Oxygen (O) IDEAL GAS $A_r = 15.9994$ Oxygen (O) $O_1(g)$

IP(O, g) = 109837.02 ± 0.06 cm^{-1}
S°(298.15 K) = 161.058 ± 0.020 $J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H^\circ$(0 K) = 246.79 ± 0.10 $kJ \cdot mol^{-1}$
$\Delta_f H^\circ$(298.15 K) = 249.17 ± 0.10 $kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^3P_2$	0	5
$^3P_1$	158.265	3
$^3P_0$	226.977	1
$^1D_2$	15867.862	5
$^1S_0$	33792.583	1

Enthalpy of Formation

The enthalpy of formation is based on the dissociation energy of $O_2(g)$, 41260 ± 15 cm^{-1} (493.579 ± 0.18 $kJ \cdot mol^{-1}$), as recommended by CODATA.[1] This value is derived from the spectroscopic study of Brix and Herzberg.[2] The products of dissociation are assumed to be oxygen atoms in their ground states. The justification for this is discussed by Gaydon[3] and Krupenie.[4]

Heat Capacity and Entropy

The electronic levles for O(g) are given in the compilation by Moore.[5] Our calcualtions indicate that, except for the five states lying below 34000 cm^{-1}, the inclusion of levels up to n=12 has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the fifth excited state lies at 73768.20 cm^{-1} above the ground state. Since the inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the lowest lying status (ϵ_i< 34000 cm^{-1}). The reported uncertainty in S°(298.15 K) is due to uncertainties in the relative atomic mass, the fundamental constants, and the position of the low lying electronic levles. The calculated value of S(298.15 K) is 0.0094 $J \cdot K^{-1} \cdot mol^{-1}$ greater than that recommended by CODATA[1] due to the use of a 1 bar standard state pressure (CODATA used 1 atm). The difference is due to our use of the current CODATA fundamental constants.[6] Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures.[7]

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

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−6.725	246.790	246.790	INFINITE
100	23.703	135.947	181.131	−4.518	247.544	242.615	−126.729
200	22.734	152.153	163.085	−2.186	248.421	237.339	−61.986
250	22.246	157.170	161.421	−1.063	248.816	234.522	−49.001
298.15	21.911	161.058	161.058	0.	249.173	231.736	−40.599
300	21.901	161.194	161.059	0.041	249.187	231.628	−40.330
350	21.657	164.551	161.324	1.129	249.537	228.673	−34.128
400	21.482	167.430	161.912	2.207	249.868	225.670	−29.469
450	21.354	169.953	162.668	3.278	250.180	222.626	−25.842
500	21.257	172.197	163.511	4.343	250.474	219.549	−22.936
600	21.124	176.060	165.291	6.462	251.013	213.312	−18.570
700	21.040	179.310	167.067	8.570	251.494	206.990	−15.446
800	20.984	182.116	168.777	10.671	251.926	200.602	−13.098
900	20.944	184.585	170.399	12.767	252.320	194.163	−11.269
1000	20.915	186.790	171.930	14.860	252.682	187.681	−9.803
1100	20.893	188.782	173.373	16.950	253.018	181.165	−8.603
1200	20.877	190.599	174.734	19.039	253.332	174.619	−7.601
1300	20.864	192.270	176.019	21.126	253.627	168.047	−6.752
1400	20.853	193.816	177.236	23.212	253.906	161.453	−6.024
1500	20.845	195.254	178.390	25.296	254.171	154.840	−5.392
1600	20.838	196.599	179.486	27.381	254.421	148.210	−4.839
1700	20.833	197.862	180.530	29.464	254.659	141.564	−4.350
1800	20.830	199.053	181.527	31.547	254.884	134.905	−3.915
1900	20.827	200.179	182.479	33.630	255.097	128.234	−3.525
2000	20.826	201.247	183.391	35.713	255.299	121.552	−3.175
2100	20.827	202.263	184.266	37.796	255.488	114.860	−2.857
2200	20.830	203.232	185.106	39.878	255.667	108.159	−2.568
2300	20.835	204.158	185.914	41.962	255.835	101.450	−2.304
2400	20.841	205.045	186.693	44.045	255.992	94.734	−2.062
2500	20.851	205.896	187.444	46.130	256.139	88.012	−1.839
2600	20.862	206.714	188.170	48.216	256.277	81.284	−1.633
2700	20.877	207.502	188.871	50.303	256.405	74.551	−1.442
2800	20.894	208.261	189.550	52.391	256.525	67.814	−1.265
2900	20.914	208.995	190.208	54.481	256.637	61.072	−1.100
3000	20.937	209.704	190.846	56.574	256.741	54.327	−0.946
3100	20.963	210.391	191.466	58.669	256.838	47.578	−0.802
3200	20.991	211.057	192.068	60.767	256.929	40.826	−0.666
3300	21.022	211.704	192.653	62.867	257.014	34.071	−0.539
3400	21.056	212.332	193.223	64.971	257.094	27.315	−0.420
3500	21.092	212.943	193.777	67.079	257.169	20.555	−0.307
3600	21.130	213.537	194.318	69.190	257.241	13.794	−0.200
3700	21.170	214.117	194.845	71.305	257.309	7.030	−0.099
3800	21.213	214.682	195.360	73.424	257.373	0.265	−0.004
3900	21.257	215.234	195.862	75.547	257.436	−6.501	0.087
4000	21.302	215.772	196.353	77.675	257.496	−13.270	0.173
4100	21.349	216.299	196.834	79.808	257.554	−20.040	0.255
4200	21.397	216.814	197.303	81.945	257.611	−26.811	0.333
4300	21.445	217.318	197.763	84.087	257.666	−33.583	0.408
4400	21.495	217.812	198.213	86.234	257.720	−40.358	0.479
4500	21.545	218.295	198.654	88.386	257.773	−47.133	0.547
4600	21.596	218.769	199.086	90.543	257.825	−53.909	0.612
4700	21.647	219.234	199.510	92.705	257.876	−60.687	0.674
4800	21.697	219.690	199.925	94.872	257.926	−67.465	0.734
4900	21.748	220.138	200.333	97.045	257.974	−74.244	0.791
5000	21.799	220.578	200.734	99.222	258.021	−81.025	0.846
5100	21.849	221.010	201.127	101.405	258.066	−87.806	0.899
5200	21.899	221.435	201.514	103.592	258.110	−94.589	0.950
5300	21.949	221.853	201.893	105.784	258.150	−101.371	0.999
5400	21.997	222.264	202.267	107.982	258.189	−108.155	1.046
5500	22.045	222.668	202.634	110.184	258.224	−114.940	1.092
5600	22.093	223.065	202.995	112.391	258.255	−121.725	1.135
5700	22.139	223.457	203.351	114.602	258.282	−128.510	1.178
5800	22.184	223.842	203.701	116.818	258.304	−135.296	1.218
5900	22.229	224.222	204.046	119.039	258.321	−142.083	1.258
6000	22.273	224.596	204.385	121.264	258.332	−148.869	1.296

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

Oxygen (O) $O_1(g)$

Oxygen, Ion (O^+) IDEAL GAS M_r = 15.99885 Oxygen, Ion (O^+) $O_1^+(g)$

IP(O^+, g) = 283240 ± 10 cm^{-1}
$S°$(298 15 K) = 154.959 ± 0.02 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1560.733 ± 0.10 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1568.786] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^4S_{3/2}$	0.0	4
$^2D_{5/2}$	26810.7	6
$^2D_{3/2}$	26830.5	4
$^2P_{3/2}$	40466.9	4
$^2P_{1/2}$	40468.4	2

Enthalpy of Formation

$\Delta_f H°$(O^+, g, 0 K) is calculated from $\Delta_f H°$(O, g, 0 K)[1] using the spectroscopic value of IP(O) = 109837 02 ± 0.06 cm^{-1}(314.040 ± 0.001 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0 01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°$(O^+, g, 298.15 K) is calculated from $\Delta_f H°$(O, g, 0 K) by using IP(O) with JANAF[1] enthalpies, $H°$(0 K)–$H°$(298 15 K), for O(g), O^+(g), and e^-(ref). $\Delta_f H°$($O \rightarrow O^+ + e^-$, 298.15 K) differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first four excited states; the next excited state is 119837.7 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first four excited states. The reported uncertainty in $S°$(298 15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

References

[1] JANAF Thermochemical Tables: O(g), 9–30–82 ; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	1560.733		
100	20.786	132.251	173.439	−4.119			
200	20.786	146.659	156.860	−2.040			
250	20.786	151.297	155.301	−1.001			
298.15	20.786	154.959	154.959	0.	1568.786	1546.912	−271.013
300	20.786	155.087	154.959	0.038	1568.835	1546.776	−269.318
350	20.786	158.291	155.212	1.078	1570.176	1542.994	−230.279
400	20.786	161.067	155.774	2.117	1571.507	1539.020	−200.975
450	20.786	163.515	156.501	3.156	1572.827	1534.879	−178.164
500	20.786	165.705	157.314	4.196	1574.135	1530.593	−159.900
600	20.786	169.495	159.038	6.274	1576.712	1521.642	−132.471
700	20.786	172.699	160.766	8.353	1579.242	1512.262	−112.846
800	20.786	175.475	162.435	10.431	1581.731	1502.524	−98.105
900	20.786	177.923	164.023	12.510	1584.185	1492.475	−86.621
1000	20 786	180.113	165.524	14.589	1586.612	1482.155	−77.420
1100	20.786	182.094	166.942	16.667	1589.014	1471.593	−69.880
1200	20.786	183.903	168.281	18.746	1591.397	1460 813	−63.588
1300	20.786	185.566	169.548	20.824	1593.763	1449.834	−58.255
1400	20.786	187.107	170.748	22.903	1596.113	1438.675	−53.678
1500	20.786	188.541	171.887	24.982	1598.450	1427.347	−49.705
1600	20.786	189.882	172.970	27.060	1600.773	1415.865	−46.223
1700	20.786	191.143	174.002	29.139	1603 085	1404.237	−43.147
1800	20.786	192.331	174.988	31.217	1605.384	1392.474	−40.409
1900	20.786	193.455	175.930	33.296	1607.671	1380.583	−37.955
2000	20.786	194.521	176.833	35.375	1609.947	1368.572	−35.743
2100	20.786	195.535	177.700	37.453	1612.212	1356.448	−33.740
2200	20.786	196.502	178.533	39.532	1614.465	1344.216	−31.916
2300	20.786	197.426	179.334	41.611	1616.707	1331.881	−30.248
2400	20.787	198.310	180.107	43.689	1618.938	1319.450	−28.717
2500	20.787	199.159	180.852	45.768	1621.157	1306.925	−27.307
2600	20.788	199.974	181.572	47.847	1623.367	1294.312	−26.003
2700	20.789	200.759	182.268	49.925	1625.565	1281.615	−24.794
2800	20.790	201.515	182.942	52.004	1627 754	1268.836	−23.670
2900	20.792	202.245	183.595	54.083	1629.933	1255.979	−22.623
3000	20.795	202.949	184.229	56.163	1632.102	1243.047	−21.643
3100	20.799	203.631	184.844	58.242	1634.263	1230.043	−20.726
3200	20.804	204.292	185.441	60.323	1636 415	1216.969	−19.865
3300	20.810	204.932	186.022	62.403	1638.558	1203.828	−19.055
3400	20.818	205.553	186.587	64.485	1640.695	1190.622	−18.292
3500	20.827	206.157	187.138	66.567	1642.823	1177.354	−17.571
3600	20.839	206.744	187.674	68.650	1644.946	1164.025	−16.890
3700	20.853	207.315	188.198	70.735	1647.062	1150.636	−16.244
3800	20.870	207.871	188.708	72.821	1649.172	1137.192	−15.632
3900	20.890	208.414	189.206	74.909	1651.278	1123.691	−15.050
4000	20.912	208.943	189.693	76.999	1653.379	1110.136	−14.497
4100	20.938	209.460	190.169	79.091	1655.476	1096.529	−13.970
4200	20.968	209.964	190.634	81.187	1657.569	1082.871	−13.467
4300	21.001	210.458	191.090	83.285	1659.659	1069.163	−12.988
4400	21.038	210.941	191.535	85.387	1661.747	1055.406	−12.529
4500	21.079	211.415	191.972	87.493	1663.832	1041.602	−12.091
4600	21.125	211.879	192.400	89.603	1665.916	1027.752	−11.670
4700	21.174	212.333	192.819	91.718	1667.998	1013.856	−11.268
4800	21.229	212.780	193.230	93.838	1670.079	999.916	−10.881
4900	21.287	213.218	193.634	95.964	1672.160	985.933	−10.510
5000	21.351	213.649	194.030	98.096	1674.240	971.908	−10.153
5100	21.418	214.072	194.418	100.234	1676.319	957.841	−9.810
5200	21.491	214 489	194.800	102.380	1678.399	943.732	−9.480
5300	21.568	214.899	195.176	104.532	1680.479	929.584	−9.162
5400	21.649	215.303	195.545	106.693	1682.560	915.397	−8.855
5500	21.735	215.701	195.908	108.862	1684.640	901.171	−8.559
5600	21.826	216.093	196.265	111.040	1686.721	886.907	−8.273
5700	21.921	216.480	196.616	113.228	1688.803	872.606	−7.997
5800	22.020	216.862	196.962	115.425	1690.885	858.269	−7.730
5900	22.123	217.240	197.302	117.632	1692.967	843.895	−7.471
6000	22.231	217.612	197.638	119.850	1695.049	829.487	−7.221

