. mole^{-1}

ΔH_m° = 410.52 ± 0.5 cal. mole^{-1}

ΔH_v° = [2.30] kcal. mole^{-1}

Heat of Formation.

The $\Delta H_{f\ 298.15}^\circ$ (S, 1) was obtained from that of the crystal by adding ΔH_m° and the difference between $H_{388.36}-H_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of the liquid phase was obtained from E. D. West, J. Am. Chem. Soc. 81, 29 (1959). No simple equation fits the curve of C_p against T which shows a peak.

The value of $S_{298.15}^\circ$ (S, 1) was obtained in a manner analogous to that of the heat of formation. The heat capacity of sulfur (liquid) below the melting point was assumed to be constant as 7.579 cal. deg.$^{-1}$ mole^{-1}; and above the boiling point, it was assumed as 7.694 cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

The heat of melting and the temperature were obtained from E. D. West, loc. cit.

Vaporization Data.

According to the international practical temperature scale, the boiling point is 717.75°K. The heat of vaporization to the equilibrium vapor mixture was estimated by D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D.C., 1956. The equilibrium vapor involves monomeric and several polymeric species; S_2 and S predominate above 1000°K. while S_8, S_6 and possible S_4 and S_3 are favored at lower temperatures.

Sulfur, Monatomic (S)

(Ideal Gas) At. Wt. = 32.064

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-1.591	66.142	66.142	INFINITE
100	5.103	34.127	45.046	-1.092	66.477	63.361	-138.468
200	5.589	37.831	40.604	-.555	66.621	60.180	-65.758
298	5.659	40.086	40.086	.000	66.680	57.004	-41.783
300	5.658	40.121	40.086	.010	66.680	56.944	-41.481
400	5.554	41.736	40.307	.572	66.143	53.718	-29.349
500	5.436	42.962	40.720	1.121	65.754	50.657	-22.141
600	5.340	43.944	41.178	1.659	65.435	47.669	-17.363
700	5.266	44.762	41.634	2.190	65.166	44.753	-13.972
800	5.211	45.461	42.069	2.713	51.864	40.586	-11.087
900	5.169	46.072	42.481	3.232	51.945	39.172	-9.512
1000	5.137	46.615	42.868	3.747	52.019	37.748	-8.250
1100	5.112	47.103	43.231	4.260	52.089	36.317	-7.215
1200	5.093	47.547	43.572	4.770	52.155	34.881	-6.352
1300	5.079	47.954	43.894	5.279	52.219	33.440	-5.622
1400	5.070	48.331	44.198	5.786	52.279	31.992	-4.994
1500	5.064	48.680	44.485	6.293	52.338	30.540	-4.449
1600	5.062	49.007	44.758	6.799	52.396	29.085	-3.973
1700	5.063	49.314	45.017	7.305	52.453	27.626	-3.551
1800	5.068	49.603	45.263	7.812	52.510	26.165	-3.177
1900	5.075	49.877	45.499	8.319	52.567	24.701	-2.841
2000	5.085	50.138	45.725	8.827	52.624	23.232	-2.539
2100	5.097	50.386	45.941	9.336	52.681	21.761	-2.265
2200	5.112	50.624	46.148	9.846	52.739	20.287	-2.015
2300	5.127	50.851	46.348	10.358	52.798	18.811	-1.787
2400	5.144	51.070	46.540	10.872	52.859	17.332	-1.578
2500	5.162	51.280	46.725	11.387	52.921	15.851	-1.386
2600	5.181	51.483	46.905	11.904	52.984	14.367	-1.208
2700	5.200	51.679	47.078	12.423	53.049	12.879	-1.042
2800	5.219	51.869	47.246	12.944	53.115	11.387	-.889
2900	5.239	52.052	47.408	13.467	53.183	9.898	-.746
3000	5.258	52.230	47.566	13.992	53.252	8.405	-.612
3100	5.277	52.403	47.719	14.519	53.324	6.908	-.487
3200	5.295	52.571	47.868	15.048	53.396	5.408	-.369
3300	5.313	52.734	48.013	15.578	53.470	3.907	-.259
3400	5.331	52.893	48.154	16.110	53.545	2.406	-.155
3500	5.347	53.047	48.292	16.644	53.621	.901	-.056
3600	5.363	53.198	48.426	17.180	53.700	-.606	.037
3700	5.378	53.345	48.557	17.717	53.778	-2.115	.125
3800	5.392	53.489	48.685	18.255	53.858	-3.628	.209
3900	5.406	53.629	48.810	18.795	53.939	-5.142	.288
4000	5.419	53.766	48.932	19.336	54.021	-6.655	.364
4100	5.430	53.900	49.052	19.879	54.105	-8.174	.436
4200	5.441	54.031	49.169	20.422	54.188	-9.694	.504
4300	5.451	54.159	49.283	20.967	54.273	-11.216	.570
4400	5.461	54.285	49.396	21.513	54.358	-12.742	.633
4500	5.470	54.408	49.506	22.059	54.443	-14.267	.693
4600	5.477	54.528	49.613	22.607	54.530	-15.795	.750
4700	5.485	54.646	49.719	23.155	54.617	-17.326	.806
4800	5.491	54.761	49.823	23.703	54.703	-18.857	.859
4900	5.497	54.875	49.925	24.253	54.791	-20.390	.909
5000	5.502	54.986	50.025	24.803	54.878	-21.927	.958
5100	5.507	55.095	50.124	25.353	54.965	-23.462	1.005
5200	5.511	55.202	50.220	25.904	55.053	-25.001	1.051
5300	5.515	55.307	50.315	26.456	55.142	-26.542	1.094
5400	5.518	55.410	50.409	27.007	55.229	-28.082	1.136
5500	5.521	55.511	50.500	27.559	55.317	-29.625	1.177
5600	5.523	55.611	50.591	28.111	55.404	-31.172	1.216
5700	5.525	55.708	50.680	28.664	55.492	-32.716	1.254
5800	5.526	55.805	50.767	29.216	55.579	-34.269	1.291
5900	5.528	55.899	50.853	29.769	55.667	-35.818	1.327
6000	5.529	55.992	50.938	30.322	55.754	-37.366	1.361

Dec. 31, 1960; June 30, 1961; Dec. 31, 1965

SULFUR, MONATOMIC (S) (IDEAL GAS) AT. WT. = 32.064

Ground State Configuration $^3P_2$

$S^\circ_{298.15}$ = 40.1 ± 0.1 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 66.14 ± 0.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 66.68 ± 0.5 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_1, cm.$^{-1}$	g_1	ϵ_1, cm.$^{-1}$	g_1	ϵ_1, cm.$^{-1}$	g_1
0.0	5	67,878.03	9	73,921.14	7
396.8	3	67,890.45	7	74,269.2	5
573.6	1	67,888.25	5	74,270.28	3
9,239.0	5	67,885.97	3	74,272.32	1
22,181.4	1	67,884.67	1	75,342.02	40
52,623.88	5	69,238.7	5	76,706.70	73
55,331.15	3	70,165.9	3	77,986.31	39
63,446.36	3	70,166.8	5	78,338.35	54
63,457.33	5	70,170.7	7	79,014.3	83
63,475.26	7	[70,706.0]	5	79,782.1	52
64,891.71	1	71.352.5	3	80,158.61	24
64,889.23	3	72,025.5	5	80,634.	89
64,892.89	5	72,382.5	3	81,089.9	29
67,816.87	3	72,572.4	1	81,405.23	84
67,825.72	5	73,911.53	3	81,864.6	101
67,843.38	7	73,915.16	5	82,353.3	25

Heat of Formation.

L. Brewer, J. Chem. Phys. 31, 1143 (1959), has reviewed the three possible values of D_0° (S_2), i.e. 4.4 e.V., 3.6 e.V. and 3.3 e.V., which were due to the ambiguity of defining the excitation state of the atomic products resulting from predissociation in the spectroscopic measurements. The value of 4.4 e.V. (101.5 kcal. mole^{-1}) was shown to be the most probable one. Since this review, further support for his value have been given by the following investigators. J. R. Marquart, Dissertation Abstract 24, 5027 (1964), has found that the value of D_0° (S_2) to be consistent with the value of 4.4 e.V. in mass spectrometric studies. R. Colin, P. Goldfinger and M. Jeunehomme, Trans. Faraday Soc. 60, 306 (1964), have found D_0° (S_2) = 97 ± 5 kcal. mole^{-1} in their mass-spectrometric studies of the vaporization of CaS, BaS, SnS and PbS, but they reported a revised value, i.e. D_0° (S_2) = 101 ± 1 kcal. mole^{-1}, which was given in the note in proof. A. N. Singh and D. K. Rai, J. Chem. Phys. 43, 2151 (1965), have selected the best value of D_0° (S_2) = 4.4 e.V. in theoretical comparisons of the potential-energy curve. As pointed out by L. Brewer, loc. cit., and A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., 2nd. Ed., London, 1953, the old vapor pressure measurements which are not consistent with D_0 (S_2) = 4.4 e.V. (101.5 kcal. mole^{-1}) are probably not reliable.

The value D_0 (S_2, g) = 4.4 e.V. (101.5 kcal. mole^{-1}) was selected as the dissociation energy of diatomic sulfur, and combination of this value with heat of formation of diatomic sulfur gives the heat of formation of monatomic sulfur, $\Delta H^\circ_{f\ 298}$ (S, g) = 66.68 kcal. mole^{-1}.

Heat Capacity and Entropy.

The ground state configuration, electronic levels and quantum weight were obtained from C. E. Moore, "Atomic Energy Levels", Vol. 1, National Bureau of Standards Circular 467, June, 1949.

ulfur, Diatomic (S_2)

Ideal Gas) Mol. Wt. = 64.128

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.141	30.805	30.805	INFINITE
100	6.964	46.623	61.075	-1.445	31.173	27.104	-59.232
200	7.265	51.515	55.204	-.738	31.094	23.040	-25.176
298	7.759	54.510	54.510	.000	30.840	19.138	-14.028
300	7.768	54.558	54.510	.014	30.834	19.066	-13.889
400	8.144	56.848	54.819	.811	29.433	15.233	-8.323
500	8.389	58.693	55.416	1.639	28.385	11.806	-5.160
600	8.549	60.238	56.094	2.486	27.518	8.575	-3.123
700	8.658	61.564	56.783	3.347	26.779	5.525	-1.725
800	8.735	62.726	57.455	4.217	.000	.000	.000
900	8.792	63.758	58.099	5.093	.000	.000	.000
1000	8.836	64.687	58.712	5.975	.000	.000	.000
1100	8.870	65.531	59.294	6.860	.000	.000	.000
1200	8.899	66.304	59.846	7.749	.000	.000	.000
1300	8.922	67.017	60.371	8.640	.000	.000	.000
1400	8.942	67.679	60.870	9.533	.000	.000	.000
1500	8.960	68.296	61.344	10.428	.000	.000	.000
1600	8.976	68.875	61.797	11.325	.000	.000	.000
1700	8.990	69.420	62.230	12.223	.000	.000	.000
1800	9.002	69.934	62.643	13.123	.000	.000	.000
1900	9.014	70.421	63.040	14.024	.000	.000	.000
2000	9.025	70.884	63.421	14.926	.000	.000	.000
2100	9.036	71.324	63.787	15.829	.000	.000	.000
2200	9.046	71.745	64.139	16.733	.000	.000	.000
2300	9.055	72.147	64.479	17.638	.000	.000	.000
2400	9.064	72.533	64.806	18.544	.000	.000	.000
2500	9.073	72.903	65.123	19.451	.000	.000	.000
2600	9.081	73.259	65.429	20.358	.000	.000	.000
2700	9.090	73.602	65.725	21.267	.000	.000	.000
2800	9.098	73.932	66.012	22.176	.000	.000	.000
2900	9.106	74.252	66.291	23.086	.000	.000	.000
3000	9.113	74.561	66.562	23.997	.000	.000	.000
3100	9.121	74.860	66.824	24.909	.000	.000	.000
3200	9.129	75.149	67.080	25.822	.000	.000	.000
3300	9.136	75.430	67.329	26.735	.000	.000	.000
3400	9.143	75.703	67.571	27.649	.000	.000	.000
3500	9.150	75.968	67.807	28.563	.000	.000	.000
3600	9.158	76.226	68.038	29.479	.000	.000	.000
3700	9.165	76.477	68.262	30.395	.000	.000	.000
3800	9.172	76.722	68.482	31.312	.000	.000	.000
3900	9.179	76.960	68.696	32.229	.000	.000	.000
4000	9.186	77.193	68.906	33.148	.000	.000	.000
4100	9.192	77.419	69.111	34.066	.000	.000	.000
4200	9.199	77.641	69.311	34.986	.000	.000	.000
4300	9.206	77.858	69.507	35.906	.000	.000	.000
4400	9.213	78.069	69.699	36.827	.000	.000	.000
4500	9.220	78.276	69.888	37.749	.000	.000	.000
4600	9.226	78.479	70.072	38.671	.000	.000	.000
4700	9.233	78.678	70.253	39.594	.000	.000	.000
4800	9.240	78.872	70.431	40.518	.000	.000	.000
4900	9.247	79.063	70.605	41.442	.000	.000	.000
5000	9.253	79.250	70.776	42.367	.000	.000	.000
5100	9.260	79.433	70.944	43.293	.000	.000	.000
5200	9.266	79.613	71.109	44.219	.000	.000	.000
5300	9.273	79.789	71.271	45.146	.000	.000	.000
5400	9.280	79.963	71.431	46.074	.000	.000	.000
5500	9.286	80.133	71.587	47.002	.000	.000	.000
5600	9.293	80.300	71.741	47.931	.000	.000	.000
5700	9.299	80.465	71.893	48.861	.000	.000	.000
5800	9.306	80.627	72.042	49.791	.000	.000	.000
5900	9.312	80.786	72.189	50.722	.000	.000	.000
6000	9.319	80.942	72.334	51.653	.000	.000	.000

Dec. 31, 1960; Dec. 31, 1965

SULFUR, DIATOMIC (S_2) (IDEAL GAS) MOL. WT. = 64.128

Ground State Configuration $^3\Sigma_g^-$

$S^\circ_{298.15}$ = 54.51 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 30.80 ± 0.2 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 30.84 ± 0.2 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ, cm.$^{-1}$	g_1
0	3

ω_e = 724.66 cm.$^{-1}$

B_e = 0.2948 cm.$^{-1}$

$\omega_e x_e$ = 2.852 cm.$^{-1}$

α_e = 0.0016 cm.$^{-1}$

σ = 2

r_e = 1.889 Å

Heat of Formation.

The standard enthalpy of formation of gaseous diatomic sulfur, $\Delta H^\circ_{f\ 298}$ = 30.84 kcal. mole^{-1}, was calculated from $\Delta H^\circ_{r\ 298}$ = -20.30 kcal. mole^{-1} for the reaction $H_2(g) + 0.5\ S_2(g) \rightarrow H_2S(g)$ with JANAF value $\Delta H^\circ_{f\ 298}(H_2S, g)$ = -4.88 ± 0.15 kcal. mole^{-1}. The $\Delta H^\circ_{r\ 298}$ was obtained by the second and third law analyses of equilibrium constants which have been determined by G. Preuner and W. Schupp (ref. 1) and M. Randall and F. R. Bichowsky (ref. 2). The results obtained are presented as follows:

Ref.	Temp. Range	Points	2nd law $\Delta H^\circ_{r\ 298}$ kcal. mole^{-1}	3rd law $\Delta H^\circ_{r\ 298}$ kcal. mole	Drift cal. mole^{-1} deg.$^{-1}$
1	1023-1405°K	5	-19.92 ± 0.13	-20.295	-0.282 ± 0.097
2	1362-1667°K	4	-20.74 ± 0.40	-20.307	+0.281 ± 0.269
3	1023-1667°K	9	-20.13 ± 0.12	-20.300	-0.066 ± 0.093

References

1. G. Preuner and W. Schupp, Z. physik Chem. 68, 157 (1910).
2. M. Randall and F. R. Bichowsky, J. Am. Chem. Soc. 40, 368 (1918).
3. Combination of above references.

The third law value of the combination set was selected to calculate the heat of formation of diatomic sulfur.

The dissociation energy of gaseous diatomic sulfur, $D^\circ_0\ (S_2)$ = 101.5 kcal. mole^{-1}, was chosen. For discussions see JANAF monatomic sulfur (g) and sulfur monoxide (g) tables.

Heat Capacity and Entropy.

The molecular constants which were taken from G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed., D. Van Nostrand Company, New York, have been modified for the natural isotopic abundances reported by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

ulfur, Octatomic (S_8)

Ideal Gas) Mol. Wt. = 256.528

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-7.487	25.137	25.137	INFINITE
100	20.831	70.614	132.035	-6.142	25.170	20.481	-44.758
200	32.066	88.909	106.096	-3.437	24.731	15.944	-17.422
298	37.296	102.823	102.823	.000	24.200	11.745	-8.609
300	37.361	103.054	102.824	.069	24.189	11.669	-8.500
400	39.841	114.183	104.324	3.944	19.272	7.755	-4.237
500	41.137	123.227	107.229	7.999	15.823	5.281	-2.308
600	41.887	130.799	110.544	12.153	13.121	3.440	-1.253
700	42.355	137.293	113.912	16.367	10.935	2.195	-.685
800	42.665	142.971	117.197	20.619	-95.413	-9.066	2.477
900	42.882	148.009	120.346	24.897	-94.639	1.681	-.408
1000	43.038	152.536	123.342	29.193	-93.871	12.346	-2.698
1100	43.154	156.643	126.186	33.503	-93.105	22.919	-4.553
1200	43.244	160.402	128.883	37.823	-92.337	33.440	-6.090
1300	43.313	163.866	131.442	42.151	-91.569	43.898	-7.380
1400	43.369	167.078	133.875	46.485	-90.811	54.288	-8.474
1500	43.414	170.072	136.189	50.824	-90.056	64.612	-9.414
1600	43.450	172.875	138.395	55.168	-89.296	74.910	-10.232
1700	43.481	175.510	140.502	59.514	-88.542	85.147	-10.946
1800	43.507	177.996	142.516	63.864	-87.792	95.339	-11.575
1900	43.528	180.349	144.446	68.216	-87.040	105.503	-12.135
2000	43.547	182.582	146.298	72.569	-86.295	115.613	-12.633
2100	43.563	184.707	148.077	76.925	-85.555	125.681	-13.079
2200	43.577	186.734	149.788	81.282	-84.814	135.735	-13.483
2300	43.589	188.672	151.437	85.640	-84.080	145.737	-13.848
2400	43.599	190.527	153.027	90.000	-83.344	155.717	-14.179
2500	43.609	192.307	154.563	94.360	-82.608	165.665	-14.482
2600	43.617	194.018	156.048	98.721	-81.879	175.580	-14.758
2700	43.625	195.664	157.485	103.083	-81.149	185.461	-15.011
2800	43.631	197.250	158.877	107.446	-80.426	195.311	-15.244
2900	43.637	198.782	160.227	111.810	-79.702	205.154	-15.460
3000	43.643	200.261	161.537	116.174	-78.986	214.974	-15.660
3100	43.648	201.692	162.809	120.538	-78.262	224.756	-15.845
3200	43.652	203.078	164.046	124.903	-77.553	234.517	-16.016
3300	43.656	204.421	165.249	129.269	-76.835	244.250	-16.175
3400	43.660	205.725	166.420	133.634	-76.126	253.985	-16.325
3500	43.663	206.990	167.562	138.000	-75.424	263.662	-16.463
3600	43.666	208.220	168.674	142.367	-74.713	273.348	-16.594
3700	43.669	209.417	169.759	146.734	-74.018	283.014	-16.716
3800	43.672	210.581	170.818	151.101	-73.315	292.650	-16.830
3900	43.674	211.716	171.852	155.468	-72.620	302.264	-16.938
4000	43.676	212.822	172.863	159.836	-71.924	311.893	-17.040
4100	43.678	213.900	173.851	164.203	-71.229	321.469	-17.135
4200	43.680	214.953	174.817	168.571	-70.541	331.044	-17.225
4300	43.682	215.981	175.762	172.939	-69.853	340.589	-17.310
4400	43.684	216.985	176.688	177.308	-69.172	350.127	-17.390
4500	43.685	217.966	177.594	181.676	-68.492	359.663	-17.467
4600	43.687	218.927	178.482	186.045	-67.811	369.158	-17.538
4700	43.688	219.866	179.353	190.413	-67.131	378.645	-17.606
4800	43.690	220.786	180.206	194.782	-66.458	388.112	-17.670
4900	43.691	221.687	181.044	199.151	-65.785	397.604	-17.733
5000	43.692	222.570	181.865	203.521	-65.119	407.033	-17.791
5100	43.693	223.435	182.672	207.890	-64.454	416.482	-17.847
5200	43.694	224.283	183.464	212.259	-63.789	425.910	-17.900
5300	43.695	225.116	184.242	216.629	-63.123	435.312	-17.950
5400	43.696	225.932	185.007	220.998	-62.466	444.722	-17.998
5500	43.697	226.734	185.758	225.368	-61.808	454.102	-18.043
5600	43.698	227.521	186.497	229.737	-61.159	463.486	-18.087
5700	43.698	228.295	187.223	234.107	-60.509	472.835	-18.129
5800	43.699	229.055	187.938	238.477	-59.859	482.193	-18.169
5900	43.700	229.802	188.641	242.847	-59.209	491.510	-18.206
6000	43.700	230.536	189.334	247.217	-58.567	500.871	-18.243

Dec. 31, 1960; June 30, 1964

SULFUR, OCTATOMIC (S_8) (IDEAL GAS) MOL. WT. = 256.528

Point group D_{4d}

$\Delta H^\circ_{f\ 0}$ = 25.14 ± 0.15 kcal. mole^{-1}

$S^\circ_{298.15}$ = 102.823 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 24.20 ± 0.15 kcal. mole^{-1}

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
475 (1)	475 (2)	243 (1)
218 (1)	152 (2)	437 (2)
471 (2)	56 (2)	248 (2)
191 (2)	411 (1)	

Bond Distance: S-S = 2.059 ± 0.002 Å

Bond Angle: S-S-S = 107.9 ± 0.6°

σ = 8

Product of the Moments of Inertia: $I_AI_BI_C = 3.90326 \times 10^{-111}$ g.^{3} cm.^{6}

Heat of Formation.

The vapor pressure of S(c) has been measured by many investigators. Using the seven more recent vapor pressure date, the respective heat of sublimation ($\Delta H^\circ_{s\ 298.15}$) was calculated by both the third and second law methods. The values obtained are tabulated as follows:

		$\Delta H^\circ_{s\ 298.15}$, kcal. mole^{-1}	
Investigator	Temperature Range, °K.	Third Law Value	Second Law Value
West-Menzies [1]	376.6 - 448.8	24.29	21.29
Neumann [2]	332.6 - 362.1	24.35	26.47
Fouretier [3]	304.1 - 351.6	24.36	24.10
Taillade [4]	303.6 - 352.5	24.29	24.87
Bradley [5]	288.3 - 305.7	24.29	23.80
Magee [6]	331.9 - 368.0	24.11	24.44
	332.7 - 367.4	24.12	23.88
Briske [7]	273.2 - 313.2	24.28	24.00

1 W. A. West and A. W. Menzies, J. Phys. Chem. 33, 1880 (1929).
2 K. Neumann, Z. physik. Chem. A171, 416 (1934).
3 G. Fouretier, Compt. rend. 218, 194 (1944).
4 M. Taillade, Compt. rend. 218, 836 (1944).
5 R. S. Bradley, Proc. Roy. Soc. (London) A 205, 553 (1951).
6 D. W. Magee, Ph. D. Thesis, The Ohio State University, 1955.
7 C. Briske, N. H. Hartshorne and D. R. Stranks, J. Chem. Soc. (London), 1200 (1960).

Due to the presence of S_6(g) in S_8(g), the measured total pressures were corrected to give the partial pressures of S_8(g) for the first five sets of vapor pressure data, according to D. W. Scott, U. S. Bureau of Mines, Bartlesville, Oklahoma, private communication, May 22, 1964. However, the magnitude of the correction is only 0.1 - 0.2 kcal. mole^{-1}. The adopted value is the weighted average of both the third and second law values.

Heat Capacity and Entropy.

The vibrational frequencies were taken from D. W. Scott, J. P. McCullough and F. H. Kruse, "Vibrational Assignment and Force Constants of S_8 (condensed States) from a Normal-Coordinate Treatment", Prepublication Report 64, U. S. Bureau of Mines, May 20, 1963. Four of the eighteen frequencies, i.e. 86(2) and 218(2) cm.$^{-1}$, were changed to 56(2) and 248(2) cm.$^{-1}$, respective, suggested by D. W. Scott, loc. cit., private communication, April 23, 1964. The molecular structure and bond distance and angle were reported by J. Donohur, A. Caron and E. Goldish, J. Am. Chem. Soc. 83, 3748 (1961). The three principle moments of inertia are: $I_A = I_B = 1.28594 \times 10^{-37}$ and $I_C = 2.36042 \times 10^{-37}$ g. cm.^{2}.

Silicon (Si)

(Reference State) GFW = 28.086

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- .769	.000	.000	.000
100	1.737	.916	7.966	- .705	.000	.000	.000
200	3.737	2.788	4.908	- .424	.000	.000	.000
298	4.780	4.498	4.498	.000	.000	.000	.000
300	4.792	4.528	4.498	.009	.000	.000	.000
400	5.292	5.983	4.693	.516	.000	.000	.000
500	5.576	7.197	5.076	1.060	.000	.000	.000
600	5.773	8.231	5.518	1.628	.000	.000	.000
700	5.928	9.133	5.971	2.213	.000	.000	.000
800	6.061	9.933	6.417	2.813	.000	.000	.000
900	6.184	10.655	6.849	3.425	.000	.000	.000
1000	6.295	11.312	7.263	4.049	.000	.000	.000
1100	6.400	11.917	7.659	4.684	.000	.000	.000
1200	6.500	12.478	8.037	5.329	.000	.000	.000
1300	6.600	13.002	8.399	5.984	.000	.000	.000
1400	6.700	13.495	8.746	6.649	.000	.000	.000
1500	6.800	13.961	9.078	7.324	.000	.000	.000
1600	6.900	14.403	9.397	8.009	.000	.000	.000
1700	6.500	21.941	9.767	20.697	.000	.000	.000
1800	6.500	22.313	10.454	21.347	.000	.000	.000
1900	6.500	22.664	11.087	21.997	.000	.000	.000
2000	6.500	22.998	11.674	22.647	.000	.000	.000
2100	6.500	23.315	12.221	23.297	.000	.000	.000
2200	6.500	23.617	12.732	23.947	.000	.000	.000
2300	6.500	23.906	13.212	24.597	.000	.000	.000
2400	6.500	24.183	13.663	25.247	.000	.000	.000
2500	6.500	24.448	14.089	25.897	.000	.000	.000
2600	6.500	24.703	14.493	26.547	.000	.000	.000
2700	6.500	24.948	14.876	27.197	.000	.000	.000
2800	6.500	25.185	15.240	27.847	.000	.000	.000
2900	6.500	25.413	15.586	28.497	.000	.000	.000
3000	6.500	25.633	15.918	29.147	.000	.000	.000
3100	6.500	25.846	16.235	29.797	.000	.000	.000
3200	6.500	26.053	16.538	30.447	.000	.000	.000
3300	6.500	26.253	16.830	31.097	.000	.000	.000
3400	6.500	26.447	17.110	31.747	.000	.000	.000
3500	6.500	26.635	17.379	32.397	.000	.000	.000
3600	5.508	52.990	18.265	125.008	.000	.000	.000
3700	5.513	53.141	19.206	125.559	.000	.000	.000
3800	5.516	53.288	20.101	126.110	.000	.000	.000
3900	5.519	53.431	20.954	126.662	.000	.000	.000
4000	5.521	53.571	21.767	127.214	.000	.000	.000
4100	5.523	53.707	22.545	127.767	.000	.000	.000
4200	5.524	53.840	23.288	128.319	.000	.000	.000
4300	5.524	53.970	24.000	128.871	.000	.000	.000
4400	5.524	54.097	24.683	129.424	.000	.000	.000
4500	5.524	54.222	25.338	129.976	.000	.000	.000
4600	5.523	54.343	25.967	130.528	.000	.000	.000
4700	5.522	54.462	26.572	131.081	.000	.000	.000
4800	5.521	54.578	27.155	131.633	.000	.000	.000
4900	5.520	54.692	27.715	132.185	.000	.000	.000
5000	5.519	54.803	28.256	132.737	.000	.000	.000
5100	5.519	54.913	28.778	133.289	.000	.000	.000
5200	5.518	55.020	29.281	133.841	.000	.000	.000
5300	5.518	55.125	29.768	134.392	.000	.000	.000
5400	5.519	55.228	30.238	134.944	.000	.000	.000
5500	5.520	55.329	30.694	135.496	.000	.000	.000
5600	5.521	55.429	31.134	136.048	.000	.000	.000
5700	5.524	55.527	31.562	136.600	.000	.000	.000
5800	5.527	55.623	31.976	137.153	.000	.000	.000
5900	5.531	55.717	32.377	137.706	.000	.000	.000
6000	5.536	55.810	32.767	138.259	.000	.000	.000