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

Oxygen, Ion (O^+) $O_1^+(g)$

Oxygen, Ion (O^-) IDEAL GAS $M_r = 15.99995$ Oxygen, Ion (O^-) $O_1^-(g)$

$EA(O, g) = 1.4611215 \pm 0.0000010$ eV
$S°(298.15\ K) = 157.790 \pm 0.001\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 105.814 \pm 0.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [101.846]\ kJ \cdot mol^{-1}$

Electonic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2P_3$	0.0	4
$^2P_1$	177.08	2

Enthalpy of Formation

$\Delta_f H°(O^-, g, 0\ K)$ is calculated from $\Delta_f H°(O, g, 0\ K)$[1] using the adopted electron affinity of $EA(O) = 1.4611215 \pm 0.0000010$ eV ($140.9757 \pm 0.0001\ kJ \cdot mol^{-1}$). This value, is assumed to be the same as that recommended by Hotop and Lineberger,[2] is based on a tunable laser photodetachment threshold study.[3] Additional information on $O^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger[2,4], Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(O^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(O, g, 0\ K)$ by using EA(O) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for $O^-(g)$, $O(g)$, and e^-(ref). $\Delta_r H°(O^- \rightarrow O + e^-, 298.15\ K)$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by $+6.197\ kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state and the fine–structure separation (177.08 ± 0.05 cm^{-1}) for $O^-(g)$ has been experimentally determined;[3] a thorough discussion of the relevant work is given by Hotop and Lineberger.[2] Massey[6] listed the hyperfine splitting of the ground state as 226 cm^{-1} based on a quadratic isoelectronic extrapolation. Use of this value would decrease the entropy at 298.15 K by $0.16\ J \cdot K^{-1} \cdot mol^{-1}$.

A comparison of the isoelectronic sequence – $O^-(g)$, $F(g)$, $Ne^+(g)$ – would suggest that stable electronic states may exist below EA(O), i.e. below 12000 cm^{-1}. These levels would greatly affect the entropy. However, lacking any experimental evidence as to the stability of these levels, we assume no stable excited states exist.

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.571	105.814		
100	22.725	133.326	177.481	−4.415			
200	22.271	149.016	159.790	−2.155			
250	21.936	153.948	158.148	−1.050			
298.15	21.692	157.790	157.790	0.	101.846	91.638	−16.055
300	21.684	157.924	157.790	0.040	101.821	91.575	−15.945
350	21.500	161.252	158.054	1.119	101.123	89.922	−13.420
400	21.364	164.114	158.636	2.191	100.407	88.371	−11.540
450	21.262	166.624	159.387	3.256	99.675	86.910	−10.088
500	21.184	168.860	160.225	4.318	98.926	85.532	−8.935
600	21.075	172.712	161.995	6.430	97.380	82.997	−7.226
700	21.005	175.955	163.764	8.534	95.778	80.726	−6.024
800	20.958	178.757	165.467	10.632	94.129	78.688	−5.138
900	20.924	181.223	167.083	12.726	92.442	76.859	−4.461
1000	20.899	183.426	168.609	14.817	90.723	75.219	−3.929
1100	20.881	185.417	170.048	16.906	88.979	73.753	−3.502
1200	20.866	187.233	171.406	18.993	87.213	72.446	−3.154
1300	20.855	188.903	172.688	21.079	85.429	71.288	−2.864
1400	20.846	190.448	173.902	23.164	83.629	70.268	−2.622
1500	20.838	191.886	175.054	25.248	81.814	69.377	−2.416
1600	20.832	193.231	176.148	27.332	79.985	68.607	−2.240
1700	20.827	194.494	177.191	29.415	78.144	67.952	−2.088
1800	20.823	195.684	178.185	31.497	76.289	67.406	−1.956
1900	20.819	196.810	179.136	33.580	74.423	66.963	−1.841
2000	20.816	197.878	180.047	35.661	72.545	66.619	−1.740
2100	20.813	198.893	180.920	37.743	70.655	66.369	−1.651
2200	20.811	199.861	181.760	39.824	68.754	66.210	−1.572
2300	20.809	200.786	182.567	41.905	66.841	66.137	−1.502
2400	20.807	201.672	183.345	43.986	64.917	66.148	−1.440
2500	20.805	202.521	184.095	46.066	62.981	66.239	−1.384
2600	20.804	203.337	184.819	48.147	61.035	66.407	−1.334
2700	20.803	204.122	185.520	50.227	59.078	66.651	−1.289
2800	20.801	204.879	186.198	52.307	57.111	66.968	−1.249
2900	20.800	205.609	186.855	54.387	55.133	67.354	−1.213
3000	20.800	206.314	187.492	56.467	53.146	67.810	−1.181
3100	20.799	206.996	188.110	58.547	51.150	68.332	−1.151
3200	20.798	207.656	188.710	60.627	49.144	68.918	−1.125
3300	20.797	208.296	189.294	62.707	47.130	69.567	−1.101
3400	20.797	208.917	189.862	64.787	45.107	70.277	−1.080
3500	20.796	209.520	190.415	66.866	43.076	71.047	−1.060
3600	20.795	210.106	190.954	68.946	41.037	71.875	−1.043
3700	20.795	210.676	191.480	71.025	38.991	72.759	−1.027
3800	20.794	211.230	191.992	73.105	36.938	73.700	−1.013
3900	20.794	211.770	192.492	75.184	34.878	74.694	−1.000
4000	20.794	212.297	192.981	77.264	32.811	75.741	−0.989
4100	20.793	212.810	193.458	79.343	30.737	76.840	−0.979
4200	20.793	213.311	193.925	81.422	28.657	77.990	−0.970
4300	20.793	213.800	194.382	83.502	26.571	79.189	−0.962
4400	20.792	214.278	194.828	85.581	24.479	80.437	−0.955
4500	20.792	214.746	195.266	87.660	22.380	81.732	−0.949
4600	20.792	215.203	195.694	89.739	20.276	83.074	−0.943
4700	20.792	215.650	196.114	91.818	18.165	84.462	−0.939
4800	20.791	216.088	196.526	93.897	16.048	85.895	−0.935
4900	20.791	216.516	196.929	95.977	13.925	87.372	−0.931
5000	20.791	216.936	197.325	98.056	11.795	88.893	−0.929
5100	20.791	217.348	197.714	100.135	9.658	90.456	−0.926
5200	20.791	217.752	198.095	102.214	7.514	92.061	−0.925
5300	20.790	218.148	198.470	104.293	5.363	93.708	−0.924
5400	20.790	218.536	198.838	106.372	3.205	95.395	−0.923
5500	20.790	218.918	199.200	108.451	1.038	97.122	−0.922
5600	20.790	219.292	199.555	110.530	−1.137	98.889	−0.922
5700	20.790	219.660	199.905	112.609	−3.321	100.694	−0.923
5800	20.790	220.022	200.248	114.688	−5.515	102.538	−0.923
5900	20.790	220.377	200.586	116.767	−7.718	104.419	−0.924
6000	20.789	220.727	200.919	118.846	−9.932	106.339	−0.926

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

Phosphorus Oxide (PO) IDEAL GAS $M_r = 46.97316$

$S°(298.15\ \mathrm{K}) = 222.776 \pm 0.021\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$

$\Delta_f H°(0\ \mathrm{K}) = -23.24 \pm 14.6\ \mathrm{kJ{\cdot}mol^{-1}}$
$\Delta_f H°(298.15\ \mathrm{K}) = -23.26 \pm 4.2\ \mathrm{kJ{\cdot}mol^{-1}}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^2\Pi_{1/2}$	0	2
$X^2\Pi_{3/2}$	224	2
$B^2\Sigma^+$	30696	2
$B'^2\Pi_i$	32884	4
$D'^2\Pi_r$	38055	4
$A^2\Sigma^+$	40485	2
$C'^2\Sigma^-$	43629	2
$C^2\Sigma^-$	47251	2
$D^2\Pi_r$	48580	4

$\omega_e = 1233.3\ \mathrm{cm^{-1}}$ $\omega_e x_e = 6.56\ \mathrm{cm^{-1}}$ $\sigma = 1$
$B_e = 0.7337\ \mathrm{cm^{-1}}$ $\alpha_e = 0.0056\ \mathrm{cm^{-1}}$ $r_e = 1.4757\ \mathrm{Å}$

Enthalpy of Formation

The dissociation energy of PO has been reported by various investigators to be from 5.15 eV to 7.4 eV. All of these values have been based on the spectroscopic properties of PO. Recently Drowart *et al.*[1] have measured the dissociation energy by a complex series of exchange reactions in a mass-spectrometer from which they calculate a dissociation energy of 142.2 ± 2.5 kcal·mol^{-1} (6.17 cal·K^{-1}·mol^{-1}). Drowart *et al.*[1] also point out the agreement with the observed predissociation in the D' state. Couet *et al.*[2] and Verma and Dixit[3] have observed this predissociation. It was thought to occur between the 0 and 1 levels but recently Verma[4] has shown that the vibrational numbering is in error. This does not affect the predissociation, however, which we take as 49210 ± 350 cm^{-1}. If this is to ground state products, the dissociation energy is 140.7 ± 1.0 kcal·mol^{-1}. The linear Birge–Sponer extrapolation (LBX) of the ground state vibrational energy levels yields $D_0^\circ = 164$ kcal·mol^{-1}, when corrected by the method of Hildenbrand[5] $D_0^\circ = 138.1$ kcal·mol^{-1}, in excellent agreement with the predissociation limit.