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1966; Mar. 31, 1967

SILICON (Si) (REFERENCE STATE) GFW = 28.086

0	to	1685°K	Crystal
1685	to	3513.8°K	Liquid
3513.8	to	6000°K	Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

ilicon (Si)

rystal) GFW = 28.086

T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- .769	.000	.000	INFINITE
100	1.737	.916	7.966	- .705	.000	.000	.000
200	3.737	2.788	4.908	- .424	.000	.000	.000
298	4.780	4.498	4.498	.000	.000	.000	.000
300	4.792	4.528	4.498	.009	.000	.000	.000
400	5.292	5.983	4.693	.516	.000	.000	.000
500	5.576	7.197	5.076	1.060	.000	.000	.000
600	5.773	8.231	5.518	1.628	.000	.000	.000
700	5.928	9.133	5.971	2.213	.000	.000	.000
800	6.061	9.933	6.417	2.813	.000	.000	.000
900	6.184	10.655	6.849	3.425	.000	.000	.000
1000	6.295	11.312	7.263	4.049	.000	.000	.000
1100	6.400	11.917	7.659	4.684	.000	.000	.000
1200	6.500	12.478	8.037	5.329	.000	.000	.000
1300	6.600	13.002	8.399	5.984	.000	.000	.000
1400	6.700	13.495	8.746	6.649	.000	.000	.000
1500	6.800	13.961	9.078	7.324	.000	.000	.000
1600	6.900	14.403	9.397	8.009	.000	.000	.000
1700	7.000	14.824	9.704	8.704	- 11.993	.106	- .014
1800	7.100	15.227	10.000	9.409	- 11.938	.817	- .099
1900	7.200	15.614	10.285	10.124	- 11.873	1.522	- .175
2000	7.300	15.985	10.561	10.849	- 11.798	2.228	- .243
2100	7.400	16.344	10.828	11.584	- 11.713	2.926	- .305
2200	7.500	16.691	11.086	12.329	- 11.618	3.619	- .360
2300	7.600	17.026	11.337	13.084	- 11.513	4.311	- .410
2400	7.700	17.352	11.581	13.849	- 11.398	4.996	- .455
2500	7.800	17.668	11.818	14.624	- 11.273	5.677	- .496

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1966

SILICON (Si) (CRYSTAL) GFW = 28.086

$\Delta Hf^\circ_0 = 0$ kcal/mol

$S^\circ_{298.15} = 4.498 \pm 0.01$ gibbs/mol

$\Delta Hf^\circ_{298.15} = 0$ kcal/mol

$T_m = 1685 \pm 3$ °K

$\Delta Hm^\circ = 12.0 \pm 0.1$ kcal/mol

$\Delta Hs^\circ_{298.15} = 107.7 \pm 1$ kcal/mol

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Low temperature heat capacities are based on the precise data (8-300°K) of Flubacher, Leadbetter and Morrison. The entropy is obtained from the heat capacity using $S^\circ_8 = 0.0003$ eu. The selected values are consistent with recent data of Keesom and Seidel (1.2 - 4.2°K) and Kalishevich et al. (60-300°K). Earlier data have been reviewed by R. Hultgren, R. L. Orr and K. K. Kelley, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," Univ. of California, Berkeley, November, 1965.

High temperature studies are summarized below, along with the pertinent low temperature studies. The selected heat capacities above 300°K are obtained from a Shomate plot of the adopted low temperature heat capacities and the enthalpies reported or derived from the work of Dennison (1963), Kantor et al. (1960), Olette (1956), Serebrennikov and Gel'd (1952), and Magnus (1923). Discrepancies are apparent in the enthalpy data, particularly in the range of 370 to 1100°K, where only the recent study of Dennison made use of a high purity sample. Enthalpies from Dennison join most smoothly with the low temperature Cp° but deviate increasingly at higher temperatures, being 1-2% lower than the other measurements above 1000°K. The selected functions agree with Dennison below 600°K, with Magnus from 600 to 1200°K, and with Kantor et al. above 1200°K. The resulting heat capacities are slightly different from those selected by Hultgren et al., loc. cit.; the latter are 0.07 gibbs/mol higher at 800°K and 0.21 gibbs/mol lower at the melting point.

Investigators	Method	Quantity Reported	T Range, °K	Sample
1. Flubacher et al. (1959)	Calorimetry	Cp°	7.7 - 300	Single crystal, 3mm pieces, Resistance (300°K) = 100 ohm cm, Carrier Concentration $\leqslant 10^{15}$ cm^{-3}
2. Keesom et al. (1959)	Calorimetry	Specific Heat	1.2 - 4.2	
3. Kalishevich et al. (1965)	Calorimetry	Cp°	60 - 300	99.999%
4. Gerlich et al. (1965)	Temperature Modulation	Cp°	300 - 900	Resistance (300°K) = 0.027 ohm cm, Carrier Concentration = 10^{19} cm^{-3}
5. Dennison (1963)	Drop Calorimetry	Specific Heat	273 - 1373	Resistance (300°K) = 107 ohm cm
6. Kantor et al. (1960)	Drop Calorimetry	Enthalpy Equation	1148 - 1685	"Highly purified"
7. Olette (1956)	Drop Calorimetry	Specific Enthalpy	1467 - 1685	99.99%
8. Serebrennikov et al.	Drop Calorimetry	Specific Enthalpy	302 - 1556	99.3%
9. Magnus (1923)	Drop Calorimetry	Specific Enthalpy	372 - 1175	99.2%

Reference:

1. P. Flubacher, A. J. Leadbetter and J. A. Morrison, Phil. Mag. 4, 273 (1959).
2. P. H. Keesom and G. Seidel, Phys. Rev. 113, 33 (1959).
3. G. I. Kalishevich, P. V. Gel'd. and R. P. Krentsis, Russ. J. Phys. Chem. 39, 1602 (1965).
4. D. Gerlich, B. Abeles and R. E. Miller, J. Appl. Phys. 36, 76 (1965).
5. D. H. Dennison quoted by H. R. Shanks et al., Phys. Rev. 130, 1743 (1963).
6. P. B. Kantor, A. M. Kisil and E. M. Fomichev, Ukrain. Fiz. Zhur. 5, 358 (1960).
7. M. Olette, Phys. Chem. Steelmaking, Proc. Dedham, Mass. 1956, 18-26 (Pub. 1958).
8. N. N. Serebrennikov and P. V. Gel'd, Doklad. Akad. Nauk SSSR 87, 1021 (1952).
9. A. Magnus, Ann. Physik 70, 303 (1923).

Melting Data.

See the Si(l) table for details.

Heat of Sublimation.

$\Delta Hs^\circ_{298.15}$ is calculated as the difference between $\Delta Hf^\circ_{298.15}$ for Si(g) and Si(c).

licon (Si)

iquid) GFW = 28.086

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	6.500	10.626	10.626	.000	11.585	9.758	-7.153
300	6.500	10.666	10.626	.012	11.588	9.747	-7.100
400	6.500	12.536	10.881	.662	11.731	9.110	-4.977
500	6.500	13.987	11.363	1.312	11.837	8.442	-3.690
600	6.500	15.172	11.902	1.962	11.919	7.754	-2.825
700	6.500	16.174	12.442	2.612	11.984	7.055	-2.203
800	6.500	17.042	12.964	3.262	12.034	6.347	-1.734
900	6.500	17.807	13.460	3.912	12.072	5.635	-1.368
1000	6.500	18.492	13.930	4.562	12.098	4.918	-1.075
1100	6.500	19.112	14.373	5.212	12.113	4.199	-.834
1200	6.500	19.677	14.792	5.862	12.118	3.479	-.634
1300	6.500	20.197	15.188	6.512	12.113	2.760	-.464
1400	6.500	20.679	15.563	7.162	12.098	2.040	-.319
1500	6.500	21.128	15.920	7.812	12.073	1.323	-.193
1600	6.500	21.547	16.258	8.462	12.038	.608	-.083
1700	6.500	21.941	16.581	9.112	.000	.000	.000
1800	6.500	22.313	16.889	9.762	.000	.000	.000
1900	6.500	22.664	17.184	10.412	.000	.000	.000
2000	6.500	22.997	17.466	11.062	.000	.000	.000
2100	6.500	23.315	17.737	11.712	.000	.000	.000
2200	6.500	23.617	17.998	12.362	.000	.000	.000
2300	6.500	23.906	18.249	13.012	.000	.000	.000
2400	6.500	24.183	18.490	13.662	.000	.000	.000
2500	6.500	24.448	18.723	14.312	.000	.000	.000
2600	6.500	24.703	18.948	14.962	.000	.000	.000
2700	6.500	24.948	19.166	15.612	.000	.000	.000
2800	6.500	25.185	19.377	16.262	.000	.000	.000
2900	6.500	25.413	19.581	16.912	.000	.000	.000
3000	6.500	25.633	19.779	17.562	.000	.000	.000
3100	6.500	25.846	19.971	18.212	.000	.000	.000
3200	6.500	26.053	20.158	18.862	.000	.000	.000
3300	6.500	26.253	20.340	19.512	.000	.000	.000
3400	6.500	26.447	20.517	20.162	.000	.000	.000
3500	6.500	26.635	20.689	20.812	.000	.000	.000
3600	6.500	26.818	20.856	21.462	-91.961	2.255	-.137
3700	6.500	26.996	21.020	22.112	-91.862	4.875	-.288
3800	6.500	27.170	21.180	22.762	-91.763	7.485	-.431
3900	6.500	27.338	21.335	23.412	-91.665	10.098	-.566
4000	6.500	27.503	21.487	24.062	-91.567	12.705	-.694
4100	6.500	27.663	21.636	24.712	-91.470	15.310	-.816
4200	6.500	27.820	21.782	25.362	-91.372	17.912	-.932
4300	6.500	27.973	21.924	26.012	-91.274	20.513	-1.043
4400	6.500	28.122	22.063	26.662	-91.177	23.113	-1.148
4500	6.500	28.269	22.199	27.312	-91.079	25.710	-1.249

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1966; Mar. 31, 1967

SILICON (Si) (LIQUID) GFW = 28.086

$S^\circ_{298.15}$ = 10.626 gibbs/mol

Tm = 1685 ± 3°K

Tb = [3513.8] °K (to monomer only)

Tb = [3492] °K (to equilibrium mixture)

$\Delta Hf^\circ_{298.15}$ = 11.585 kcal/mol

ΔHm° = 12.0 ± 0.1 kcal/mol

ΔHv° = [92.047] kcal/mol

ΔHv° = [85.8] kcal/mol

Heat of Formation.

The heat of formation is obtained from that of the crystal by adding ΔHm° and the difference between $H^\circ_{Tm} - H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

Enthalpy data for high purity samples in quartz or vitreous silica capsules have been reported for the range 1698-1915°K by P.B. Kantor, A. M. Kisil and E. M. Fomichev, Ukrain. Fiz. Zhur. 5, 358 (1960), and for the range 1686-1825°K by M. Olette, Phys. Chem. Steelmaking, Proc. Dedham, Mass. 1956, 18-26 (Pub. 1958). Due to the limited temperature range and the experimental uncertainty, the data do not appear to justify more than a constant heat capacity. A value of 6.5 gibbs/mol is selected, intermediate between the values of 6.75 and 6.15 obtained from the separate experiments. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data.

Modern determinations of the melting point range from 1683 ± 1 to 1690 ± 4 °K, the former from the specific volume study of L. D. Lucas and G. Urbain, Compt. Rend. 255, 2414 (1962), and the latter from the enthalpy study of Kantor et al. The selected value of Tm = 1685°K is taken from R. Hultgren, R. L. Orr and K. K. Kelley, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," Univ. of California, Berkeley, November, 1965, who have reviewed the melting data. The heat of melting is calculated from the selected enthalpy of the crystal and the liquid enthalpy measurements of Kantor et al. and Olette, who reported comparable values of ΔHm° = 11.95 ± 0.18 and 12.095 ± 0.1 kcal/mol, respectively.

Vaporization Data.

Tb is calculated as the temperature for which the ΔGr° = 0 for Si(l) = Si(g). ΔHv° is calculated as the difference between ΔHf°(g) and ΔHf°(l) at Tb. The normal boiling for the equilibrium vapor is calculated as the temperature at which Si, Si_2 and Si_3 attain a total pressure of one atm. ΔHv° at this temperature is calculated as the enthalpy of vaporization of one GFW of liquid to vapor containing 92.1, 7.0 and 0.9 mole percent of monomer, dimer and trimer, respectively. Tetramer and higher polymers, which are ignored in the equilibrium calculation, are probably negligible at this temperature.

icon, Monatomic (Si)

deal Gas) GFW - 28.086

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-1.805	106.664	106.664	INFINITE
100	6.697	33.646	45.140	-1.149	107.256	103.983	-227.254
200	5.687	37.931	40.617	-.537	107.587	100.558	-109.885
298	5.318	40.121	40.121	.000	107.700	97.079	-71.161
300	5.314	40.154	40.121	.010	107.701	97.013	-70.674
400	5.166	41.660	40.328	.533	107.717	93.446	-51.057
500	5.095	42.804	40.713	1.045	107.685	89.882	-39.287
600	5.056	43.729	41.141	1.553	107.625	86.326	-31.444
700	5.033	44.506	41.568	2.057	107.544	82.783	-25.846
800	5.019	45.178	41.978	2.560	107.447	79.251	-21.650
900	5.012	45.768	42.367	3.061	107.336	75.734	-18.391
1000	5.011	46.296	42.734	3.562	107.213	72.229	-15.786
1100	5.016	46.774	43.080	4.064	107.080	68.737	-13.657
1200	5.027	47.211	43.406	4.566	106.937	65.257	-11.885
1300	5.043	47.614	43.715	5.069	106.785	61.790	-10.388
1400	5.063	47.988	44.007	5.574	106.625	58.335	-9.107
1500	5.087	48.338	44.284	6.082	106.458	54.892	-7.998
1600	5.113	48.668	44.548	6.592	106.283	51.459	-7.029
1700	5.142	48.978	44.799	7.105	94.108	48.145	-6.189
1800	5.171	49.273	45.040	7.620	93.973	45.445	-5.518
1900	5.202	49.553	45.270	8.139	93.842	42.753	-4.918
2000	5.232	49.821	45.491	8.660	93.713	40.067	-4.378
2100	5.261	50.077	45.703	9.185	93.588	37.388	-3.891
2200	5.289	50.322	45.908	9.713	93.466	34.715	-3.449
2300	5.316	50.558	46.105	10.243	93.346	32.046	-3.045
2400	5.341	50.785	46.295	10.776	93.229	29;384	-2.676
2500	5.364	51.003	46.479	11.311	93.114	26.726	-2.336
2600	5.386	51.214	46.657	11.848	93.001	24.073	-2.024
2700	5.406	51.418	46.830	12.388	92.891	21.422	-1.734
2800	5.423	51.615	46.997	12.930	92.783	18.779	-1.466
2900	5.439	51.805	47.160	13.473	92.676	16.139	-1.216
3000	5.454	51.990	47.318	14.017	92.570	13.499	-.983
3100	5.466	52.169	47.471	14.563	92.466	10.865	-.766
3200	5.478	52.343	47.621	15.111	92.364	8.236	-.562
3300	5.487	52.511	47.766	15.659	92.262	5.610	-.372
3400	5.495	52.675	47.908	16.208	92.161	2.986	-.192
3500	5.502	52.835	48.047	16.758	92.061	.361	-.023
3600	5.508	52.990	48.182	17.308	.000	.000	.000
3700	5.513	53.141	48.314	17.859	.000	.000	.000
3800	5.516	53.288	48.443	18.411	.000	.000	.000
3900	5.519	53.431	48.569	18.963	.000	.000	.000
4000	5.521	53.571	48.692	19.515	.000	.000	.000
4100	5.523	53.707	48.813	20.067	.000	.000	.000
4200	5.524	53.840	48.931	20.619	.000	.000	.000
4300	5.524	53.970	49.047	21.172	.000	.000	.000
4400	5.524	54.097	49.160	21.724	.000	.000	.000
4500	5.524	54.222	49.271	22.276	.000	.000	.000
4600	5.523	54.343	49.380	22.829	.000	.000	.000
4700	5.522	54.462	49.487	23.381	.000	.000	.000
4800	5.521	54.578	49.592	23.933	.000	.000	.000
4900	5.520	54.692	49.695	24.485	.000	.000	.000
5000	5.519	54.803	49.796	25.037	.000	.000	.000
5100	5.519	54.913	49.895	25.589	.000	.000	.000
5200	5.518	55.020	49.993	26.141	.000	.000	.000
5300	5.518	55.125	50.089	26.693	.000	.000	.000
5400	5.519	55.228	50.183	27.245	.000	.000	.000
5500	5.520	55.329	50.275	27.797	.000	.000	.000
5600	5.521	55.429	50.367	28.349	.000	.000	.000
5700	5.524	55.527	50.456	28.901	.000	.000	.000
5800	5.527	55.623	50.544	29.453	.000	.000	.000
5900	5.531	55.717	50.631	30.006	.000	.000	.000
6000	5.536	55.810	50.717	30.560	.000	.000	.000

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1966; Mar. 31, 1967

Ground State Configuration $^3P_0$ ΔHf°_0 = 106.66 ± 1 kcal/mol

$S^\circ_{298.15}$ = 40.121 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 107.7 ± 1 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	1	45,303	15	50,533	9	56,699	9	58,782	28	61,489	75
77.12	3	47,284	3	51,612	1	56,780	3	58,802	3	62,720	117
223.16	5	47,352	5	53,362	7	57,094	15	58,893	7	62,727	69
6,298.86	5	48,161	15	53,387	3	57,402	9	59,077	15	63,405	18
15,394.37	1	49,128	9	54,226	15	57,489	21	59,108	56	63,653	81
33,326	5	49,400	3	54,425	9	57,542	3	59,674	21	63,707	45
39,860	9	49,966	21	54,871	3	57,798	5	60,706	36	64,456	75
40,992	3	50,189	5	56,503	5	58,311	1	61,278	72	[65,300]	[200]

Heat of Formation.

The heat of formation is the heat of sublimation, $\Delta Hs^\circ_{298.15}$ = 107.7 kcal/mol, selected from third law analyses of the vapor pressure data reviewed below. Langmuir, Knudsen and transport studies are all in satisfactory agreement throughout the range of 1400 - 2000°K. In addition, O. C. Trulson and P. O. Schissel, Condensation Evaporation Solids Proc. Symp., Dayton, Ohio 1962, 313-17 (Pub. 1964), have experimentally verified that the vaporization coefficient is about 0.8 at 1300°K. This was accomplished by mass spectrometric determination of the Langmuir and Knudsen rates of sublimation from a single crystal sample in a cell designed to give Knudsen effusion from one end and free evaporation from the other end.

The recent studies confirm the mass spectrometric data of R. E. Honig, J. Chem. Phys. 22, 1610 (1954), and substantiate the author's postulate that vapor pressures obtained in early boiling point experiments are too large due to reaction or decomposition of the alumina and silicon carbide containers. In their review of the earlier experiments, R. Hultgren, R. L Orr and K. K. Kelley, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," Univ. of California, Berkeley, November, 1965, calculated apparent heats of sublimation of less than 90 kcal/mol from the data. Neither these values nor the value of 92 kcal/mol, obtained from the Knudsen data (1485 - 1593°K) of A. V. Tseplyaeva, Yu. A. Priselkov and V. V. Karelin, Vestnik Moskov. Univ., Ser. 2 Khim. 15, No. 5, 36 (1960), were considered in the JANAF selection. It is not clear why Tseplyaeva et al. obtain pressures larger by a factor of 200 from their molybdenum cell.

		Container	T Range	No. of	ΔHs°_{298} (kcal/mol)		Drift
Source	Method	or Support	(°K)	Points	2nd Law	3rd Law	eu
1. Gulbransen (1966)	Langmuir	Quartz fiber	1373-1623	10	104.9 ± 4.1	107.15	1.0 ± 2.8
2. Nannichi (1963)	Langmuir	Tantalum	1399-1527	4	95.3 ± 6.0	107.99	8.6 ± 4.1
3. Batdorf (1959)	Langmuir	Tantalum	1473-1600	12	108.8 ± 5.7	109.02	0.5 ± 3.7
4. Davis (1961)	Knudsen	SiC-lined graphite	1848-2003*	11	112.6 ± 12	108.50	-2.2 ± 6.2
5. Grieveson (1959)	Knudsen	SiC-lined graphite	1640-1684	3	97.5 ± 0.2	107.72	6.1 ± 0.1
Grieveson (1959)	Knudsen	SiC-lined graphite	1701-1900*	9	109.7 ± 0.1	107.74	-1.1 ± 0.04
Grieveson (1959)	Transport	SiC-lined graphite and $MoSi_2$	1853*	14	-	107.73	-
6. Drowart (1960)	Mass Spec.	SiC-lined graphite	1703-2160*	12	108 ± 1.0	107.00	-0.5 ± 0.5

*Data for liquid phase.

1. E. A. Gulbransen, K. F. Andrew and F. A. Brassart, J. Electrochem. Soc. 113, 834 (1966).
2. Y. Nannichi, Japan J. Appl. Phys. 2, 586 (1963), data given graphically.
3. R. L. Batdorf and F. M. Smits, J. Appl. Phys. 30, 259 (1959), data given graphically.
4. S. G. Davis, D. F. Anthrop and A. W. Searcy, J. Chem. Phys. 34, 659 (1961).
5. P. Grieveson and C. B. Alcock, Special Ceramics, Proc. Symposium Brit. Ceram. Research Assoc., Stoke-on-Trent 1959, 183-208 (Pub. 1960). Points above 1900°K are omitted.
6. J. Drowart and G. De Maria, pp. 16-23 in "Silicon Carbide," Edited by J. R. O'Connor and J. Smiltens, Pergamon Press, London, 1960.

Heat Capacity and Entropy.

Electronic levels and quantum weights are from L. J. Radziemski and K. L. Andrew, J. Opt. Soc. Am. 55, 474 (1965), and V. Kaufman, L. J. Radziemski and K. L. Andrew, ibid. 56, 911 (1966). An additional level with quantum weight of 200 is estimated above the observed levels and below the dissociation limit; however, the effect of this level on the entropy at 6000°K is negligible. Levels above 39000 cm^{-1} are averaged.

Silicon, Diatomic (Si_2)

(Ideal Gas) GFW = 56.172

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.214	140.324	140.324	INFINITE
100	7.029	46.655	61.829	-1.517	140.893	136.410	-298.124
200	7.692	51.715	55.632	-.783	141.065	131.837	-144.064
298	8.234	54.895	54.895	.000	141.000	127.315	-93.325
300	8.242	54.946	54.895	.015	140.997	127.230	-92.687
400	8.658	57.375	55.224	.861	140.829	122.665	-67.021
500	9.079	59.352	55.857	1.747	140.627	118.148	-51.643
600	9.499	61.045	56.584	2.676	140.420	113.671	-41.404
700	9.567	62.537	57.330	3.645	140.219	109.230	-34.103
800	10.151	63.875	58.066	4.647	140.021	104.814	-28.634
900	10.343	65.082	58.779	5.672	139.822	100.428	-24.387
1000	10.453	66.178	59.465	6.713	139.615	96.061	-20.994
1100	10.502	67.177	60.122	7.761	139.393	91.716	-18.222
1200	10.507	68.091	60.748	8.812	139.154	87.392	-15.916
1300	10.485	68.932	61.346	9.861	138.893	83.087	-13.968
1400	10.447	69.707	61.916	10.908	138.610	78.806	-12.302
1500	10.401	70.427	62.460	11.951	138.303	74.545	-10.861
1600	10.354	71.096	62.979	12.988	137.970	70.306	-9.603
1700	10.309	71.723	63.475	14.022	113.628	66.298	-8.523
1800	10.268	72.311	63.950	15.050	113.356	63.523	-7.713
1900	10.232	72.865	64.404	16.075	113.081	60.761	-6.989
2000	10.200	73.389	64.841	17.097	112.803	58.017	-6.340
2100	10.174	73.886	65.260	18.116	112.522	55.284	-5.753
2200	10.153	74.359	65.663	19.132	112.238	52.563	-5.222
2300	10.135	74.810	66.050	20.146	111.952	49.857	-4.737
2400	10.122	75.241	66.425	21.159	111.665	47.165	-4.295
2500	10.112	75.654	66.785	22.171	111.377	44.482	-3.889
2600	10.106	76.050	67.134	23.182	111.088	41.813	-3.515
2700	10.101	76.432	67.472	24.192	110.798	39.151	-3.169
2800	10.099	76.799	67.798	25.202	110.508	36.507	-2.849
2900	10.099	77.153	68.115	26.212	110.218	33.870	-2.552
3000	10.100	77.496	68.422	27.222	109.928	31.235	-2.276
3100	10.103	77.827	68.720	28.232	109.638	28.619	-2.018
3200	10.107	78.148	69.009	29.242	109.348	26.014	-1.777
3300	10.111	78.459	69.291	30.253	109.059	23.414	-1.551
3400	10.117	78.761	69.565	31.265	108.771	20.823	-1.338
3500	10.124	79.054	69.832	32.277	108.483	18.239	-1.139
3600	10.131	79.339	70.092	33.289	-75.727	20.181	-1.225
3700	10.139	79.617	70.346	34.303	-75.815	22.845	-1.349
3800	10.147	79.887	70.594	35.317	-75.903	25.515	-1.467
3900	10.156	80.151	70.835	36.332	-75.992	28.181	-1.579
4000	10.165	80.408	71.071	37.349	-76.080	30.856	-1.686
4100	10.175	80.660	71.302	38.365	-76.169	33.523	-1.787
4200	10.185	80.905	71.528	39.383	-76.255	36.200	-1.884
4300	10.195	81.145	71.749	40.402	-76.340	38.879	-1.976
4400	10.206	81.379	71.965	41.422	-76.426	41.560	-2.064
4500	10.218	81.609	72.177	42.444	-76.508	44.249	-2.149
4600	10.229	81.833	72.384	43.466	-76.590	46.934	-2.230
4700	10.241	82.053	72.588	44.489	-76.673	49.621	-2.307
4800	10.254	82.269	72.787	45.514	-76.752	52.306	-2.382
4900	10.266	82.481	72.983	46.540	-76.830	54.995	-2.453
5000	10.279	82.688	73.175	47.567	-76.907	57.683	-2.521
5100	10.293	82.892	73.363	48.596	-76.982	60.381	-2.588
5200	10.306	83.092	73.548	49.626	-77.056	63.074	-2.651
5300	10.320	83.288	73.730	50.657	-77.127	65.772	-2.712
5400	10.335	83.481	73.909	51.690	-77.198	68.467	-2.771
5500	10.349	83.671	74.085	52.724	-77.268	71.161	-2.828
5600	10.364	83.858	74.258	53.760	-77.336	73.864	-2.883
5700	10.379	84.041	74.428	54.797	-77.403	76.571	-2.936
5800	10.395	84.222	74.595	55.836	-77.470	79.269	-2.987
5900	10.410	84.400	74.760	56.876	-77.536	81.965	-3.036
6000	10.426	84.575	74.922	57.918	-77.600	84.670	-3.084

Dec. 31, 1960; Dec. 31, 1962; Mar. 31, 1967

SILICON, DIATOMIC (Si_2) (IDEAL GAS) GFW = 56.172

Ground State Configuration ${}^3\Sigma_g^-$

$S^\circ_{298.15}$ = 54.895 gibbs/mol

ΔHf°_0 = 140.3 ± 3 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 141 ± 3 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
${}^3\Sigma_g^-$	0	3	$[{}^1\Delta_g]$	[10000]	[2]	${}^3\Pi_g$	[30000]	6
${}^3\Pi_u$	[2000]	6	$[{}^1\Sigma_g^+]$	[13000]	[1]	${}^3\Sigma_u^-$	30769	3
$[{}^1\Sigma_g^+]$	[6000]	[1]	$[{}^3\Sigma_u^+]$	[20000]	[3]	$[{}^1\Pi_g]$	[40000]	[2]
$[{}^1\Pi_u]$	[8000]	[2]	${}^3\Sigma_u^-$	24583	3	$[{}^1\Sigma_u^+]$	[45000]	[1]
						${}^3\Sigma_u^-$	46762	3

ω_e = 510.98 cm^{-1} $\omega_e x_e$ = 2.02 cm^{-1} σ = 2

B_e = 0.2390 cm^{-1} α_e = 0.0013 cm^{-1} r_e = 2.246 Å

Heat of Formation.