The much shorter extrapolation of the $B^2\Sigma^+$ levels yields $D_0^\circ = 157.5$,[3] 155.0[6] and 152.7[7] kcal·mol^{-1} using the LBX method, a non-linear extrapolation[8] yields 151.0 kcal·mol^{-1}. All these values assume ground state atoms as the products, which must be the case since a $^2\Sigma^+$ state exists which correlates with those products and the $B^2\Sigma^+$ state must be this state or be formed by an avoided crossing. It is possible then that these values are high due to a potential maximum in the $B^2\Sigma^+$ state.

The adopted value is $D_0^\circ = 140.7 \pm 1$ kcal·mol^{-1} and this yields $\Delta_f H°(\mathrm{PO, g, 298.15\ K}) = -23.548$ kJ·mol^{-1}.

Heat Capacity and Entropy

The ground-state constants are from Verma[9] and Verma and Dixit.[3] The ground-state splitting is from Rao[10] who also reported the excitation energy of the A state. The energy of the B state is due to Singh,[11] while that of the B' state is from Verma.[9] The C state energy is due to Dressler[6] while Narisimham[12] reported the C' state energy. Verma and Dixit[3] reported the D state energy and Verma[4] the D' state energy, which is considerably different from earlier reports. The E' state reported by Santaram and Rao[13] has been shown to coincide with the D' state by Verma and Dixit.[3] States above 50000 cm^{-1} were not included. Other states in the 40,000 cm^{-1} region have been proposed[14] from perturbation analyses.

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Phosphorus Oxide (PO) $O_1P_1(g)$

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.395	−23.241	−23.241	INFINITE
100	32.287	187.462	251.313	−6.385	−22.571	−30.883	16.131
200	32.204	210.041	225.686	−3.129	−23.033	−39.268	10.256
250	31.821	217.180	223.299	−1.530	−23.255	−43.303	9.048
298.15	31.762	222.776	222.776	0.	−23.548	−47.139	8.258
300	31.765	222.972	222.776	0.059	−23.560	−47.285	8.233
350	31.970	227.882	223.164	1.651	−24.642	−51.140	7.632
400	32.329	232.173	224.027	3.258	−25.098	−54.894	7.168
450	32.754	236.005	225.149	4.885	−25.546	−58.592	6.801
500	33.193	239.479	226.411	6.534	−25.985	−62.240	6.502
600	34.005	245.604	229.113	9.895	−26.836	−69.410	6.043
700	34.678	250.898	231.855	13.330	−27.660	−76.441	5.704
800	35.213	255.565	234.533	16.826	−28.466	−83.354	5.442
900	35.636	259.738	237.106	20.369	−29.258	−90.168	5.233
1000	35.973	263.511	239.561	23.950	−30.040	−96.893	5.061
1100	36.244	266.953	241.897	27.562	−30.816	−103.541	4.917
1200	36.465	270.116	244.118	31.197	−95.159	−109.040	4.746
1300	36.649	273.042	246.232	34.853	−95.153	−110.197	4.428
1400	36.803	275.764	248.245	38.526	−95.150	−111.354	4.155
1500	36.934	278.308	250.166	42.213	−95.150	−112.512	3.918
1600	37.047	280.695	252.000	45.912	−95.155	−113.669	3.711
1700	37.146	282.944	253.755	49.622	−95.164	−114.826	3.528
1800	37.233	285.070	255.436	53.341	−95.179	−115.982	3.366
1900	37.311	287.085	257.049	57.068	−95.201	−117.137	3.220
2000	37.381	289.001	258.599	60.803	−95.229	−118.291	3.089
2100	37.445	290.826	260.091	64.544	−95.263	−119.444	2.971
2200	37.504	292.570	261.528	68.292	−95.305	−120.594	2.863
2300	37.558	294.238	262.914	72.045	−95.355	−121.742	2.765
2400	37.608	295.837	264.253	75.803	−95.412	−122.889	2.675
2500	37.655	297.374	265.547	79.566	−95.478	−124.032	2.592
2600	37.699	298.851	266.800	83.334	−95.551	−125.173	2.515
2700	37.741	300.275	268.013	87.106	−95.631	−126.310	2.444
2800	37.781	301.648	269.190	90.882	−95.720	−127.445	2.378
2900	37.819	302.975	270.332	94.662	−95.816	−128.577	2.316
3000	37.856	304.257	271.442	98.446	−95.919	−129.705	2.258
3100	37.892	305.499	272.521	102.234	−96.030	−130.829	2.204
3200	37.926	306.703	273.570	106.024	−96.147	−131.950	2.154
3300	37.960	307.870	274.592	109.819	−96.272	−133.067	2.106
3400	37.993	309.004	275.587	113.616	−96.402	−134.180	2.061
3500	38.025	310.106	276.558	117.417	−96.539	−135.289	2.019
3600	38.057	311.177	277.505	121.221	−96.681	−136.394	1.979
3700	38.089	312.221	278.429	125.029	−96.829	−137.495	1.941
3800	38.121	313.237	279.332	128.839	−96.982	−138.592	1.905
3900	38.153	314.227	280.214	132.653	−97.141	−139.685	1.871
4000	38.186	315.194	281.076	136.470	−97.303	−140.774	1.838
4100	38.219	316.137	281.920	140.290	−97.471	−141.858	1.807
4200	38.252	317.059	282.746	144.114	−97.642	−142.939	1.778
4300	38.286	317.959	283.554	147.941	−97.818	−144.015	1.749
4400	38.322	318.840	284.346	151.771	−97.998	−145.088	1.722
4500	38.358	319.701	285.122	155.605	−98.181	−146.156	1.697
4600	38.396	320.545	285.883	159.443	−98.368	−147.220	1.672
4700	38.435	321.371	286.630	163.284	−98.558	−148.280	1.648
4800	38.476	322.180	287.362	167.130	−98.752	−149.336	1.625
4900	38.519	322.974	288.080	170.980	−98.949	−150.387	1.603
5000	38.563	323.753	288.786	174.834	−99.150	−151.435	1.582
5100	38.610	324.517	289.479	178.692	−99.354	−152.479	1.562
5200	38.659	325.267	290.160	182.556	−99.561	−153.519	1.542
5300	38.710	326.004	290.830	186.424	−99.772	−154.554	1.523
5400	38.763	326.728	291.488	190.298	−99.987	−155.586	1.505
5500	38.820	327.440	292.135	194.177	−100.205	−156.614	1.487
5600	38.879	328.140	292.772	198.062	−100.427	−157.637	1.470
5700	38.941	328.829	293.398	201.953	−100.653	−158.657	1.454
5800	39.005	329.506	294.015	205.850	−100.883	−159.672	1.438
5900	39.073	330.174	294.622	209.754	−101.118	−160.684	1.423
6000	39.144	330.831	295.220	213.665	−101.357	−161.691	1.408

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

Lead Oxide, Red (PbO) CRYSTAL(RED) $M_r = 223.1994$ Lead Oxide, Red (PbO) $O_1Pb_1(cr)$

$S°(298.15\ K) = 66.316 \pm 0.8\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs} = 762 \pm 1\ K$

$\Delta_f H°(0\ K) = -217.297 \pm 0.8\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -219.409 \pm 0.8\ kJ{\cdot}mol^{-1}$
$\Delta_{trs} H° = 0.167 \pm 0.29\ kJ{\cdot}mol^{-1}$

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−9.109	−217.297	−217.297	INFINITE
100	26.870	24.765	101.583	−7.682	−219.089	−209.218	109.284
200	40.476	48.028	69.262	−4.247	−219.634	−199.037	51.983
298.15	45.773	66.316	66.316	0.000	−219.409	−189.283	33.162
300	45.866	66.600	66.317	0.085	−219.401	−189.096	32.925
400	50.375	80.434	68.173	4.904	−218.796	−179.077	23.385
500	53.430	92.066	71.821	10.123	−217.921	−169.245	17.681
600	55.396	101.992	76.042	15.570	−216.942	−159.601	13.894
700	56.651	110.626	80.380	21.172	−220.789	−149.325	11.143
762.000	57.430	115.466	83.040	24.709	-------- I <--> II --------		
800	57.907	118.273	84.647	26.900	−219.747	−139.186	9.088
900	59.162	125.166	88.773	32.754	−218.581	−129.185	7.498
1000	60.417	131.464	92.731	38.733	−217.288	−119.320	6.233
1100	61.672	137.281	96.520	44.837	−215.863	−109.591	5.204
1200	62.927	142.701	100.145	51.067	−214.301	−99.998	4.353
1300	64.183	147.788	103.616	57.423	−212.608	−90.540	3.638
1400	65.438	152.590	106.944	63.904	−210.796	−81.218	3.030

PREVIOUS: March 1962 CURRENT: December 1971

Enthalpy of Formation

The difference in the enthalpies of formation of red and yellow PbO has been determined directly, using a solution calorimeter, by Knacke and Prescher[1] as 394 ± 70 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ by dissolving both forms in nitric acid. This difference and $\Delta_f H°$(PbO, yellow, 298.15 K) = −52.12 ± 0.15 $kcal{\cdot}mol^{-1}$ yields $\Delta_f H°$(PbO, red, 298.15 K) = −52.51 ± 0.2 $kcal{\cdot}mol^{-1}$. Smith and Woods[2] have measured the emf of reversible cells to obtain the Gibbs energy of the reaction PbO(red, cr) + H_2(g) → Pb(cr) + H_2O(l) at two temperatures. From a 2nd law analysis of these data, we obtain $\Delta_r H°$ = −15.91 $kcal{\cdot}mol^{-1}$ which yields $\Delta_f H°$(PbO, red, 298.15 K) = −52.41 ± 0.2 $kcal{\cdot}mol^{-1}$.

If we assume the entropy to be accurately known, then the enthalpy of formation can be calculated directly from the Gibbs energies of reaction. Smith and Woods,[2] for the reaction given above, found $\Delta_r G°$(298.15 K) = −11.513 $kcal{\cdot}mol^{-1}$, in combination with $\Delta_f G°$(H_2O, l, 298.15 K) = −56.687 $kcal{\cdot}mol^{-1}$ [3] yields $\Delta_f G°$(PbO, red, 298.15 K) = −45.182 $kcal{\cdot}mol^{-1}$. This Gibbs energy with JANAF entropies[4] is equivalent to $\Delta_f H°$(PbO, red, 298.15 K) = −52.45 $kcal{\cdot}mol^{-1}$. Spencer and Mote[5] measured the Gibbs energy of the reaction Pb(cr) + HgO(cr) → PbO(red, cr) + Hg(l) by means of a reversible cell and obtained $\Delta_r G°$(298.15 K) = −31.265 $kcal{\cdot}mol^{-1}$. This value combined with $\Delta_f G°$(HgO, cr, 298.15 K) = −13.983 $kcal{\cdot}mol^{-1}$ [4] yields $\Delta_f G°$(PbO, red, 298.15 K) = −45.248 $kcal{\cdot}mol^{-1}$, which with JANAF entropies[4] is equivalent to $\Delta_f H°$(PrO, red, 298.15 K) = 52.52 kcal $\cdot mol^{-1}$.

It is apparent that the data for enthalpy, Gibbs energy and entropy are all in excellent agreement, thus we adopt $\Delta_f H°$(PbO, red, 298.15 K) = −52.44 ± 0.2 $kcal{\cdot}mol^{-1}$. The adopted value was selected within all the uncertainties to assure the correct crossover of the red and yellow forms at 762 K.