The selected value is based on the spectroscopic and equilibrium data summarized below. Verma and Warsop[1] concluded from analysis of the absorption spectra that D°_0 = 70 ± 4 kcal/mol. Predissociation of the H state suggested the upper limit $D^\circ_0 \leq 74.0$, while linear Birge-Sponer extrapolations of the H and K states gave 78.4 and 68.9 kcal/mol for the ground state. By assuming that the true extrapolation would not reduce the linear extrapolation for the H state by more than half, i.e. from 26 to 13 kcal, the authors arrived at the lower limit of $D^\circ_0 \geq 65.5$ for the ground state.

Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor equilibria over the systems SiC-graphite[2], SiC-silicon[3] and boron-carbon-silicon[4]. Third law analysis of the partial pressures of Si_2 and Si over the three systems yields D°_0 values of 73.3, 74.3 and 70.4 kcal/mol, which are in good agreement with the spectroscopic values. The selected value, ΔHf°_{298} = 141 ± 3 kcal/mol, corresponds to D°_0 = 73.0 kcal/mol.

Source	Method	Range, T°K	No. of Points	ΔHr°_{298} (kcal/mol)* 2nd law	3rd law	Drift (eu)	ΔHf°_{298} (kcal/mol)
Verma (1963)	Prediss. of H state		-		≤75.4	-	≥140.0
	LBX of K state		-		70.3		145.1
	Extrap. of H state		-		≥66.9		≤148.5
Drowart (1958)	Mass Spec.	2149-2316	7	95.3±7.1	74.68	-9±3	140.7
Drowart (1960)	Mass Spec.	1703-2160	9	81.0±1.1	75.71	-2.7±0.6	139.7
Verhaegen (1964)	Mass Spec.	2166-2344	4	68 ± 16	71.76	2±7	143.6

*For the reaction $Si_2(g) = 2\ Si(g)$

Heat Capacity and Entropy.

Vibrational and rotational constants are those obtained by Verma and Warsop[1] through combination of their data for the H-X system with those of Douglas[5]. Observation of the same H-X system in matrix isolation by Weltner and McLeod[6] confirms that the lower state is the ground state. Comparison with the isoelectronic molecules C_2, BN, BeO and MgO (7,8,9,10) suggests that there are several possible low-lying excited states in Si_2. Tentative estimates for these levels are given above, based on this comparison and on the observed states (1,5). These estimates are relatively uncertain and probably yield an upper limit for the entropy at temperatures where Si_2 is significant. A probable lower limit may be obtained by increasing the two ${}^3\Pi$ states by 8000 cm^{-1} and omitting the other estimated levels. This would reduce the entropy by 1.7 eu at 2000°K, corresponding to a change of 3.4 kcal/mol in ΔHr° values based on equilibrium data.

References.

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licon, Triatomic (Si_3)

deal Gas) GFW = 84.258

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 3.088	151.219	151.219	INFINITE
100	9.357	51.599	74.779	- 2.318	151.797	146.912	- 321.076
200	11.927	58.983	65.172	- 1.238	152.034	141.910	- 155.072
298	13.158	64.002	64.002	.000	152.000	136.941	- 100.380
300	13.174	64.084	64.002	.024	151.997	136.847	- 99.693
400	13.811	67.971	64.528	1.377	151.829	131.820	- 72.023
500	14.162	71.094	65.539	2.777	151.597	126.846	- 55.444
600	14.371	73.696	66.688	4.205	151.321	121.919	- 44.409
700	14.504	75.922	67.852	5.649	151.010	117.044	- 36.543
800	14.594	77.865	68.985	7.104	150.665	112.212	- 30.655
900	14.656	79.587	70.069	8.567	150.292	107.432	- 26.088
1000	14.702	81.134	71.099	10.035	149.888	102.690	- 22.443
1100	14.738	82.537	72.076	11.507	149.455	97.990	- 19.469
1200	14.766	83.821	73.002	12.982	148.995	93.331	- 16.998
1300	14.790	85.004	73.881	14.460	148.508	88.711	- 14.914
1400	14.814	86.101	74.715	15.940	147.993	84.131	- 13.133
1500	14.838	87.123	75.508	17.423	147.451	79.591	- 11.596
1600	14.863	88.082	76.264	18.908	146.881	75.084	- 10.256
1700	14.893	88.984	76.986	20.396	110.305	70.931	- 9.119
1800	14.926	89.836	77.677	21.886	109.845	68.631	- 8.333
1900	14.964	90.644	78.338	23.381	109.390	66.351	- 7.632
2000	15.007	91.413	78.973	24.879	108.938	64.100	- 7.005
2100	15.055	92.146	79.583	26.382	108.49.	61.869	- 6.439
2200	15.107	92.847	80.170	27.890	108.049	59.558	- 5.926
2300	15.164	93.520	80.736	29.404	107.613	57.468	- 5.461
2400	15.224	94.167	81.282	30.923	107.182	55.299	- 5.036
2500	15.288	94.790	81.810	32.449	106.758	53.143	- 4.646
2600	15.354	95.390	82.321	33.981	106.340	51.009	- 4.288
2700	15.423	95.971	82.816	35.520	105.929	48.886	- 3.957
2800	15.493	96.533	83.296	37.066	105.525	46.786	- 3.652
2900	15.564	97.078	83.762	38.618	105.127	44.694	- 3.368
3000	15.636	97.607	84.214	40.178	104.737	42.613	- 3.104
3100	15.707	98.121	84.655	41.746	104.355	40.547	- 2.859
3200	15.777	98.621	85.083	43.320	103.979	38.500	- 2.629
3300	15.847	99.107	85.501	44.901	103.610	36.462	- 2.415
3400	15.915	99.581	85.908	46.489	103.248	34.432	- 2.213
3500	15.981	100.044	86.305	48.084	102.893	32.406	- 2.024
3600	16.046	100.495	86.693	49.685	- 173.339	37.171	- 2.257
3700	16.108	100.935	87.072	51.293	- 173.384	43.022	- 2.541
3800	16.168	101.366	87.443	52.907	- 173.423	48.869	- 2.811
3900	16.225	101.786	87.805	54.526	- 173.460	54.718	- 3.066
4000	16.279	102.198	88.160	56.152	- 173.490	60.570	- 3.309
4100	16.331	102.600	88.507	57.782	- 173.519	66.417	- 3.540
4200	16.380	102.995	88.847	59.418	- 173.539	72.266	- 3.760
4300	16.426	103.381	89.181	61.058	- 173.555	78.120	- 3.970
4400	16.469	103.759	89.508	62.703	- 173.569	83.972	- 4.171
4500	16.509	104.129	89.829	64.352	- 173.576	89.840	- 4.363
4600	16.547	104.493	90.144	66.005	- 173.579	95.686	- 4.546
4700	16.582	104.849	90.453	67.661	- 173.582	101.542	- 4.722
4800	16.614	105.198	90.756	69.321	- 173.578	107.395	- 4.890
4900	16.643	105.541	91.055	70.984	- 173.571	113.250	- 5.051
5000	16.670	105.878	91.348	72.649	- 173.562	119.093	- 5.206
5100	16.694	106.208	91.636	74.318	- 173.549	124.959	- 5.355
5200	16.716	106.532	91.919	75.988	- 173.535	130.811	- 5.498
5300	16.735	106.851	92.198	77.661	- 173.515	136.662	- 5.635
5400	16.752	107.164	92.472	79.335	- 173.497	142.511	- 5.768
5500	16.767	107.471	92.742	81.011	- 173.477	148.361	- 5.895
5600	16.780	107.774	93.008	82.688	- 173.456	154.217	- 6.019
5700	16.791	108.071	93.270	84.367	- 173.433	160.074	- 6.138
5800	16.800	108.363	93.527	86.046	- 173.413	165.922	- 6.252
5900	16.807	108.650	93.781	87.727	- 173.391	171.765	- 6.363
6000	16.813	108.933	94.031	89.408	- 173.369	177.613	- 6.470

Dec. 31, 1960; Dec. 31, 1962; Mar. 31, 1967

SILICON, TRIATOMIC (Si_3) (IDEAL GAS) GFW = 84.258

Point Group $[D_{\infty h}]$

$S^\circ_{298.15}$ = [64.0] gibbs/mol

ΔHf°_0 = 151.2 ± 10 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 152 ± 10 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	3
[10000]	[6]
[18000]	[2]
21460	3

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[360] (1)
[200] (2)
[630] (1)

Bond Distance: Si-Si = [2.25] Å

Bond Angle: Si-Si-Si = [180°]

σ = [2]

Rotational Constant: B_0 = [0.05928] cm^{-1}

Heat of Formation.

The selected value is an average based on the equilibrium data summarized below. Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor species over the systems SiC-graphite[1] and SiC-silicon[2]. Third law analysis of the partial pressures of Si_3 and Si yields the values 154.0 and 149.9 kcal/mol. Both drifts suggest that the entropy may be lower than the tabulated values. It is unlikely that the entropy is in error by more than 5 eu so that most of the drift is inherent in the data. The adopted value of ΔHf°_{298} = 152 ± 10 kcal/mol includes allowance for an error of up to 5 eu.

Source	Method	Range, T°K	No. of Points	ΔHr°_{298} (kcal/mol)* 2nd Law	3rd Law	Drift (eu)	ΔHf°_{298} (kcal/mol)
Drowart (1958)	Mass Spec.	2230-2316	2	209	169.1	-18	154.0
Drowart (1960)	" "	1703-1890	4	204±3	173.2	-17±2	149.9

*For reaction $Si_3(g) = 3\ Si(g)$

Heat Capacity and Entropy.

Weltner and McLeod[3] observed an absorption band near 4660 Å in matrix isolation studies. Their tentative assignment of this band as the ${}^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ transition of Si_3 is adopted here. A ${}^1\Pi_u$ state is assumed at 18000 cm^{-1}, which is 7000 and 2000 cm^{-1} below the analogous levels[3] for C_3 and C_2Si. Also a ${}^3\Pi_u$ level is assumed at 10000 cm^{-1}, presumably arising from the same molecular orbital configuration as the ${}^1\Pi_u$ state. The molecule is assumed to be linear with a bond distance equal to that in Si_2. Vibrational frequencies are estimated from a valence bond calculation using $k_1 = 2.16 \times 10^5$ and $k\delta/l^2 = 0.11 \times 10^5$ dyn/cm. The stretching force constant is obtained from Si_2, while the bending force constant is based on C_2Si and the ${}^1\Pi_u$ excited state[3] of C_3. The moment of inertia is 47.22×10^{-39} g cm^2.

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2. J. Drowart and G. DeMaria, pp. 16-23 in "Silicon Carbide," Edited by J. R. O'Connor and J. Smiltens, Pergamon Press, New York, 1960.
3. W. Weltner, Jr. and D. McLeod, Jr., J. Chem. Phys. 41, 235 (1964); 40, 1305 (1964); 45, 3096 (1966).

Titanium (Ti)

(Reference State) GFW = 47.90

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol −(G°−H°298)/T	kcal/mol H°−H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0	.000	.000	INFINITE	- 1.152	.000	.000	.000
100	3.412	1.969	12.152	- 1.018	.000	.000	.000
200	5.333	5.069	7.870	- .560	.000	.000	.000
298	5.987	7.325	7.325	.000	.000	.000	.000
300	5.996	7.362	7.325	.011	.000	.000	.000
400	6.341	9.139	7.565	.629	.000	.000	.000
500	6.559	10.578	8.028	1.275	.000	.000	.000
600	6.755	11.791	8.557	1.941	.000	.000	.000
700	6.976	12.848	9.096	2.627	.000	.000	.000
800	7.229	13.796	9.625	3.337	.000	.000	.000
900	7.499	14.663	10.137	4.073	.000	.000	.000
1000	7.767	15.467	10.631	4.837	.000	.000	.000
1100	8.025	16.220	11.105	5.626	.000	.000	.000
1200	7.068	17.741	11.592	7.378	.000	.000	.000
1300	7.210	18.312	12.087	8.092	.000	.000	.000
1400	7.367	18.852	12.551	8.821	.000	.000	.000
1500	7.540	19.366	12.989	9.566	.000	.000	.000
1600	7.730	19.859	13.403	10.329	.000	.000	.000
1700	7.940	20.333	13.797	11.112	.000	.000	.000
1800	8.160	20.793	14.173	11.917	.000	.000	.000
1900	8.390	21.240	14.533	12.744	.000	.000	.000
2000	8.500	23.977	14.956	18.042	.000	.000	.000
2100	8.500	24.392	15.396	18.892	.000	.000	.000
2200	8.500	24.787	15.814	19.742	.000	.000	.000
2300	8.500	25.165	16.212	20.592	.000	.000	.000
2400	8.500	25.527	16.593	21.442	.000	.000	.000
2500	8.500	25.874	16.957	22.292	.000	.000	.000
2600	8.500	26.207	17.307	23.142	.000	.000	.000
2700	8.500	26.528	17.642	23.992	.000	.000	.000
2800	8.500	26.837	17.965	24.842	.000	.000	.000
2900	8.500	27.136	18.276	25.692	.000	.000	.000
3000	8.500	27.424	18.576	26.542	.000	.000	.000
3100	8.500	27.703	18.866	27.392	.000	.000	.000
3200	8.500	27.972	19.147	28.242	.000	.000	.000
3300	8.500	28.234	19.418	29.092	.000	.000	.000
3400	8.500	28.488	19.681	29.942	.000	.000	.000
3500	8.500	28.734	19.936	30.792	.000	.000	.000
3600	8.146	57.276	20.257	133.268	.000	.000	.000
3700	8.283	57.501	21.260	134.090	.000	.000	.000
3800	8.417	57.723	22.217	134.925	.000	.000	.000
3900	8.548	57.944	23.130	135.773	.000	.000	.000
4000	8.676	58.162	24.003	136.634	.000	.000	.000
4100	8.799	58.378	24.839	137.508	.000	.000	.000
4200	8.919	58.591	25.640	138.394	.000	.000	.000
4300	9.035	58.802	26.409	139.292	.000	.000	.000
4400	9.146	59.011	27.147	140.201	.000	.000	.000
4500	9.252	59.218	27.858	141.121	.000	.000	.000
4600	9.354	59.423	28.542	142.051	.000	.000	.000
4700	9.451	59.625	29.201	142.991	.000	.000	.000
4800	9.544	59.825	29.837	143.941	.000	.000	.000
4900	9.631	60.022	30.451	144.900	.000	.000	.000
5000	9.713	60.218	31.044	145.867	.000	.000	.000
5100	9.791	60.411	31.618	146.842	.000	.000	.000
5200	9.864	60.602	32.174	147.825	.000	.000	.000
5300	9.933	60.790	32.712	148.815	.000	.000	.000
5400	9.996	60.977	33.234	149.812	.000	.000	.000
5500	10.056	61.161	33.740	150.814	.000	.000	.000
5600	10.111	61.342	34.231	151.823	.000	.000	.000
5700	10.161	61.522	34.708	152.836	.000	.000	.000
5800	10.208	61.699	35.172	153.855	.000	.000	.000
5900	10.251	61.874	35.623	154.878	.000	.000	.000
6000	10.289	62.046	36.062	155.905	.000	.000	.000