Heat Capacity and Entropy

The heat capacity has been reported by King[6] from 53 to 296 K and the entropy was obtained by integration of these data based on $S°$(51 K) = 2.73 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$. This extrapolated portion was obtained by use of a Debye Einstein fit of the measured data. The value was then corrected by analogy with the 0.25 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ difference between the extrapolation for PbO(cr, yellow) by King[6] and the measured amount. The justification for this procedure is the similarity of the two curves at all other temperatures. The high temperature heat capacities were obtained by fitting an orthogonal polynomial through the low temperature data of King[6] and the enthalpies of Spencer and Spicer.[7]

Transition Data

The temperature of transition has been reported by Cohen and Addink[8] and Petersen.[9] The enthalpy of transition is calculated from the adopted enthalpy at 298.15 K and the enthalpy difference, $H°$(762 K)–$H°$(298.15 K), between PbO yellow and red.

Vaporization Data

The vapor species over PbO(cr, l) consists of $(PbO)_x$ where x = 1–6;[10, 11] thus a value for the heat of sublimation is not given.

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Lead Oxide, Yellow (PbO) **CRYSTAL(YELLOW)** **M_r = 223.1994** **Lead Oxide, Yellow (PbO)** **O_1Pb_1(cr)**

$S°(298.15 \text{ K}) = 68.701 \pm 0.21$ J·K^{-1}·mol^{-1}
$T_{fus} = 1159 \pm 5$ K

$\Delta_f H°$(0lthsp;lK) = −216.080 kJ·mol^{-1}
$\Delta_f H°(298.15 \text{ K}) = -218.062 \pm 0.63$ kJ·mol^{-1}
$\Delta_{fus} H° = 25.522 \pm 0.4$ kJ·mol^{-1}

Enthalpy of Formation

Espada *et al.*[1] have measured calorimetrically the heat of the reaction PbO(yellow, cr) + H_2(g) → Pb(cr) + H_2O(l) as $\Delta_f H°(298.15 \text{ K}) = -16.20 \pm 0.07$ kcal·mol^{-1} which yields the adopted enthalpy of formation.

Spencer and Mote[2] have measured the Gibbs energy of the cell reaction Pb(cr) + HgO(cr) → PbO(yellow, cr) + Hg(l) as −31.120 kcal·mol^{-1}. With JANAF auxillary data[3] we obtain $\Delta_f G°$PbO(yellow, 298.15 K) = −45.103 kcal·mol^{-1} which corresponds to $\Delta_f H°$PbO, yellow, 298.15 K) = −52.13 kcal·mol^{-1} in excellent agreement with the adopted value.

Charette and Flengas[13] measured the Gibbs form of energy directly in a high temperature electrolytic cell. Alcock and Bedford[14] measured the Gibbs energy of the reactions (a)PbO(cr) + Ni(cr) → NiO(cr) + Pb(l) and (b)Cu_2O(cr) + Pb(l) = PbO(cr) + 2 Cu(cr) in high temperature electrolytic cells.

Source	T/K	$\Delta_r H°$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(PbO, 298.15 K), kcal·mol^{-1}
[13]	770–1160	−52.3	−52.93 ± 0.26	−0.6 ± 0.2	−52.93 ± 0.26
[14a]	780–1070	−3.9	2.27 ± 1.8	6.6 ± 0.2	−54.0 ± 0.7
[14b]	710–1050	−12.1	−12.61 ± 0.25	−0.6 ± 0.2	−52.28 ± 0.7

These values indicate that the overall consistency between enthalpies of formation, enthalpies, entropy and Gibbs energies is generally within the experimental error.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 12.5 K to 302.7 K by Kostryukov and Morozova[4] and from 54.1 K to 296.1 K by King.[5] the two sets of data are in reasonable agreement with differences up to 0.5%. A line fitted through both data sets yields an entropy within the stated uncertainty of the Russian set, whose results we adopted.

The high temperature heat capacity was derived from the enthalpy measurements of Rodigina *et al.*[6] by curve fitting with orthogonal polynomials. The curve was constrained to join smoothly with the low temperature heat capacities. The adopted values are in good agreement with enthalpies reported by Regnault,[7] Magnus[8] and Kopp.[9] The enthalpies reported by Spencer and Spicer[10] lie about 3% higher than the adopted values are, admitted to be not too accurate. The values reported by Knacke and Prescher[11] lie 5 to 6% higher than the adopted values.

Fusion Data

The melting point was selected by Schnedier[12] in his review of metal oxide melting points. The enthalpy of melting was calculated from the enthalpy equation derived from the work of Rodigina *et al.*[6] for crystal and liquid. Knacke and Prescher[11] report a heat of melting of 6.57 kcal·mol^{-1} from their enthalpy measurements.

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

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.000	0.000	INFINITE	−9.238	−216.080	−216.080	INFINITE
100	27.698	28.284	105.269	−7.699	−217.759	−208.239	108.773
200	40.041	51.547	72.990	−4.289	−218.329	−198.435	51.826
298.15	45.773	68.701	68.701	0.000	−218.062	−188.647	33.050
300	45.834	68.985	68.702	0.085	−218.054	−188.464	32.815
400	48.526	82.565	70.536	4.812	−217.541	−178.675	23.333
500	50.463	93.609	74.080	9.765	−216.931	−169.027	17.658
600	52.103	102.958	78.133	14.895	−216.270	−159.508	13.886
700	53.605	111.104	82.274	20.181	−220.433	−149.304	11.141
762.000	54.495	115.690	84.808	23.532	-------- I <--> II	-------	
800	55.028	118.355	86.339	25.613	−219.687	−139.192	9.088
900	56.409	124.917	90.266	31.185	−218.803	−129.182	7.498
1000	57.764	130.930	94.036	36.894	−217.779	−119.277	6.230
1100	59.099	136.499	97.646	42.738	−216.615	−109.482	5.199
1159.000	59.884	139.607	99.704	46.248	----- II <--> LIQUID	-----	
1200	60.421	141.698	101.103	48.714	−215.307	−99.800	4.344
1300	61.739	146.586	104.415	54.822	−213.861	−90.232	3.626
1400	63.049	151.209	107.594	61.061	−212.291	−80.780	3.014
1500	64.350	155.604	110.650	67.431	−210.606	−71.445	2.488

PREVIOUS. March 1962 CURRENT December 1971

Lead Oxide, Yellow (PbO) **O_1Pb_1(cr)**

$S°(298.15\ K) = [73.376]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 1159 \pm 5\ K$

$\Delta_fH°(298.15\ K) = [-202.249]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 25.522 \pm 0.4\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(l, 298.15\ K)$ is calculated from that of PbO (yellow, cr) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1159\ K)–H°(298.15\ K)$, between PbO(yellow, cr) and PbO(l). Direct measurements of the Gibbs energy chang in the reaction $PbO(l) + C(cr) \rightarrow Pb(l) + CO(g)$ have been reported by Kvyatkovskii *et al.*[1] Charette and Flengas[2] and Delimarskii and Andreeva[3] have also determined the Gibbs energy of formation of the liquid directly in a high temperature cell. 2nd- and 3rd law analysis of these data are summarized below.

Source	T/K	$\Delta_rH°$, kcal·mol⁻¹ 2nd law	3rd law	Drift cal·K⁻¹·mol⁻¹	$\Delta_fH°(PbO, l, 298.15\ K)$ kcal·mol⁻¹
1	1173–1423	34.5 ± 6.5	22.81 ± 2.49	−8.6 ± 4.9	−48.20 ± 2.5
2	1160–1371	−49.9 ± 0.2	−49.24 ± 0.13	0.5 ± 0.1	−49.24 ± 0.13
3	1173–1253	−46.9 ± 5.6	−48.51 ± 0.39	−1.5 ± 4.6	−48.51 ± 0.39

Heat Capacity and Entropy

The heat capacity was obtained from the enthalpy determinations of Rodigina *et al.*[4] and Knacke and Prescher.[5] The absolute enthalpy values differ by 2–3% but the constant heat capacities derived from each set agree very well. The entropy at 298.15 K is calculated from that of the yellow crystal in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the yellow–crystal table for details.

Vaporizaton Data

Refer to the red–crystal table for details.

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	64.998	73.376	73.376	0.000	−202.249	−174.228	30.524
300	64.998	73.778	73.378	0.120	−202.205	−174.054	30.306
400	64.999	92.478	75.927	6.620	−199.920	−165.018	21.549
500	65.000	106.982	80.742	13.120	−197.763	−156.545	16.354
600	65.000	118.833	86.133	19.620	−195.732	−148.494	12.928
700	65.000	128.853	91.538	26.120	−198.681	−139.976	10.445
800	65.000	137.532	96.757	32.620	−196.867	−131.714	8.600
900	65.000	145.188	101.721	39.120	−195.055	−123.678	7.178
1000	65.000	152.036	106.416	45.620	−193.240	−115.845	6.051
1100	65.000	158.232	110.850	52.120	−191.419	−108.193	5.138
1159.000	65.000	161.628	113.349	55.955	----- II <--> LIQUID -----		
1200	65.000	163.887	115.037	58.620	−189.588	−100.708	4.384
1300	65.000	169.090	118.998	65.120	−187.750	−93.376	3.752
1400	65.000	173.907	122.750	71.620	−185.919	−86.185	3.216
1500	65.000	178.392	126.312	78.120	−184.104	−79.124	2.755
1600	65.000	182.587	129.699	84.620	−182.310	−72.184	2.357
1700	65.000	186.527	132.927	91.120	−180.542	−65.356	2.008
1800	65.000	190.243	136.009	97.620	−178.801	−58.631	1.701
1900	65.000	193.757	138.957	104.120	−177.091	−52.001	1.430
2000	65.000	197.091	141.781	110.620	−175.412	−45.461	1.187
2100	65.000	200.262	144.491	117.120	−350.987	−31.889	0.793
2200	65.000	203.286	147.095	123.620	−348.984	−16.741	0.397
2300	65.000	206.176	149.602	130.120	−347.080	−1.682	0.038
2400	65.000	208.942	152.017	136.620	−345.278	13.296	−0.289
2500	65.000	211.595	154.347	143.120	−343.578	28.201	−0.589

PREVIOUS: March 1962   CURRENT December 1971

Lead Oxide (PbO) CRYSTAL(RED-YELLOW)-LIQUID $M_r = 223.1994$ Lead Oxide (PbO) $O_1Pb_1(cr,l)$

0 to 762 K crystal, red
762 to 1159 K crystal, yellow
above 1159 K liquid

Refer to the individual tables for details.

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.000	0.000	INFINITE	−9.109	−217.297	−217.297	INFINITE
100	26.870	24.765	101.583	−7.682	−219.089	−209.218	109.284
200	40.476	48.028	69.262	−4.247	−219.634	−199.037	51.983
298.15	45.773	66.316	66.316	0.000	−219.409	−189.283	33.162
300	45.866	66.600	66.317	0.085	−219.401	−189.096	32.925
400	50.375	80.434	68.173	4.904	−218.796	−179.077	23.385
500	53.430	92.066	71.821	10.123	−217.921	−169.245	17.681
600	55.396	101.992	76.042	15.570	−216.942	−159.601	13.894
700	56.651	110.626	80.380	21.172	−220.789	−149.325	11.143
762.000	57.430	115.466	83.040	24.709	I <- -> II		
762.000	54.495	115.690	83.040	24.880	TRANSITION		
800	55.028	118.355	84.654	26.961	−219.687	−139.192	9.088
900	56.409	124.917	88.769	32.533	−218.803	−129.182	7.498
1000	57.764	130.930	92.689	38.242	−217.779	−119.277	6.230
1100	59.099	136.499	96.421	44.085	−216.615	−109.482	5.199
1159.000	59.884	139.607	98.541	47.595	II <- -> LIQUID		
1159.000	65.000	161.628	98.541	73.117	TRANSITION		
1200	65.000	163.887	100.735	75.782	−189.586	−100.706	4.384
1300	65.000	169.090	105.796	82.282	−187.748	−93.374	3.752
1400	65.000	173.907	110.491	88.782	−185.918	−86.183	3.216
1500	65.000	178.392	114.870	95.282	−184.103	−79.123	2.755
1600	65.000	182.587	118.973	101.782	−182.309	−72.183	2.357
1700	65.000	186.527	122.832	108.282	−180.540	−65.354	2.008
1800	65.000	190.243	126.475	114.782	−178.800	−58.629	1.701
1900	65.000	193.757	129.924	121.282	−177.089	−52.000	1.430
2000	65.000	197.091	133.200	127.782	−175.410	−45.459	1.187
2100	65.000	200.262	136.318	134.282	−350.985	−31.887	0.793
2200	65.000	203.286	139.294	140.782	−348.982	−16.739	0.397
2300	65.000	206.176	142.140	147.282	−347.078	−1.681	0.038
2400	65.000	208.942	144.866	153.782	−345.276	13.298	−0.289
2500	65.000	211.595	147.482	160.282	−343.577	28.203	−0.589

PREVIOUS: CURRENT: December 1971

Lead Oxide (PbO) $O_1Pb_1(cr,l)$

Lead Oxide (PbO) **IDEAL GAS** **$M_r = 223.1994$ Lead Oxide (PbO)** **$O_1Pb_1(g)$**

$S°(298.15\ K) = 240.039 \pm 0.021\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 72.55 \pm 7.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 70.29 \pm 7.1\ kJ \cdot mol^{-1}$

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

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}	$\omega_e x_e/B_e$	$\omega_e/\omega_e x_e$
X O^+	0	1	1.922	0.3074	0.00212	721.8	3.70	12.036	195.08
A O^+	20088	1	2.095	0.2587	0.00138	451.7	3.33	12.872	135.65
B 1	22531	2	2.071	0.2646	0.0026	493.5	2.26	8.541	218.36
C O^+	24108	1	2.11	0.254	0.002	[534]	[3.9]	[15.354]	136.92
C'1	25720	2	2.14	0.248	0.0018	[475]	[2.7]	[10.887]	175.92
D 1	30464	2	2.046	0.2711	0.0031	530.5	2.92	10.771	181.68
E O^+	34680	1	[2.183]	[0.2382]	[0.0014]	[440]	[2.6]	169.23	

Enthalpy of Formation

A value for the dissociation energy can be calculated by applying the Hildenbrand formula[1] to the linear Birge Sponer extrapolation of the ground state vibrational levels. This procedure yields a $D° = 91.4\ kcal \cdot mol^{-1}$, corresponding to $\Delta_f H°(0\ K) = 14.5\ kcal \cdot mol^{-1}$.

Recently, Singh and Nair[3] have calculated $D_0^\circ = 99.2\ kcal \cdot mol^{-1}$ from a special potential energy curve which takes into account the electronegativity of the atoms.

The enthalpy of sublimation of PbO(yellow, cr) to monomeric PbO has been measured mass spectrometrically by Drowart *et al.*[2] Our analysis of their vapor pressure data yields $\Delta_{sub} H°(298.15\ K) = 68.9 \pm 1.5\ kcal \cdot mol^{-1}$, which yields $\Delta_f H°(PbO, g, 298.15\ K) = 16.8 \pm 1.7\ kcal \cdot mol^{-1}$. This value is adopted and corresponds to a dissociation energy at 0 K of 88.6 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The tabulated molecular and electronic constants are taken from Barrow *et al.*[4] The state designations are those used by Barrow *et al.* who interpret the spectra in terms of type c coupling, when the state designations Σ, Π, etc. no longer have meaning. The estimated values for $\omega_e x_e$ for the C' and E states were obtained from the B_e values by averaging the $\omega_e x_e/B_e$ ratio for the known states. The functions were calculated from the partition function $Q = Q_u \Sigma Q_r^i Q_v^i g_i \exp(-c_2 \epsilon_i/T)$, the values for Q_r^i and Q_v^i were calculated with first order anharmonic corrections.

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−8.961	72.550	72.550	INFINITE
100	29.136	207.019	267.535	−6.052	72.241	63.887	−33.371
200	30.424	227.495	242.946	−3.090	71.222	55.926	−14.606
250	31.516	234.401	240.568	−1.542	70.736	52.159	−10.898
298.15	32.508	240.039	240.039	0.	70.291	48.622	−8.518
300	32.544	240.240	240.039	0.060	70.275	48.487	−8.442
350	33.415	245.324	240.439	1.710	69.832	44.891	−6.700
400	34.123	249.834	241.337	3.399	69.399	41.358	−5.401
450	34.692	253.887	242.510	5.120	68.965	37.879	−4.397
500	35.149	257.567	243.834	6.866	68.523	34.448	−3.599
600	35.822	264.039	246.677	10.417	67.605	27 719	−2.413
700	36.281	269.597	249.564	14.024	61.762	21.946	−1.638
800	36.608	274.464	252.378	17.669	60.722	16.329	−1.066
900	36.852	278.791	255.077	21.342	59.707	10.841	−0.629
1000	37.040	282.684	257.646	25.038	58.717	5.465	−0.285
1100	37.191	286.222	260.086	28.749	57.749	0.187	−0.009
1200	37.315	289.463	262.401	32.475	56.807	−5.004	0.218
1300	37.420	292.454	264.599	36.212	55.881	−10.118	0.407
1400	37.510	295.231	266.689	39.958	54.958	−15.160	0.566
1500	37.590	297.821	268.679	43.713	54.029	−20.136	0.701
1600	37.662	300.250	270.577	47.476	53.085	−25.050	0.818
1700	37.727	302.535	272.390	51.245	52.123	−29.904	0.919
1800	37.788	304.693	274.126	55.021	51.139	−34.701	1.007
1900	37.844	306.738	275.789	58.803	50.131	−39.442	1.084
2000	37.898	308.680	277.385	62.590	49.097	−44.130	1.153
2100	37.951	310.530	278.920	66.382	−129.185	−41.650	1.036
2200	38.003	312.297	280.397	70.180	−129.884	−37.465	0.890
2300	38.054	313.988	281.821	73.983	−130.678	−33.247	0.755
2400	38.108	315.608	283.195	77.791	−131.568	−28.993	0.631
2500	38.164	317.165	284.523	81.605	−132.554	−24.699	0.516
2600	38.224	318.663	285.808	85.424	−133.636	−20.363	0.409
2700	38.290	320.107	287.051	89.250	−134.811	−15.985	0.309
2800	38.362	321.501	288.257	93.082	−136.073	−11.561	0.216
2900	38.444	322.848	289.427	96.922	−137.418	−7.091	0.128
3000	38.536	324.153	290.563	100.771	−138.838	−2.573	0.045
3100	38.641	325.418	291.667	104.630	−140.326	1.994	−0.034
3200	38.760	326.647	292.741	108.500	−141.875	6.609	−0.108
3300	38.895	327.842	293.786	112.383	−143.474	11.274	−0.178
3400	39.048	329.005	294.805	116.280	−145.115	15.988	−0.246
3500	39.220	330.139	295.799	120.193	−146.789	20.751	−0.310
3600	39.413	331.247	296.768	124.124	−148.487	25.562	−0.371
3700	39.629	332.330	297.714	128.076	−150.200	30.420	−0.429
3800	39.869	333.390	298.639	132.051	−151.919	35.325	−0.486
3900	40.134	334.429	299.544	136.051	−153.635	40.275	−0.539
4000	40.425	335.448	300.429	140.079	−155.342	45.268	−0.591
4100	40.743	336.450	301.295	144.137	−157.030	50.304	−0.641
4200	41.088	337.436	302.144	148.228	−158.693	55.381	−0.689
4300	41.461	338.407	302.976	152.355	−160.324	60.498	−0.735
4400	41.862	339.365	303.792	156.521	−161.917	65.652	−0.779
4500	42.290	340.311	304.593	160.729	−163.466	70.841	−0.822
4600	42.746	341.245	305.380	164.980	−164.965	76.064	−0.864
4700	43.229	342.169	306.153	169.279	−166.410	81.320	−0.904
4800	43.738	343.085	306.913	173.627	−167.797	86.606	−0.942
4900	44.272	343.992	307.660	178.027	−169.121	91.920	−0.980
5000	44.830	344.892	308.396	182.482	−170.380	97.260	−1.016
5100	45.410	345.786	309.120	186.994	−171.571	102.625	−1.051
5200	46.012	346.673	309.834	191.565	−172.690	108.012	−1.085
5300	46.634	347.555	310.537	196.197	−173.736	113.420	−1.118
5400	47.273	348.433	311.231	200.892	−174.708	118.847	−1.150
5500	47.928	349.306	311.915	205.652	−175.605	124.292	−1.180
5600	48.596	350.176	312.591	210.478	−176.425	129.752	−1.210
5700	49.277	351.042	313.258	215.372	−177.168	135.226	−1.239
5800	49.966	351.905	313.917	220.334	−177.834	140.713	−1.267
5900	50.663	352.765	314.568	225.365	−178.423	146.210	−1.294
6000	51.364	353.623	315.212	230.466	−178.938	151.717	−1.321

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

Sulfur Oxide (SO) IDEAL GAS $M_r = 48.0594$ Sulfur Oxide (SO) $O_1S_1(g)$

$S°(298.15\ K) = 221.944 \pm 0.04\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = 5.03 \pm 1.3\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = 5.01 \pm 1.3\ kJ{\cdot}mol^{-1}$

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

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	ω_ex_e, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^3\Sigma^-$	0	3	1148.19	6.12	0.72082	0.00574	1.4811
$a^1\Delta$	6350	2	[1148.19]	[6.12]	0.7119	[0.00574]	1.494
$b^1\Sigma^+$	10510	1	1067.66	7.8	0.70261	0.00635	1.5005
$A^3\Pi_0$	38292	2	415.2	1.6	0.6067	0.0194	
$A^3\Pi_1$	38455	2	413.3	1.6	0.6107	0.0194	1.6094
$A^3\Pi_2$	38616	2	412.7	1.7	0.6164	0.0204	
$B^3\Sigma^-$	41629	3	630.4	4.8	0.502	0.0062	1.775
$C^3\Pi$	42200	6	170	[0]	[0.5]	[0]	2.2