Dec. 31, 1960; Sept. 30, 1966

TITANIUM (Ti) (REFERENCE STATE) GFW = 47.90

0	to	1155°K	Crystal alpha
1155	to	1933°K	Crystal beta
1933	to	3591°K	Liquid
3591	to	6000°K	Ideal Monatomic Gas

See crystal, liquid and monatomic gas for details.

itanium, Alpha (Ti)
Crystal) GFW = 47.90

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.152	.000	.000	.000
100	3.412	1.969	12.152	-1.018	.000	.000	.000
200	5.333	5.069	7.870	-.560	.000	.000	.000
298	5.987	7.325	7.325	.000	.000	.000	.000
300	5.996	7.362	7.325	.011	.000	.000	.000
400	6.341	9.139	7.565	.629	.000	.000	.000
500	6.559	10.578	8.028	1.275	.000	.000	.000
600	6.755	11.791	8.557	1.941	.000	.000	.000
700	6.976	12.848	9.096	2.627	.000	.000	.000
800	7.229	13.796	9.625	3.337	.000	.000	.000
900	7.499	14.663	10.137	4.073	.000	.000	.000
1000	7.767	15.467	10.631	4.837	.000	.000	.000
1100	8.025	16.220	11.105	5.626	.000	.000	.000
1200	8.296	16.929	11.561	6.442	-.936	.038	-.007
1300	8.556	17.603	12.000	7.284	-.807	.114	-.019
1400	8.816	18.247	12.423	8.153	-.668	.179	-.028
1500	9.076	18.864	12.832	9.048	-.518	.235	-.034
1600	9.336	19.458	13.228	9.968	-.361	.281	-.038
1700	9.596	20.032	13.611	10.915	-.197	.315	-.040
1800	9.856	20.588	13.984	11.887	-.030	.339	-.041
1900	10.116	21.128	14.346	12.886	.142	.355	-.041
2000	10.376	21.653	14.698	13.910	-4.132	.516	-.056

Dec. 31, 1960; Sept. 30, 1966

TITANIUM, ALPHA (Ti) (CRYSTAL) GFW = 47.90

$\Delta Hf°_0$ = 0 kcal/mol

$S°_{298.15}$ = 7.325 ± 0.02 gibbs/mol

$\Delta Hf°_{298.15}$ = 0 kcal/mol

Tt = 1155 ± 3 °K

$\Delta Ht°$ = 0.99 kcal/mol

$\Delta Hs°_{298.15}$ = 113.0 ± 1.0 kcal/mol

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The low temperature heat capacities, 1.1 - 305.51°K, have been measured by many investigators. Their measured temperature range, specimen purity and value of $S°_{298.15}$ reported are listed in the following table. The Cp values, below 298°K, adopted were mainly derived from the data obtained from references 3, 5 and 6, which are in good agreement with other sets of Cp data.

Investigator	Temperature, °K	Purity, %	$S°_{298.15}$, eu
1. K. K. Kelley (1944)	53.5 - 295.1	98.75	7.24 ± 0.07
2. Estermann et al. (1952)	1.8 - 4.2	99	-
3. Kothen and Johnston (1953)	15.44 - 305.51	99.96	7.33 ± 0.02
4. Aven et al. (1956)	3.95 - 15.76	99.95	-
5. Wolcott (1957)	1.17 - 20.95	99.98	-
6. Clusius and Franzosini (1958)	13.72 - 271.92	99.88	-
7. Burk et al. (1958)	22.5 - 200.0	99	-
8. Kneip et al. (1963)	1.1 - 4.5	99.86	-
9. Hake and Cape (1964)	1.2 - 4.5	99.92	-

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2. I. Estermann, S. A. Friedberg and J. E. Goldman, Phys. Rev. 87, 582 (1952).
3. C. W. Kothen and H. L. Johnston, J. Am. Chem. Soc. 75, 3101 (1953). $S°_{15}$ = 0.013 eu.
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5. N. M. Wolcott, Phil. Mag. 2, 1246 (1957).
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8. G. D. Kneip, Jr., J. O. Betterton, Jr. and J. O. Scarbrough, Phys. Rev. 130, 1687 (1963).
9. R. P. Hake and J. A. Cape, Phys. Rev. 135, A1151 (1964).

The high temperature heat capacities, 320-1856°K, have also been determined by many investigators. The values above Tt are not in good agreement. The measured temperature range, method used, and kind of data reported by these investigators are presented in the table below.

Investigator	Temperature, °K	Method	Property Measured
1. Jaeger et al. (1936)	492.9 - 1475.6	drop calorimetry	$H°_T - H°_{293.15}$
2. Kothen (1952)	1067.0 - 1856.0	drop calorimetry	$H°_T - H°_{298.15}$
3. Scott (1957)	333.2 - 1233.2	adiabatic calorimetry	Cp
4. Backhurst (1958)	873.2 - 1353.2	adiabatic calorimetry	Cp
5. Golutvin (1959)	388.0 - 1401.9	drop calorimetry	$H_T° - H°_{298.15}$
6. Holland (1963)	599.0 - 1345.0	resistance measurement	Cp
7. Kohlhaas et al. (1965)	320.0 - 1800.0	adiabatic calorimetry	Cp

1. F. M. Jaeger, E. Rosenbohm and R. Fonteyne, Rec. trav. chim, 55, 615 (1936).
2. C. W. Kothen, Ph. D. Dissertation, The Ohio State University, 1952. Sample purity 99.96%.
3. J. L. Scott, ORNL -2328, Oak Ridge National Laboratory, July 1957.
4. I. Backhurst, J. Iron Steel Inst. (London) 189, 124 (1958).
5. Y. M. Golutvin, Russ. J. Phys. Chem. 33, 164 (1959).
6. L. R. Holland, J. Appl. Phys. 34, 2350 (1963).
7. R. Kohlhaas, M. Braun and O. Vollmer, Z. Naturforsch. 20A, 1077 (1965). Sample purity 99.8%.

The adopted Cp values, 298.15 - 1155°K, were mainly derived from the Cp data reported by reference 7. The low temperature and high temperature Cp data were joined smoothly at 298°K. The Cp values above 1155°K were estimated by graphical extrapolation. $S°_{298.15}$ was derived from the adopted Cp, based on $S°_{13}$ = 0.015 eu.

Transition Data.

See the Ti (β , c) table for details.

Heat of Sublimation.

$\Delta Hs°_{298.15}$ is calculated as the difference between $\Delta Hf°_{298.15}$ for Ti(g) and Ti (α ,c).

Titanium, Beta (Ti)

(Crystal) GFW = 47.90

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	6.205	8.691	8.691	.000	1.433	1.026	-.752
300	6.206	8.729	8.691	.011	1.433	1.023	-.746
400	6.280	10.525	8.935	.636	1.440	.885	-.484
500	6.358	11.934	9.399	1.268	1.426	.748	-.327
600	6.439	13.101	9.922	1.907	1.399	.613	-.223
700	6.525	14.100	10.449	2.556	1.362	.485	-.151
800	6.618	14.977	10.961	3.213	1.309	.364	-.099
900	6.718	15.762	11.452	3.879	1.239	.250	-.061
1000	6.825	16.475	11.919	4.556	1.152	.144	-.032
1100	6.940	17.131	12.363	5.245	1.052	.050	-.010
1200	7.068	17.741	12.786	5.945	.000	.000	.000
1300	7.210	18.312	13.190	6.659	.000	.000	.000
1400	7.367	18.852	13.575	7.387	.000	.000	.000
1500	7.540	19.366	13.944	8.133	.000	.000	.000
1600	7.730	19.858	14.298	8.896	.000	.000	.000
1700	7.940	20.333	14.639	9.679	.000	.000	.000
1800	8.160	20.793	14.969	10.484	.000	.000	.000
1900	8.390	21.240	15.287	11.311	.000	.000	.000
2000	8.630	21.677	15.596	12.162	-4.447	.153	-.017
2100	8.860	22.103	15.895	13.037	-4.422	.385	-.040
2200	9.090	22.521	16.187	13.934	-4.375	.611	-.061
2300	9.312	22.930	16.471	14.855	-4.304	.836	-.079
2400	9.530	23.331	16.749	15.797	-4.212	1.058	-.096
2500	9.750	23.724	17.020	16.761	-4.098	1.277	-.112

Sept. 30, 1966

TITANIUM, BETA (Ti) (CRYSTAL) GFW = 47.90

ΔHf°_{0} = Unknown

$S^{\circ}_{298.15}$ = 8.691 gibbs/mol

$\Delta Hf^{\circ}_{298.15}$ = 1.433 kcal/mol

Tt = 1155 ± 3 °K

ΔHt° = 0.99 kcal/mol

Tm = 1933 ± 10 °K

ΔHm° = [4.45] kcal/mol

$\Delta Hs^{\circ}_{298.15}$ = [111.57] kcal/mol

Heat of Formation.

The heat of formation ($\Delta Hf^{\circ}_{298.15}$) was obtained from $\Delta Hf^{\circ}_{298.15}$ (α , c) by adding ΔHt° and the difference $H^{\circ}_{Tt} - H^{\circ}_{298.15}$ for Ti (α, c) and Ti (β, c).

Heat Capacity and Entropy.

The heat capacities, 1155 - 1856°K, have been determined by many investigators. See the Ti (α, c) table for details. The selected Cp values were evaluated based on the data reported by C. W. Kothen, Ph. D. dissertation, The Ohio State University, 1952, and R. Kohlhaas, M. Braun and O. Vollmer, Z. Naturforsch. 20A, 1077 (1965). The heat capacities below 1155°K and above 1800°K were estimated by graphical extrapolation. The entropy was obtained in a manner analogous to that of the heat of formation.

Transition Data.

Titanium has two crystal forms, i.e. the hexagonal close-packed low-temperature form and the body-centered cubic high-temperature form. The α→ β transition temperature has been determined and reported over a range of temperatures, 1154-1167°K, by many investigators. The value of Tt is affected by the impurities in the specimen or adsorbed by the specimen during the measurement and the method used for the determination. The following table indicates the values of Tt reported by different investigators. Also included are the heats of transition (ΔHt°), purity of specimen and property measured. The value of Tt adopted is 1155 ± 3°K, and the value of ΔHt° is selected as 0.99 kcal/mol.

Investigator	Tt, °K	ΔHt°, kcal/mol	Purity, %	Method or Property Measured
1. Fast (1939)	1158 ± 10	-	Iodide	electrical resistance
2. Greiner and Ellis (1949)	1158 ± 2	-	99.9	electrical resistance
3. McQuillan (1950)	1155.7 ± 1	-	99.93	hydrogen solubility
4. Duwez (1951)	1155 ± 4	-	Iodide	cooling curve
5. Worner (1951)	1158 ± 2	-	99.93	thermoelectric power
6. Kothen (1952)	1154	0.943	99.96	dropping calorimetry
7. Edwards et al. (1953)	1157 ± 3.5	-	99.88	cooling curve
8. Schofield (1956)	1158	0.814	-	rate of heating
9. Scott (1957)	1156 ± 2	0.978 ± 0.025	Iodide	adiabatic calorimetry
10. Backhurst (1958)	-	0.880	Commercial	adiabatic calorimetry
11. Golutvin (1959)	1155	0.820 ± 0.020	Iodide	dropping calorimetry
12. Kohlhaas, et al. (1965)	1167	0.992	99.8	adiabatic calorimetry

1. J. D. Fast, Rec. trav. chim. 58, 973 (1939).
2. E. S. Greiner and W. C. Ellis, Trans. Am. Inst. Min. Met. Eng. 180, 657 (1949).
3. A. D. McQuillan, J. Inst. Metals, 78, 249 (1950).
4. P. Duwez, J. Metals, 3, 765 (1951).
5. H. W. Worner, Australian J. Sci. Res. 4, 62 (1951).
6. C. W. Kothen, Ph. D. Dissertation, The Ohio State University, 1952.
7. J. W. Edwards, H.L. Johnston and W. E. Ditmars, J. Am. Chem. Soc. 75, 2467 (1953).
8. T. H. Schofield, J. Inst. Metals, 85, 68 (1956).
9. J. L. Scott, ORNL - 2328, Oak Ridge National Laboratory, July 1957.
10. I. Backhurst, J. Iron Steel Inst. (London) 189, 124 (1958).
11. Y. M. Golutvin, Russ J. Phys, Chem. 33, 164 (1959).
12. R. Kohlhaas, M. Braun and D. Vollmer, Z. Naturforsch. 20A, 1077 (1965).

Melting Data.

See the Ti(l) table for details.

Heat of Sublimation.