Enthalpy of Formation

The selection for $\Delta_fH°(0\ K)$ of SO(g), 1.2 ± 3 kcal·mol^{-1}, was derived from one of the two independent means, pointed out by Okabe[1] that employs principally spectroscopic data: $\Delta_fH°(SO, g, 0\ K) = 1/2\ D_0°(S_2) + 1/2\ D_0°(O_2) - D_0°(SO) + 1/2\ \Delta_fH°(S_2, g, 0\ K)$. The data employed are as follows. Ricks and Barrow[2] give $D_0°(S_2) = 100.69 \pm 0.01$ kcal·mol^{-1}. Brix and Herzberg[3] give $D_0°(O_2) = 117.97 \pm 0.046$ kcal·mol^{-1}. On the basis of analysis of spectroscopic data to 1964, JANAF[4] gives $D_0°(SO) = 123.5 \pm 0.3$ kcal·mol^{-1}. NBS[5] gives $\Delta_fH°(S_2, g, 0\ K) = 30.65 \pm 0.2$ kcal·mol^{-1}. Assuming the dissociation products of SO are $S(^1D_2)$ and $O(^3P)$, Colin[6] concludes $D_0°(SO) = 123.56 \pm 0.23$ kcal·mol^{-1}. A systematic error of 0.65 kcal·mol^{-1} is incurred if the assumption is wrong. Support for this assumption is as follows: 1) Okabe[7] concludes that $D_0°(OS\text{–}O) = 130.06 \pm 0.5$ kcal·mol^{-1}assuming the predissociation of SO_2 is to ground state products. Using $\Delta_fH°(SO_2, g, 0\ K) = -70.336$ kcal·mol^{-1} from[5] and the relation: $\Delta_fH°(SO, g, 0\ K) = D_0°(OS\text{–}O) - 1/2\ D_0°(O_2) + \Delta_fH°(SO_2, g, 0\ K)$, one obtains $\Delta_fH°(SO, g, 0\ K) = 0.7 \pm 0.7$ kcal·mol^{-1}; 2) Assuming the threshold energy for fluorescence of SO, 217.00 ± 0.7 kcal·mol^{-1} (see Okabe),[8] corresponds to the minimum energy for the reaction $OSCl_2 = SO(A^3\Pi_0) + 2\ Cl(^3P_{3/2})$ and using 108.43 kcal·mol^{-1} for the difference in energy between the lowest vibrational levels of $SO(A^3\Pi_0)$ and $SO(X^3\Sigma^-)$ (Colin)[6] one obtains $\Delta_fH°(SO, g, 0\ K) = 1.3 \pm 0.7$ kcal·mol^{-1}. This is based on $\Delta_fH°(OSCl_2, g, 0\ K) = -50.07$ kcal·mol^{-1}[15] and $D_0°(Cl_2, 0\ K) = 57.177 \pm 0.005$ kcal·mol^{-1} given by Douglas *et al*);[9] 3) Re-examination of the photoionization–yield curves of SO_2^+ and SO^+ obtained by Dibeler and Liston[10] suggests that their reported threshold for $SO \rightarrow SO^+ + O + e-$ should be increased from 15.81 ± 0.02 cal·K^{-1}·mol^{-1} to 16.00 eV. Using the latter and the ionization energy of SO given by Jonathon *et al.*[11] of 10.34 ± 0.02 eV and the relation $\Delta_fH°(SO, g, 0\ K) = D_0°(S\text{–}O) - 1/2\ D_0°(O_2) + \Delta_fH°(SO_2, g, 0\ K)$, one obtains $\Delta_fH°(SO, g, 0\ K) = 1.20 \pm 0.5$ kcal·mol^{-1}.

Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels were taken from Rosen.[12] The thermodynamic functions are calculated using first–order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_u\Sigma Q_r^iQ_v^ig_i\exp(-c_2\epsilon_i/T)$. The National Bureau of Standards prepared this table[13] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_fH°$ selected by NBS,[13] we recalculate the table in terms of 1973 fundamental constants,[14] 1975 atomic weights,[15] and current JANAF reference states for the elements.

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0	INFINITE	−8.733	5.028	5.028	INFINITE
100	29.106	189.916	248.172	−5.826	5.793	−3.281	1.714
200	29.269	210.114	224.668	−2.911	5.610	−12.337	3.222
250	29.634	216.680	222.437	−1.439	5.333	−16.793	3.509
298.15	30.173	221.944	221.944	0.	5.007	−21.026	3.684
300	30.197	222.130	221.944	0.056	4.994	−21.187	3.689
350	30.867	226.835	222.314	1.582	4.616	−25.521	3.809
400	31.560	231.002	223.144	3.143	1.998	−29.711	3.880
450	32.221	234.758	224.230	4.738	0.909	−33.619	3.902
500	32.826	238.184	225.456	6.364	−0.238	−37.391	3.906
600	33.838	244.263	228.097	9.699	−2.067	−44.643	3.887
700	34.612	249.540	230.791	13.124	−3.617	−51.614	3.851
800	35.206	254.202	233.432	16.616	−5.005	−58.374	3.811
900	35.672	258.377	235.976	20.161	−59.419	−63.886	3.708
1000	36.053	262.155	238.408	23.748	−59.420	−64.382	3.363
1100	36.379	265.607	240.726	27.369	−59.424	−64.878	3.081
1200	36.672	268.785	242.933	31.022	−59.432	−65.374	2.846
1300	36.946	271.731	245.037	34.703	−59.446	−65.869	2.647
1400	37.210	274.479	247.043	38.411	−59.462	−66.362	2.476
1500	37.469	277.055	248.959	42.145	−59.482	−66.854	2.328
1600	37.725	279.482	250.791	45.905	−59.505	−67.345	2.199
1700	37.980	281.776	252.547	49.690	−59.528	−67.834	2.084
1800	38.232	283.954	254.232	53.501	−59.552	−68.323	1.983
1900	38.482	286.028	255.851	57.336	−59.575	−68.809	1.892
2000	38.727	288.008	257.410	61.197	−59.597	−69.294	1.810
2100	38.967	289.904	258.912	65.082	−59.618	−69.779	1.736
2200	39.200	291.722	260.363	68.990	−59.636	−70.262	1.668
2300	39.425	293.469	261.764	72.921	−59.652	−70.745	1.607
2400	39.641	295.152	263.121	76.875	−59.666	−71.227	1.550
2500	39.847	296.774	264.434	80.849	−59.678	−71.708	1.498
2600	40.043	298.341	265.709	84.844	−59.687	−72.189	1.450
2700	40.229	299.856	266.945	88.857	−59.694	−72.670	1.406
2800	40.404	301.322	268.147	92.889	−59.699	−73.150	1.365
2900	40.568	302.742	269.316	96.938	−59.702	−73.631	1.326
3000	40.721	304.120	270.453	101.002	−59.705	−74.111	1.290
3100	40.864	305.458	271.561	105.082	−59.707	−74.591	1.257
3200	40.996	306.757	272.640	109.175	−59.708	−75.072	1.225
3300	41.119	308.021	273.693	113.281	−59.710	−75.552	1.196
3400	41.232	309.250	274.721	117.398	−59.712	−76.032	1.168
3500	41.336	310.447	275.725	121.527	−59.716	−76.512	1.142
3600	41.432	311.613	276.706	125.665	−59.722	−76.991	1.117
3700	41.520	312.749	277.665	129.813	−59.730	−77.471	1.094
3800	41.601	313.857	278.603	133.969	−59.741	−77.950	1.071
3900	41.676	314.939	279.520	138.133	−59.755	−78.429	1.050
4000	41.745	315.995	280.419	142.304	−59 774	−78.908	1.030
4100	41.810	317.027	281.299	146.482	−59.796	−79.386	1.011
4200	41.871	318.035	282.162	150.666	−59.824	−79.863	0.993
4300	41.929	319.021	283.008	154.856	−59.857	−80.340	0.976
4400	41.986	319.985	283.837	159.051	−59.896	−80.816	0.959
4500	42.042	320.930	284.651	163.253	−59.941	−81.291	0.944
4600	42.098	321.854	285.450	167.460	−59.992	−81.765	0.928
4700	42.156	322.760	286.234	171.673	−60.049	−82.238	0.914
4800	42.217	323.648	287.004	175.891	−60.113	−82.709	0.900
4900	42.282	324.520	287.761	180.116	−60.183	−83.179	0.887
5000	42.352	325.374	288.505	184.348	−60.259	−83.648	0.874
5100	42.429	326.214	289.236	188.587	−60.342	−84.114	0.862
5200	42.514	327.039	289.955	192.834	−60.430	−84.580	0.850
5300	42.608	327.849	290.663	197.090	−60.524	−85.043	0.838
5400	42.712	328.647	291.359	201.356	−60.623	−85.505	0.827
5500	42.829	329.431	292.044	205.633	−60.726	−85.965	0.816
5600	42.959	330.204	292.718	209.922	−60.832	−86.423	0.806
5700	43.104	330.966	293.383	214.225	−60.941	−86.879	0.796
5800	43.265	331.717	294.037	218.543	−61.051	−87.333	0.787
5900	43.444	332.458	294.682	222.879	−61.162	−87.786	0.777
6000	43 642	333.190	295.318	227.233	−61.271	−88.235	0.768

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

Sulfur Oxide (S_2O) IDEAL GAS $M_r = 80.1194$ Sulfur Oxide (SSO) $O_1S_2(g)$

$S°(298.15\ K) = 267.020\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-58.86 \pm 33.5]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-56.48 \pm 33.5]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
679(1)
388(1)
1165(1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: C_s
Bond Distances: S–S = 1.884 Å S–O = 1.465 Å
Bond Angle: S–S–O = 118°
Product of the Moments of Inertia: $I_A I_B I_C = 6.270091 \times 10^{-115}\ g^3 \cdot cm^6$

Enthalpy of Formation

There is no direct measurement of the standard enthalpy of formation for $S_2O(g)$. Blukis and Myers[1] have discussed the discrepancy of the values of $\Delta_f H°(0\ K)$ which vary from −1 to −35 kcal·mol^{-1}. Hagman[2] reported $\Delta_f H° = -17$ kcal·mol^{-1} from his ionization and appearance potential measurements by mass spectrometry. Steudel and Schenk[3] estimated the enthalpy of formation as −22.7 kcal·mol^{-1}. If the bond dissociation energies $D_0^\circ(S\text{–}O) = 123.5$ kcal·mol^{-1} and $D_0^\circ(S\text{–}S) = 101$ kcal·mol^{-1} were used to estimate the dissociation energy of S_2O (i.e., $D_0^\circ(S_2O) = 224.5$ kcal·mol^{-1}), one will obtain $\Delta_f H = -35.3$ kcal m,uccirclol^{-1} Jones[4] reported the predissociation energy, 91 kcal·mol^{-1} for sulfur monoxide from the infrared and ultraviolet spectra. [Meschi and Myers[5] have concluded from their experiment that the so-called sulfur monoxide is S_2O.] Therefore, if $SO(g) + S(g)$ were the dissociation products, the $\Delta_f H°$ would be −25.4 kcal·mol^{-1} and if $S_2(g) + O(g)$ were the products, the $\Delta_f H°$ would be −1.2 kcal·mol^{-1}. (All JANAF auxiliary data used in calculation.)

Dewing and Richardson[6] have investigated the gas phase equilibria in the sulfur–oxygen vapor at 1250° and 1500°C, respectively. Blukis and Myers[1] recalculated their data based on the assumption that the S_2O (instead of SO) was the major product in the equilibrium, and obtained $\Delta_f H° = -13$ kcal·mol^{-1} for $S_2O(g)$ which is adopted in this table.

Heat Capacity and Entropy

The bond distance, angle, and vibrational frequencies were obtained from the microwave and infrared spectra measurements by Meschi and Myers[5] and Blukis and Myers.[1] The principal moments of inertia are: $I_A = 2.0209 \times 10^{-39}$, $I_B = 16.6326 \times 10^{-39}$ and $I_C = 18.6536 \times 10^{-39}\ g \cdot cm^2$.

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.128	−58.859	−58.859	INFINITE
100	34.286	225.094	302.941	−7.785	−57.657	−70.249	36.694
200	39.425	250.369	270.911	−4.108	−57.078	−83.076	21.697
250	41.949	259.442	267 734	−2.073	−56.791	−89.608	18.723
298.15	44.114	267.020	267.020	0.	−56.484	−95.956	16.811
300	44.191	267.293	267.020	0.082	−56.472	−96.201	16.750
350	46.136	274.255	267.566	2.341	−56.117	−102.850	15.350
400	47.797	280.527	268.800	4.691	−57.945	−109.465	14.295
450	49 199	286.240	270.425	7.116	−58.203	−115.898	13.453
500	50.379	291.486	272.273	9.607	−58.487	−122.290	12.776
600	52.201	300.842	276.274	14.741	−58.517	−135.040	11.756
700	53.497	308.992	280.378	20.029	−58.203	−147.815	11.030
800	54.436	316.200	284.414	25.429	−57.683	−160.651	10.489
900	55 131	322.653	288.311	30.909	−110.163	−172.478	10.010
1000	55.656	328.491	292.041	36.449	−108.209	−179.507	9.376
1100	56.061	333.815	295.600	42.036	−106.248	−186.732	8.867
1200	56.379	338.707	298.992	47.658	−104.287	−194.135	8.450
1300	56.632	343.230	302.223	53.309	−102.330	−201 702	8.104
1400	56.836	347.435	305.304	58.983	−100.381	−209.419	7.814
1500	57.004	351.362	308.245	64.676	−98.443	−217.275	7.566
1600	57.143	355.045	311.056	70.383	−96.517	−225.260	7.354
1700	57.259	358.513	313.747	76.103	−94.606	−233.365	7.170
1800	57.358	361.789	316.325	81.834	−92.709	−241.582	7.011
1900	57.442	364.893	318.801	87.574	−90.828	−249.904	6.870
2000	57.514	367.841	321.180	93.322	−88.963	−258.325	6.747
2100	57.576	370.648	323.469	99.077	−87.113	−266.839	6.637
2200	57.630	373.328	325.675	104.837	−85.280	−275.440	6.540
2300	57.678	375.891	327.803	110.603	−83.462	−284.124	6.453
2400	57.720	378.347	329.858	116.373	−81.659	−292.888	6.375
2500	57.757	380.704	331.845	122.146	−79.871	−301.726	6.304
2600	57.790	382.970	333.768	127.924	−78.098	−310.635	6.241
2700	57.819	385.151	335.631	133.704	−76.338	−319.612	6.183
2800	57.846	387.254	337.437	139.488	−74.591	−328.654	6.131
2900	57.869	389.285	339.190	145.273	−72.858	−337.759	6.084
3000	57 891	391.247	340.893	151.061	−71.137	−346.922	6.040
3100	57.910	393.145	342.548	156.851	−69.428	−356.143	6.001
3200	57.928	394.984	344.158	162.643	−67.731	−365.420	5.965
3300	57.944	396.767	345.726	168.437	−66.045	−374.749	5.932
3400	57.959	398.497	347.252	174.232	−64.369	−384.128	5.901
3500	57.972	400.177	348.741	180.029	−62.705	−393.557	5.874
3600	57.985	401.811	350.192	185.827	−61.051	−403.034	5.848
3700	57.996	403.400	351.609	191.626	−59.408	−412.556	5.824
3800	58.007	404.946	352.992	197.426	−57.775	−422.122	5.802
3900	58.017	406.453	354.344	203.227	−56.152	−431.731	5.782
4000	58.026	407.922	355.665	209.029	−54.539	−441.382	5.764
4100	58.034	409.355	356.957	214.832	−52.937	−451.073	5.747
4200	58.042	410.754	358.221	220.636	−51.345	−460.803	5.731
4300	58.049	412.120	359.459	226.440	−49.763	−470.570	5.716
4400	58.056	413.454	360.671	232.246	−48.193	−480.375	5.703
4500	58.062	414.759	361.859	238.052	−46.633	−490.215	5.690
4600	58.068	416.035	363.022	243.858	−45.084	−500.090	5.679
4700	58.074	417.284	364.164	249.665	−43.547	−509.998	5.668
4800	58.079	418.507	365.283	255.473	−42.022	−519.938	5.658
4900	58.084	419.704	366.382	261.281	−40.509	−529.910	5.649
5000	58.088	420.878	367.460	267.090	−39.008	−539.913	5.640
5100	58.093	422.028	368.519	272.899	−37.521	−549.946	5.633
5200	58.097	423.156	369.559	278.708	−36.047	−560.008	5.625
5300	58.101	424.263	370.580	284.518	−34.587	−570.098	5.619
5400	58.104	425.349	371.584	290.328	−33.141	−580.216	5.612
5500	58.108	426.415	372.572	296.139	−31.711	−590.360	5.607
5600	58.111	427.462	373.543	301.950	−30.295	−600.530	5.602
5700	58.114	428.491	374.498	307.761	−28.896	−610.725	5.597
5800	58.117	429.502	375.437	313.573	−27.513	−620.945	5.592
5900	58.120	430.495	376.362	319.385	−26.147	−631.189	5.588
6000	58.123	431.472	377.272	325 197	−24.798	−641.455	5.584

PREVIOUS: September 1965 (1 atm) CURRENT· September 1965 (1 bar)

Silicon Oxide (SiO) IDEAL GAS $M_r = 44.0849$ Silicon Oxide (SiO) $O_1Si_1(g)$

$S°(298.15\ K) = 211.579\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -101.57 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -100.42 \pm 8.4\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1
	[30000]	6
	42640	2

$\omega_e = 1241.44\ cm^{-1}$
$B_e = 0.7273\ cm^{-1}$
$\omega_e x_e = 5.92\ cm^{-1}$
$\alpha_e = 0.00508\ cm^{-1}$
$\sigma = 1$
$r_e = 1.509\ Å$

Enthalpy of Formation

The adopted value is based on equilibrium data summarized below. The more reliable results from three different reactions lie in the range from about −23 to −28 kcal·mol^{-1}. Extreme values, including −20 and −32 kcal·mol^{-1}, can be discounted on experimental grounds. Margrave[1] recently reported $\Delta_r H°(298.15\ K) = 82.8 \pm 1.5$ kcal·mol^{-1} for $0.5\ SiO_2(s) + 0.5\ Si(s) = SiO(g)$, but details are not yet available. Assuming that this corresponds to reaction A below, we calculate $\Delta_f H(298.15\ K) = -25.4$ kcal·mol^{-1}. Reaction A involves the nominal composition SiO(s) which is treated as an intimate mixture of 0.5 Si(cr) + 0.5 SiO_2(high cristobalite). X-ray studies[13 14] suggest that the condensed "SiO" used in[4,8] is probably a mixture of Si and amorphous or vitreous SiO_2. The adopted $\Delta_f H°$ corresponds to $D_0° = 190 \pm 3$ kcal·mol^{-1}. This may be compared with $D_0^{\prime\prime} = 179$ kcal·mol^{-1}obtained by linear Birge–Sponer extrapolation of the ground state vibrational constants and with $D_0° = 185 \pm 7$ kcal·mol^{-1} obtained by Barrow[15] from $D_0^{\prime o}(LBX) = 77.5$ kcal·mol^{-1} for the excited state at 52580 cm^{-1}. Barrow assumed $D_0^{\prime\prime}/D_0^{\prime o}(LBX) = 0.456$ based on related molecules.

Source	Reaction	Method	T/K	Data Points	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1}		Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Ramstad[2]	A	Carrier gas	1510–1758	6	80.2 ± 2.3	85.08	3.0 ± 1.4	−23.1
Bergman[3]	A	$\Delta_{sub}H°$ by explosion	–	–	–	87 ± 2	–	−22
Gunther[4]	A*	Knudsen wt. gain	1202–1520	18	97.0 ± 0.7	86.76	−7.6 ± 0.5	−21.5
Porter[5]	A**	Knudsen mass spec.	1345–1463	2	105.1	87.35	−13	−20.9
Tombs [6]	A	Carrier gas	1573–1920	7	66.4 ± 1.1	84.75	11 ± 1	−23.5
Schafer[7]	A	Knudsen wt. loss	1336–1460	21	78.7 ± 1.5	82.74	2.9 ± 1.0	−25.5
Gel'd [8]	A*	Knudsen wt. loss	1173–1428	11	77.2 ± 1.8	85.87	6.8 ± 1.4	−22.3
Ramstad[2]	B***	Carrier gas	1698–1873	4	142.6 ± 0.7	133.79	−4.9 ± 0.4	−24.8
Bowles[2]	B***	Carrier gas	1703–1898	–	135	132.3	−2	−26.3
Tombs [6]	B***	Carrier gas	1501–1926	23	88 ± 3	127.3	22 ± 2	−31.3
Grube [9]	B***	Carrier gas	1473–1773	4	112 ± 3	134.4	13 ± 2	−24.2
Nesmeyanov[10]	C**	Knudsen collection	1653–1739	24	–	–	–	−20.5
Yang [11]	C	Knudsen wt. loss	1818–1960	15	199.3 ± 3.4	194.5	−2 ± 1.8	−21.9
Porter[5]	C	Knudsen mass spec.	1800–1900	2	130	184.4	29	−32.0
Cochran[12]	D	Knudsen effusion	?	–	–	11.5	–	−25.3

A) $0.5\ SiO_2(\text{high cristo.}) + 0.5\ Si(cr, l) = SiO(g)$
B) $SiO_2(\text{high cristo.}) + H_2(g) = H_2O(g) + SiO(g)$
C) $SiO_2(\text{high cristo.}) = 0.5\ O_2(g) + SiO(g)$
D) $SiO_2(l) + Mg(g) = MgO(cr) + SiO(g)$
*Starting material was "SiO" **Starting material was tridymite ***Starting material was quartz

Heat Capacity and Entropy

All constants for the ground state and the $A^1\Pi$ State at 42640 cm^{-1} are taken from the analysis of the A→X system reported by Lagerqvist.[16] An intercombination transition has been observed and assigned as $^1\Sigma^-$ a $^3\Pi_r$ by Verma.[17] The value of the a–X excitation energy is unknown but is estimated here as 30000 ± 5000 cm^{-1} by comparison with the a and A states of CO and Al Cl. Several additional states are known[15,16] to lie near or above the A state, but they are omitted because their contribution to the thermal functions is negligible.