$\Delta Hs^{\circ}_{298.15}$ is calculated as the difference between $\Delta Hf^{\circ}_{298.15}$ for Ti(g) and Ti(β, c).

itanium (Ti)
Liquid) GFW = 47.90

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	6.205	10.695	10.695	.000	5.433	4.428	- 3.246
300	6.206	10.733	10.695	.011	5.433	4.422	- 3.222
400	6.280	12.529	10.939	.636	5.440	4.084	- 2.231
500	6.358	13.938	11.403	1.268	5.426	3.746	- 1.637
600	6.439	15.105	11.926	1.907	5.399	3.411	- 1.242
700	6.525	16.104	12.453	2.556	5.362	3.082	- .962
800	6.618	16.981	12.965	3.213	5.309	2.761	- .754
900	6.718	17.766	13.456	3.879	5.239	2.447	- .594
1000	6.825	18.479	13.923	4.556	5.152	2.140	- .468
1100	6.940	19.135	14.367	5.245	5.052	1.845	- .367
1200	7.068	19.745	14.790	5.945	4.000	1.595	- .291
1300	8.500	20.316	15.194	6.659	4.000	1.395	- .234
1400	8.500	20.946	15.582	7.509	4.121	1.189	- .186
1500	8.500	21.532	15.960	8.359	4.226	.977	- .142
1600	8.500	22.081	16.325	9.209	4.313	.758	- .103
1700	8.500	22.596	16.679	10.059	4.380	.533	- .068
1800	8.500	23.082	17.021	10.909	4.425	.305	- .037
1900	8.500	23.541	17.353	11.759	4.448	.076	- .009
2000	8.500	23.977	17.673	12.609	.000	.000	.000
2100	8.500	24.392	17.983	13.459	.000	.000	.000
2200	8.500	24.788	18.284	14.309	.000	.000	.000
2300	8.500	25.165	18.575	15.159	.000	.000	.000
2400	8.500	25.527	18.857	16.009	.000	.000	.000
2500	8.500	25.874	19.131	16.859	.000	.000	.000
2600	8.500	26.208	19.396	17.709	.000	.000	.000
2700	8.500	26.528	19.655	18.559	.000	.000	.000
2800	8.500	26.837	19.906	19.409	.000	.000	.000
2900	8.500	27.136	20.150	20.259	.000	.000	.000
3000	8.500	27.424	20.388	21.109	.000	.000	.000
3100	8.500	27.703	20.619	21.959	.000	.000	.000
3200	8.500	27.973	20.845	22.809	.000	.000	.000
3300	8.500	28.234	21.065	23.659	.000	.000	.000
3400	8.500	28.488	21.279	24.509	.000	.000	.000
3500	8.500	28.734	21.489	25.359	.000	.000	.000
3600	8.500	28.974	21.693	26.209	- 101.615	.258	- .016
3700	8.500	29.207	21.893	27.059	- 101.585	3.088	- .182
3800	8.500	29.433	22.089	27.909	- 101.569	5.918	- .340
3900	8.500	29.654	22.280	28.759	- 101.566	8.745	- .490
4000	8.500	29.869	22.467	29.609	- 101.576	11.576	- .632
4100	8.500	30.079	22.650	30.459	- 101.599	14.402	- .768
4200	8.500	30.284	22.829	31.309	- 101.634	17.230	- .897
4300	8.500	30.484	23.005	32.159	- 101.680	20.061	- 1.020
4400	8.500	30.679	23.177	33.009	- 101.738	22.896	- 1.137
4500	8.500	30.870	23.346	33.859	- 101.807	25.732	- 1.250

Dec. 31, 1960; Sept. 30, 1966

TITANIUM (Ti) (LIQUID) GFW = 47.90

$S^\circ_{298.15}$ = [10.695] gibbs/mol

Tm = 1933 ± 10°K

Tb = [3591]°K

$\Delta Hf^\circ_{298.15}$ = [5.433] kcal/mol

ΔHm° = [4.45] kcal/mol

ΔHv° = [101.63] kcal/mol

Heat of Formation.

The heat of formation ($\Delta Hf^\circ_{298.15}$) was obtained from $\Delta Hf^\circ_{298.15}$ (β, c) by adding ΔHm° and the difference between $H^\circ_{Tm} - H^\circ_{298.15}$ for Ti (β, c) and Ti(l).

Heat Capacity and Entropy.

A glass transition temperature at 1300°K was assumed. The heat capacities below 1300°K were obtained from those for Ti (β, c). The Cp value above 1300°K was estimated by comparison with those for the other transition elements and assumed to be constant in the temperature range 1300 - 4500°K. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

Because of the highly reactive nature of Ti(c), the accurate determination of the melting point is difficult. The results reported by different investigators show wide discrepancies. The Tm value adopted was determined by Schofield and Bacon (1953) and later confirmed by Westrum and Feick (1963). The other values of Tm reported are presented in the table below. The heat of melting was calculated based on an estimated entropy of melting, ΔSm°_{1933} = 2.3 eu.

Tm, °K	Investigator
2068 ± 15	G. K. Burgess and R. G. Waltenberg, Z. anorg. Chem. 82, 361 (1913).
1993	J. D. Fast, Rec. trav. chim. 58, 973 (1939).
1993 ± 25	M. Hansen, H. D. Kessler and D. J. McPherson, Trans. Am. Soc. Metals, 44, 518 (1952).
1973 ± 15	H. K. Adenstedt, J. R. Pequignot and J. M. Raymer, Trans. Am. Soc. Metals, 44, 990 (1952).
1953 ± 10	D. J. Maykuth, H. R. Ogden and R. I. Jaffee, Trans. Am. Inst. Min. Met. Eng. 197, 231 (1953).
1933 ± 10	T. H. Schofield and A. E. Bacon, J. Inst. Metals, 82, 167 (1953).
1945 ± 4	R. A. Oriani and T. S. Jones, Rev. Sci. Instr. 25, 248 (1954).
1941 ± 10	D. K. Deardorff and E. T. Hayes, J. Metals, 8, 509 (1956).
1933	E. F. Westrum, Jr. and G. Feick, ASD-TDR-62-204, Part II, University of Michigan, Ann Arbor, Michigan, May 1963.

Vaporization Data.

Tb is the temperature at which the gibbs energy change (ΔGr°) for the reaction Ti(l) = Ti(g) approaches zero. The difference between ΔHf° (Ti,g) and ΔHf° (Ti,l) at Tb is ΔHv°.

Titanium (Ti)

(Ideal Gas) GFW = 47.90

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 1.902	112.350	112.350	INFINITE
100	6.447	36.123	48.584	- 1.246	112.772	109.357	- 238.998
200	6.330	40.635	43.615	- .596	112.964	105.851	- 115.668
298	5.839	43.066	43.066	.000	113.000	102.344	- 75.020
300	5.831	43.102	43.066	.011	113.000	102.278	- 74.509
400	5.522	44.733	43.291	.577	112.948	98.710	- 53.933
500	5.344	45.945	43.706	1.120	112.845	95.161	- 41.595
600	5.237	46.909	44.162	1.648	112.707	91.636	- 33.379
700	5.170	47.711	44.613	2.168	112.541	88.137	- 27.518
800	5.128	48.398	45.044	2.683	112.346	84.664	- 23.129
900	5.104	49.001	45.451	3.194	112.121	81.217	- 19.722
1000	5.096	49.538	45.833	3.704	111.867	77.796	- 17.002
1100	5.106	50.024	46.193	4.214	111.588	74.404	- 14.783
1200	5.132	50.469	46.531	4.726	110.348	71.074	- 12.944
1300	5.176	50.881	46.850	5.241	110.149	67.810	- 11.400
1400	5.237	51.267	47.152	5.762	109.941	64.560	- 10.078
1500	5.313	51.631	47.438	6.289	109.723	61.326	- 8.935
1600	5.403	51.977	47.711	6.825	109.496	58.107	- 7.937
1700	5.504	52.307	47.972	7.370	109.258	54.902	- 7.058
1800	5.616	52.625	48.222	7.926	109.009	51.711	- 6.279
1900	5.737	52.932	48.461	8.494	108.750	48.535	- 5.583
2000	5.864	53.229	48.692	9.074	104.032	45.528	- 4.975
2100	5.996	53.518	48.915	9.666	103.774	42.610	- 4.434
2200	6.132	53.801	49.131	10.273	103.531	39.700	- 3.944
2300	6.271	54.076	49.340	10.893	103.301	36.806	- 3.497
2400	6.413	54.346	49.543	11.527	103.085	33.920	- 3.089
2500	6.557	54.611	49.740	12.176	102.884	31.041	- 2.714
2600	6.701	54.871	49.933	12.839	102.697	28.170	- 2.368
2700	6.847	55.126	50.120	13.516	102.524	25.309	- 2.049
2800	6.993	55.378	50.304	14.208	102.365	22.451	- 1.752
2900	7.140	55.626	50.483	14.915	102.223	19.602	- 1.477
3000	7.286	55.871	50.659	15.636	102.094	16.753	- 1.220
3100	7.432	56.112	50.831	16.372	101.980	13.912	- .981
3200	7.578	56.350	50.999	17.122	101.880	11.071	- .756
3300	7.722	56.585	51.165	17.887	101.795	8.237	- .546
3400	7.866	56.818	51.328	18.667	101.725	5.403	- .347
3500	8.007	57.048	51.488	19.461	101.669	2.570	- .160
3600	8.146	57.276	51.645	20.268	.000	.000	.000
3700	8.283	57.501	51.801	21.090	.000	.000	.000
3800	8.417	57.723	51.954	21.925	.000	.000	.000
3900	8.548	57.944	52.105	22.773	.000	.000	.000
4000	8.676	58.162	52.253	23.634	.000	.000	.000
4100	8.799	58.378	52.400	24.508	.000	.000	.000
4200	8.919	58.591	52.545	25.394	.000	.000	.000
4300	9.035	58.802	52.688	26.292	.000	.000	.000
4400	9.146	59.011	52.829	27.201	.000	.000	.000
4500	9.252	59.218	52.969	28.121	.000	.000	.000
4600	9.354	59.423	53.107	29.051	.000	.000	.000
4700	9.451	59.625	53.244	29.991	.000	.000	.000
4800	9.544	59.825	53.379	30.941	.000	.000	.000
4900	9.631	60.022	53.512	31.900	.000	.000	.000
5000	9.713	60.218	53.644	32.867	.000	.000	.000
5100	9.791	60.411	53.775	33.842	.000	.000	.000
5200	9.864	60.602	53.905	34.825	.000	.000	.000
5300	9.933	60.790	54.033	35.815	.000	.000	.000
5400	9.996	60.977	54.160	36.812	.000	.000	.000
5500	10.056	61.161	54.285	37.814	.000	.000	.000
5600	10.111	61.342	54.410	38.823	.000	.000	.000
5700	10.161	61.522	54.533	39.836	.000	.000	.000
5800	10.208	61.699	54.655	40.855	.000	.000	.000
5900	10.251	61.874	54.776	41.878	.000	.000	.000
6000	10.289	62.046	54.895	42.905	.000	.000	.000

Dec. 31, 1960; Sept. 30, 1966; June 30, 1967

TITANIUM (Ti) (IDEAL GAS) GFW = 47.90

Ground State Configuration $^3F_2$

ΔHf°_0 = 112.4 ± 1.0 kcal/mol

$S^\circ_{298.15}$ = 43.066 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 113.0 ± 1.0 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0.00	5	11639.82	7	17467.00	15	35943.00	147
170.13	7	11776.82	9	18101.00	9	37685.00	105
386.87	9	[12000.00]	[1]	18392.00	76	38939.00	161
6556.86	3	12118.46	9	19789.00	44	40121.00	80
6598.83	5	13981.75	3	21381.00	38	41471.00	190
6661.00	7	14028.47	5	22270.00	12	42106.00	216
6742.79	9	14105.68	7	25405.00	87	43734.00	145
6843.00	11	15108.15	7	27178.00	123	44732.00	127
7255.29	5	15156.80	9	28745.00	65	46284.00	213
8436.63	1	15220.40	11	30144.00	89	48513.00	330
8492.44	3	16008.00	21	31849.00	76		
8602.35	5	16371.00	24	33751.00	54		
11531.81	5	17046.00	35	34698.00	28		

Heat of Formation

The vapor pressure of Ti(β), 1510-1822°K, has been measured in three separate investigations. Based on the reported vapor pressures, the enthalpies of sublimation ($\Delta Hs^\circ_{298.15}$) are evaluated by both the second and third law methods. The results obtained are presented in the following table. The adopted value of $\Delta Hf^\circ_{298.15}$ for Ti(g) is 113.0 ± 1.0 kcal/mol.

Reference	Temperature, °K	$\Delta Hr^\circ_{298.15}$, kcal/mol Second Law Value	Third Law Value	Drift eu	$\Delta Hf^\circ_{298.15}$* kcal/mol
1	1510 - 1822	112.23 ± 1.91	110.26 ± 0.81	-1.3 ± 1.2	111.69
2	1658 - 1808	112.41 ± 6.30	110.71 ± 1.10	-1.1 ± 3.7	112.14
3	1587 - 1764	112.26 ± 1.12	111.79 ± 0.18	-0.2 ± 0.6	113.22

*Calculation based on the third law ΔHr°_{298} and $\Delta Hf^\circ_{298}(\beta)$ = 1.43 kcal/mol.

1. J. M. Blocher, Jr., and I. E. Campbell, J. Am. Chem. Soc. 71, 4040 (1949).
2. L. G. Carpenter and W. N. Mair, Proc. Phys. Soc. 64, 57 (1951). The preliminary results were reported by L. G. Carpenter and F. R. Reavell, Nature, 163, 527 (1949).
3. J. W. Edwards, H. L. Johnston and W. E. Ditmars, J. Am. Chem. Soc. 75, 2467 (1953).

Heat Capacity and Entropy

The electronic levels and quantum weights are obtained from C. E. Moore, National Bureau of Standards Circular 467 (1949). However, above the level ϵ_i = 15877.17 cm^{-1}, the values of ϵ_i and g_i listed in the above table are average values calculated from those given by Moore. The $^1S_0$ level of the ground multiplet which has not been observed is estimated to lie at 12000 cm^{-1} by comparison with the corresponding levels for Ti^{++} ion, Zr and Zr^{++} ion reported by C. E. Moore, loc. cit.

anium Unipositive Ion (Ti^+)

eal Gas) GFW = 47.89945

, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	6.257	43.854	43.854	.000	271.840	259.462	- 190.190
300	6.257	43.893	43.854	.012	271.850	259.395	- 188.961
400	6.245	45.692	44.100	.637	272.354	255.153	- 139.409
500	6.177	47.079	44.562	1.258	272.826	250.797	- 109.623
600	6.060	48.196	45.078	1.871	273.270	246.349	- 89.733
700	5.931	49.120	45.591	2.470	273.679	241.928	- 75.502
800	5.812	49.904	46.093	3.057	274.053	237.253	- 64.814
900	5.712	50.583	46.546	3.633	274.390	232.533	- 56.491
000	5.633	51.180	46.980	4.200	274.690	227.974	- 49.824
100	5.573	51.714	47.387	4.760	274.958	223.293	- 44.364
200	5.529	52.197	47.768	5.315	274.258	218.624	- 39.817
300	5.499	52.639	48.126	5.867	274.592	213.972	- 35.972
400	5.481	53.045	48.463	6.416	274.909	209.297	- 32.673
500	5.474	53.423	48.781	6.963	275.208	204.600	- 29.810
600	5.475	53.776	49.082	7.511	275.490	199.884	- 27.303
700	5.484	54.109	49.368	8.059	275.752	195.150	- 25.088
800	5.499	54.422	49.640	8.608	275.992	190.401	- 23.118
900	5.521	54.720	49.900	9.159	276.213	185.641	- 21.354
000	5.547	55.004	50.148	9.712	271.965	181.023	- 19.781
100	5.578	55.276	50.396	10.268	272.168	176.470	- 18.365
200	5.613	55.536	50.614	10.828	272.375	171.909	- 17.077
300	5.650	55.786	50.834	11.391	272.584	167.336	- 15.901
400	5.690	56.027	51.045	11.958	272.798	162.757	- 14.821
500	5.731	56.261	51.249	12.529	273.016	158.167	- 13.827
600	5.773	56.486	51.446	13.104	273.238	153.569	- 12.909
700	5.817	56.705	51.637	13.684	273.465	148.963	- 12.058
800	5.860	56.917	51.822	14.267	273.695	144.346	- 11.267
900	5.904	57.124	52.001	14.856	273.930	139.725	- 10.530
000	5.946	57.324	52.175	15.449	274.169	135.091	- 9.841
100	5.988	57.520	52.344	16.045	274.413	130.452	- 9.197
200	6.029	57.711	52.509	16.646	274.661	125.804	- 8.592
300	6.069	57.897	52.669	17.251	274.913	121.149	- 8.023
400	6.107	58.079	52.825	17.859	275.167	116.487	- 7.488
500	6.144	58.256	52.979	18.472	275.427	111.815	- 6.982
600	6.179	58.430	53.128	19.088	174.064	107.400	- 6.520
700	6.212	58.600	53.273	19.708	174.359	105.540	- 6.234
800	6.243	58.766	53.416	20.330	174.643	103.676	- 5.963
900	6.273	58.928	53.555	20.956	174.918	101.809	- 5.705
000	6.300	59.087	53.691	21.585	175.182	99.929	- 5.460
100	6.325	59.243	53.825	22.216	175.436	98.044	- 5.226
200	6.351	59.396	53.955	22.850	175.681	96.154	- 5.003
300	6.373	59.546	54.084	23.486	175.916	94.256	- 4.791
400	6.394	59.692	54.210	24.125	176.143	92.355	- 4.587
500	6.414	59.836	54.333	24.765	176.359	90.448	- 4.393
600	6.432	59.978	54.454	25.407	176.568	88.540	- 4.207
700	6.448	60.116	54.573	26.051	176.769	86.523	- 4.028
800	6.463	60.252	54.690	26.697	176.962	84.701	- 3.857
900	6.477	60.385	54.805	27.344	177.147	82.776	- 3.692
000	6.490	60.516	54.918	27.992	177.324	80.853	- 3.534
100	6.502	60.645	55.029	28.642	177.496	78.918	- 3.382
200	6.513	60.771	55.138	29.293	177.661	76.987	- 3.236
300	6.523	60.896	55.246	29.945	177.820	75.045	- 3.095
400	6.533	61.018	55.351	30.597	177.972	73.107	- 2.959
500	6.541	61.138	55.455	31.251	178.121	71.165	- 2.828
600	6.549	61.255	55.558	31.906	178.263	69.211	- 2.701
700	6.557	61.371	55.659	32.561	178.402	67.272	- 2.579
800	6.563	61.486	55.758	33.217	178.535	65.317	- 2.461
900	6.570	61.598	55.856	33.874	178.667	63.354	- 2.347
000	6.576	61.708	55.953	34.531	178.794	61.409	- 2.237

Dec. 31, 1967

TITANIUM UNIPOSITIVE ION (Ti^+) (IDEAL GAS) GFW = 47.89945

Ground State Configuration $^4F_{3/2}$

ΔHf°_0 = 269.62 ± 1.0 kcal/mol

$S^\circ_{298.15}$ = 43.854 ± 0.01 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 271.84 ± 1.0 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	4	9508.611	14	46339.691	42
93.94	6	9970.051	16	52658.791	26
225.47	8	12722.863	32	56744.104	36
393.22	10	15593.028	24	62717.485	42
907.96	4	22558.664	26	65139.311	54
983.80	6	30448.862	64	65650.954	46
1087.21	8	32094.291	44	67896.381	58
1215.58	10	36951.357	36	69610.661	48
4782.319	14	40329.191	38		
8945.376	28	43558.293	40		

Heat of Formation

The heat of formation is calculated from the reaction $Ti(g) = Ti^+(g) + e^-(g)$ with the JANAF auxiliary value for Ti(g) and an ionization potential = 6.82 eV or 157.276 kcal/mol, obtained from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. III, 1958.

Heat Capacity and Entropy

The electronic levels and quantum weights are taken from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. I, 1949. The electronic levels above 4700 cm^{-1} are averaged. The $H^\circ - H^\circ_{298}$ value at 0°K is -1.888 kcal/mol.

rconium (Zr)

eference State) GFW = 91.22

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-1.321	.000	.000	.000
100	4.466	3.352	14.443	-1.109	.000	.000	.000
200	5.754	6.946	9.862	-.583	.000	.000	.000
298	6.068	9.314	9.314	.000	.000	.000	.000
300	6.097	9.352	9.314	.011	.000	.000	.000
400	6.367	11.143	9.556	.634	.000	.000	.000
500	6.642	12.593	10.023	1.285	.000	.000	.000
600	6.919	13.828	10.557	1.963	.000	.000	.000
700	7.197	14.916	11.103	2.669	.000	.000	.000
800	7.475	15.895	11.642	3.402	.000	.000	.000
900	7.753	16.791	12.165	4.164	.000	.000	.000
1000	8.032	17.623	12.670	4.953	.000	.000	.000
1100	8.311	18.401	13.156	5.770	.000	.000	.000
1200	6.886	19.888	13.667	7.466	.000	.000	.000
1300	6.997	20.444	14.167	8.160	.000	.000	.000
1400	7.108	20.966	14.634	8.865	.000	.000	.000
1500	7.219	21.461	15.073	9.581	.000	.000	.000
1600	7.330	21.930	15.487	10.309	.000	.000	.000
1700	7.441	22.378	15.879	11.047	.000	.000	.000
1800	7.552	22.806	16.252	11.797	.000	.000	.000
1900	7.663	23.218	16.608	12.558	.000	.000	.000
2000	7.774	23.613	16.949	13.330	.000	.000	.000
2100	7.885	23.995	17.275	14.113	.000	.000	.000
2200	8.000	26.719	17.669	19.910	.000	.000	.000
2300	8.000	27.075	18.071	20.710	.000	.000	.000
2400	8.000	27.415	18.453	21.510	.000	.000	.000
2500	8.000	27.742	18.818	22.310	.000	.000	.000
2600	8.000	28.056	19.167	23.110	.000	.000	.000
2700	8.000	28.358	19.502	23.910	.000	.000	.000
2800	8.000	28.649	19.824	24.710	.000	.000	.000
2900	8.000	28.929	20.133	25.510	.000	.000	.000
3000	8.000	29.201	20.430	26.310	.000	.000	.000
3100	8.000	29.463	20.718	27.110	.000	.000	.000
3200	8.000	29.717	20.995	27.910	.000	.000	.000
3300	8.000	29.963	21.263	28.710	.000	.000	.000
3400	8.000	30.202	21.522	29.510	.000	.000	.000
3500	8.000	30.434	21.774	30.310	.000	.000	.000
3600	8.000	30.659	22.017	31.110	.000	.000	.000
3700	8.000	30.878	22.254	31.910	.000	.000	.000
3800	8.000	31.092	22.484	32.710	.000	.000	.000
3900	8.000	31.299	22.707	33.510	.000	.000	.000
4000	8.000	31.502	22.924	34.310	.000	.000	.000
4100	8.000	31.700	23.136	35.110	.000	.000	.000
4200	8.000	31.892	23.342	35.910	.000	.000	.000
4300	8.000	32.081	23.543	36.710	.000	.000	.000
4400	8.000	32.264	23.739	37.510	.000	.000	.000
4500	8.000	32.444	23.931	38.310	.000	.000	.000
4600	8.000	32.620	24.118	39.110	.000	.000	.000
4700	8.000	32.792	24.301	39.910	.000	.000	.000
4800	9.020	62.511	24.622	181.867	.000	.000	.000
4900	9.073	62.697	25.397	182.771	.000	.000	.000
5000	9.122	62.881	26.145	183.681	.000	.000	.000
5100	9.169	63.062	26.867	184.596	.000	.000	.000
5200	9.212	63.240	27.564	185.515	.000	.000	.000
5300	9.252	63.416	28.239	186.438	.000	.000	.000
5400	9.288	63.590	28.892	187.365	.000	.000	.000
5500	9.322	63.760	29.525	188.296	.000	.000	.000
5600	9.352	63.929	30.138	189.229	.000	.000	.000
5700	9.379	64.094	30.732	190.166	.000	.000	.000
5800	9.403	64.258	31.308	191.105	.000	.000	.000
5900	9.424	64.419	31.866	192.046	.000	.000	.000
6000	9.442	64.577	32.412	192.990	.000	.000	.000

Dec. 31, 1960; June 30, 1961; Dec. 31, 1967

ZIRCONIUM (Zr) (REFERENCE STATE) GFW = 91.22

0	to	1135°K	Crystal alpha
1135.	to	2125°K	Crystal beta
2125	to	4776.9°K	Liquid
4776.9	to	6000°K	Ideal Monatomic gas

See crystal, liquid and monatomic gas for details.

ectron Gas (e$^-$)

ference State) At. Wt. = 0.00054876.

T, °K.	cal. mole^{-1}deg.$^{-1}$ C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	kcal. mole^{-1} $H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	4.968	4.989	4.989	.000	.000	.000	.000
300	4.968	5.019	4.989	.009	.000	.000	.000
400	4.968	6.449	5.184	.506	.000	.000	.000
500	4.968	7.557	5.552	1.003	.000	.000	.000
600	4.968	8.463	5.964	1.500	.000	.000	.000
700	4.968	9.229	6.377	1.996	.000	.000	.000
800	4.968	9.892	6.776	2.493	.000	.000	.000
900	4.968	10.477	7.155	2.990	.000	.000	.000
000	4.968	11.001	7.514	3.487	.000	.000	.000
100	4.968	11.474	7.853	3.984	.000	.000	.000
200	4.968	11.906	8.173	4.480	.000	.000	.000
300	4.968	12.304	8.475	4.977	.000	.000	.000
400	4.968	12.672	8.762	5.474	.000	.000	.000
500	4.968	13.015	9.034	5.971	.000	.000	.000
600	4.968	13.336	9.293	6.467	.000	.000	.000
700	4.968	13.637	9.540	6.964	.000	.000	.000
800	4.968	13.921	9.776	7.461	.000	.000	.000
900	4.968	14.189	10.001	7.958	.000	.000	.000
000	4.968	14.444	10.217	8.455	.000	.000	.000
100	4.968	14.686	10.424	8.951	.000	.000	.000
200	4.968	14.918	10.623	9.448	.000	.000	.000
300	4.968	15.138	10.814	9.945	.000	.000	.000
400	4.968	15.350	10.999	10.442	.000	.000	.000
500	4.968	15.553	11.177	10.939	.000	.000	.000
600	4.968	15.746	11.349	11.435	.000	.000	.000
700	4.968	15.935	11.516	11.932	.000	.000	.000
800	4.968	16.116	11.677	12.429	.000	.000	.000
900	4.968	16.290	11.833	12.926	.000	.000	.000
000	4.968	16.458	11.984	13.423	.000	.000	.000
100	4.968	16.621	12.131	13.919	.000	.000	.000
200	4.968	16.779	12.274	14.416	.000	.000	.000
300	4.968	16.932	12.413	14.913	.000	.000	.000
400	4.968	17.080	12.548	15.410	.000	.000	.000
500	4.968	17.224	12.679	15.907	.000	.000	.000
600	4.968	17.364	12.808	16.403	.000	.000	.000
700	4.968	17.500	12.933	16.900	.000	.000	.000
800	4.968	17.633	13.055	17.397	.000	.000	.000
900	4.968	17.762	13.174	17.894	.000	.000	.000
000	4.968	17.888	13.290	18.390	.000	.000	.000
100	4.968	18.010	13.404	18.887	.000	.000	.000
200	4.968	18.130	13.515	19.384	.000	.000	.000
300	4.968	18.247	13.623	19.881	.000	.000	.000
400	4.968	18.361	13.730	20.378	.000	.000	.000
500	4.968	18.473	13.834	20.874	.000	.000	.000
600	4.968	18.582	13.936	21.371	.000	.000	.000
700	4.968	18.689	14.036	21.868	.000	.000	.000
800	4.968	18.793	14.134	22.365	.000	.000	.000
900	4.968	18.896	14.230	22.862	.000	.000	.000
000	4.968	18.996	14.324	23.358	.000	.000	.000
100	4.968	19.095	14.417	23.855	.000	.000	.000
200	4.968	19.191	14.508	24.352	.000	.000	.000
300	4.968	19.286	14.597	24.849	.000	.000	.000
400	4.968	19.379	14.685	25.346	.000	.000	.000
500	4.968	19.470	14.771	25.842	.000	.000	.000
600	4.968	19.559	14.856	26.339	.000	.000	.000
700	4.968	19.647	14.939	26.836	.000	.000	.000
800	4.968	19.734	15.021	27.333	.000	.000	.000
900	4.968	19.818	15.102	27.830	.000	.000	.000
000	4.968	19.902	15.181	28.326	.000	.000	.000

Mar. 31, 1965

ELECTRON GAS (e$^-$) (REFERENCE STATE) AT. WT. = 0.00054876

0 to 6000°K. IDEAL GAS

$S^\circ_{298.15}$ = 4.988 cal. deg.$^{-1}$ mole^{-1} $\Delta H^\circ_{f\ 298.15}$ = 0

Electronic Levels and Multiplicities

ϵ_i cm.$^{-1}$,	g_i
0	2

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Calculated by assuming to be an ideal monatomic gas of mass 0.00054876 with two equivalent spin states. The enthalpy between 298 and 0°K. is 1.481 kcal. mole^{-1} as for all unexcited monatomic gases.