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Continued on page 1813

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.715	−101.571	−101.571	INFINITE
100	29.105	179.626	237.700	−5.807	−100.382	−109.296	57.090
200	29.204	199.813	214.286	−2.894	−100.103	−118.385	30.919
250	29.466	206.354	212.069	−1.429	−100.217	−122.945	25.688
298.15	29.899	211.579	211.579	0.	−100.416	−127.305	22.303
300	29.918	211.764	211.580	0.055	−100.425	−127.472	22.195
350	30.500	216.419	211.946	1.565	−100.688	−131.959	19.694
400	31.135	220.533	212.767	3.106	−100.981	−136.407	17.813
450	31.768	224.236	213.839	4.679	−101.291	−140.817	16.346
500	32.365	227.615	215.050	6.282	−101.612	−145.191	15.168
600	33.399	233.611	217.656	9.572	−102.278	−153.845	13.393
700	34.213	238.823	220.316	12.955	−102.971	−162.385	12.117
800	34.845	243.434	222.923	16.409	−103.694	−170.824	11.154
900	35.336	247.568	225.436	19.919	−104.449	−179.170	10.399
1000	35.722	251.312	227.839	23.473	−105.237	−187.431	9.790
1100	36.030	254.731	230.131	27.061	−106.059	−195.610	9.289
1200	36.279	257.877	232.314	30.677	−106.917	−203.714	8.867
1300	36.484	260.790	234.393	34.315	−107.810	−211.744	8.508
1400	36.655	263.500	236.377	37.972	−108.742	−219.705	8.197
1500	36.800	266.034	238.270	41.645	−109.714	−227.597	7.926
1600	36.923	268.413	240.081	45.332	−110.727	−235.423	7.686
1700	37.031	270.655	241.814	49.029	−161.960	−242.737	7.458
1800	37.125	272.774	243.476	52.737	−162.830	−247.464	7.181
1900	37.209	274.784	245.071	56.454	−163.703	−252.142	6.932
2000	37.283	276.694	246.605	60.179	−164.579	−256.774	6.706
2100	37.351	278.515	248.081	63.910	−165.459	−261.362	6.501
2200	37.412	280.254	249.504	67.649	−166.345	−265.908	6.313
2300	37.469	281.918	250.878	71.393	−167.236	−270.414	6.141
2400	37.521	283.514	252.205	75.142	−168.132	−274.881	5.983
2500	37.569	285.046	253.488	78.897	−169.035	−279.310	5.836
2600	37.615	286.521	254.730	82.656	−169.943	−283.703	5.700
2700	37.658	287.941	255.934	86.420	−170.858	−288.061	5.573
2800	37.700	289.312	257.102	90.188	−171.778	−292.385	5.455
2900	37.739	290.635	258.235	93.960	−172.705	−296.677	5.344
3000	37.778	291.915	259.337	97.735	−173.637	−300.935	5.240
3100	37.816	293.155	260.408	101.515	−174.575	−305.163	5.142
3200	37.853	294.356	261.450	105.299	−175.518	−309.361	5.050
3300	37.891	295.521	262.465	109.086	−176.466	−313.529	4.963
3400	37.929	296.653	263.454	112.877	−177.418	−317.668	4.880
3500	37.968	297.753	264.418	116.672	−178.375	−321.779	4.802
3600	38.009	298.823	265.359	120.470	−563.487	−315.402	4.576
3700	38.052	299.865	266.278	124.273	−564.037	−308.503	4.355
3800	38.097	300.880	267.175	128.081	−564.591	−301.589	4.146
3900	38.145	301.871	268.052	131.893	−565.149	−294.661	3.947
4000	38.196	302.837	268.910	135.710	−565.709	−287.718	3.757
4100	38.251	303.781	269.749	139.532	−566.272	−280.761	3.577
4200	38.311	304.703	270.570	143.360	−566.835	−273.791	3.405
4300	38.375	305.606	271.374	147.195	−567.399	−266.807	3.241
4400	38.445	306.489	272.162	151.036	−567.962	−259.810	3.084
4500	38.521	307.353	272.935	154.884	−568.524	−252.800	2.934
4600	38.602	308.201	273.692	158.740	−569.084	−245.778	2.791
4700	38.690	309.032	274.435	162.604	−569.642	−238.744	2.653
4800	38.785	309.848	275.165	166.478	−570.196	−231.698	2.521
4900	38.887	310.648	275.881	170.362	−570.746	−224.639	2.395
5000	38.997	311.435	276.584	174.256	−571.291	−217.571	2.273
5100	39.114	312.208	277.275	178.161	−571.832	−210.491	2.156
5200	39.239	312.969	277.954	182.079	−572.367	−203.401	2.043
5300	39.372	313.718	278.622	186.009	−572.897	−196.300	1.935
5400	39.513	314.455	279.279	189.953	−573.421	−189.190	1.830
5500	39.662	315.181	279.925	193.912	−573.937	−182.070	1.729
5600	39.820	315.897	280.561	197.886	−574.448	−174.940	1.632
5700	39.986	316.604	281.187	201.876	−574.951	−167.801	1.538
5800	40.161	317.301	281.803	205.884	−575.448	−160.654	1.447
5900	40.343	317.989	282.411	209.909	−575.938	−153.499	1.359
6000	40.534	318.668	283.010	213.953	−576.420	−146.334	1.274

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

Silicon Oxide (SiO) $O_1Si_1(g)$

Strontium Oxide (SrO) CRYSTAL $M_r = 103.6194$ Strontium Oxide (SrO) $O_1Sr_1(cr)$

$\Delta_fH°(0\ K) = -589.80 \pm 3.3\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = 55.52 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -592.04 \pm 3.3\ kJ \cdot mol^{-1}$
$T_{fus} = 2938 \pm 20\ K$ $\Delta_{fus}H° = [75.312]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_fH°$ is from U.S. Natl. Bur. Stand. Tech.[1] The adopted value was derived[2] from $\Delta_fH° = -198.1\ kcal \cdot mol^{-1}$ for $SrCl_2(cr)$, $\Delta_{sol}H°$ of $SrCl_2$ in HCl(aq), and calorimetric data for $\Delta_rH°$ of $SrO(cr) + (x+2)HCl(n\ H_2O) \rightarrow [SrCl_2(aq) + H_2O(aq) + x\ HCl(n'\ H_2O)]$. Data of Adami and Conway[3] yield $\Delta_fH°(SrO, cr) = -141.3\ kcal \cdot mol^{-1}$, while those of Monaenkova and Vorob'ev[4] yield = 141.7 $kcal \cdot mol^{-1}$. Flidlider *et al.*[5] derived $-140.5\ kcal \cdot mol^{-1}$ from their (unpublished) data for SrO(cr) and similar measurements for Sr(cr) by Guntz and Benoit.[6] Brisi and Abbattistra[7] omit the mole ratios necessary for treatment of their data, but an approximate calculation suggests consistency with the adopted value. We omit from this discussion the early data which Parker[1 2] reviewed in selecting the adopted value.

Direct measurements of $\Delta_cH°$ of Sr(cr) by Mah[8] gave $-144.44 \pm 0.4\ kcal \cdot mol^{-1}$. The negative bias of about 3 $kcal \cdot mol^{-1}$ presumably resulted from inadequate allowance for side reactions, e.g., with combustion products of Mylar used to contain the Sr. Parker[2] noted that the combustion value is incompatible with data for $SrCl_2(cr)$ and related compounds. We find that the combustion value is also less consistent with equilibrium data for $SrCl_2$(l and g). There is a similar, but much larger, discrepancy for Ba compunds (cf, BaO, crystal). Although impurity effects are of concern in all studies, the evidence predominantly favors the solution calorimetry.

Heat Capacity and Entropy

$C_p°$ is based on data (1.4–310 K) of Gmelin[9] who reported smoothed values only in the range 4 to 300 K. Based on Gmelin's graphs, we have corrected several typographical errors and resmoothed $C_p°$ above 250 K where the scatter increases significantly. The entropy is obtained by integration of our adopted $C_p°$ using $S° = 0.0003\ cal \cdot K^{-1} \cdot mol^{-1}$ at 4 K. Gmelin reported $S°(273.15\ K) = 12.40 \pm 0.02\ cal \cdot K^{-1} \cdot mol^{-1}$ compared with 12.33 from our integration. $C_p°$ data (58–298 K) of Anderson[10] are lower at all temperatures with deviations ranging from −4.7% (61 K) to −0.3% (223 K) and −0.7% (298 K).

$C_p°$ above 300 K is from constrained fitting of enthalpy data (363–1266 K) of Lander.[11] The calorimeter[11] was calibrated with Pt, but details are lacking to assess the bias due to minor changes in the enthalpy of Pt.[12] Deviations of Lander's data from the adopted curve range from −0.7 to +1.1%.

Fusion Data

Refer to the liquid table for details.

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.000	0.000	INFINITE	−8.675	−589.801	−589.801	INFINITE
100	24.949	15.242	91.864	−7.662	−591.740	−581.794	303.898
200	40.409	38.334	59.542	−4.242	−592.263	−571.540	149.271
298.15	45.409	55.522	55.522	0.000	−592.036	−561.402	98.355
500	50.534	80.376	60.880	9.748	−590.937	−540.947	56.512
600	52.049	89.728	64.929	14.880	−590.315	−531.007	46.228
700	53.262	97.845	69.064	20.147	−589.709	−521.171	38.890
800	54.300	105.026	73.119	25.526	−589.138	−511.419	33.392
900	55.220	111.476	77.029	31.002	−589.238	−501.664	29.116
1000	56.074	117.338	80.771	36.568	−588.437	−491.977	25.698
1100	56.873	122.720	84.343	42.215	−595.481	−482.006	22.889
1200	57.639	127.702	87.751	47.941	−595.475	−471.690	20.532
1300	58.379	132.345	91.005	53.742	−595.412	−461.376	18.538
1400	59.103	136.698	94.115	59.616	−595.291	−451.070	16.830
1500	59.810	140.800	97.092	65.562	−595.112	−440.775	15.349
1600	60.509	144.682	99.946	71.578	−594.876	−430.493	14.054
1700	61.199	148.371	102.687	77.664	−731.497	−419.048	12.876
1800	61.881	151.889	105.323	83.818	−729.287	−400.732	11.629
1900	62.559	155.253	107.863	90.040	−727.026	−382.541	10.517
2000	63.229	158.479	110.314	96.329	−724.717	−364.469	9.519
2100	63.898	161.580	112.682	102.685	−722.365	−346.515	8.619
2200	64.563	164.568	114.973	109.109	−719.974	−328.672	7.804
2300	65.229	167.452	117.192	115.598	−717.551	−310.940	7.062
2400	65.890	170.242	119.345	122.154	−715.100	−293.314	6.384
2500	66.551	172.945	121.435	128.776	−712.631	−275.791	5.762
2600	67.208	175.568	123.467	135.464	−710.151	−258.366	5.191
2700	67.864	178.117	125.444	142.218	−707.669	−241.036	4.663
2800	68.517	180.597	127.370	149.037	−705.195	−223.799	4.175
2900	69.174	183.013	129.247	155.921	−702.739	−206.650	3.722
2938.000	69.425	183.915	129.948	158.555	--- CRYSTAL <--> LIQUID ---		
3000	69.827	185.369	131.079	162.871	−700.309	−189.585	3.301
3100	70.479	187.669	132.867	169.887	−697.917	−172.600	2.908
3200	71.132	189.917	134.615	176.967	−695.572	−155.692	2.541
3300	71.785	192.116	136.324	184.113	−693.282	−138.857	2.198
3400	72.438	194.269	137.997	191.324	−691.058	−122.089	1.876
3500	73.086	196.378	139.635	198.600	−688.907	−105.387	1.573
3600	73.739	198.446	141.240	205.942	−686.837	−88.744	1.288

PREVIOUS: CURRENT: December 1972

Strontium Oxide (SrO) LIQUID $M_r = 103.6194$

$S°(298.15\ K) = [80.846]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2938 \pm 20\ K$

$\Delta_f H°(298.15\ K) = [-517.292]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [75.312]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(SrO, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(2938\ K)-H°(298.15\ K)$, between the crystal and the liquid.

Heat Capacity and Entropy

$C_p°$ of the liquid is estimated as β cal·K^{-1} g atom^{-1} by comparison with other oxides $C_p°$ is taken from the crystal in the range from 298 K up to the glass transition assumed at 2000 K. $S°(298.15\ K)$ is calculated in a manner analogous to that used for $\Delta_f H°$.

Fusion Data

Foex[1,2] obtained $T_{fus} = 2660°C$ from a solar furnace study using SrO as its own container. We adopt this result but increase it by 5 for conversion to IPTS 68. The much lower value (2420°C) of Schumacher[3,4] probably resulted from contamination by WO_3 from tungsten supports of the sample. $\Delta_{fus} H°$ is estimated such that $\Delta_{fus} S°$ is 6 cal·K^{-1} g atom^{-1}. Phase data for the binary system SrO $SrZrO_3$[2] yield $\Delta_{fus} H° = 10 \pm 2$ kcal·mol^{-1} assuming ideal behavior in the liquid. Comparison with the very non ideal behavior of other mixed oxides suggests that the SrO data[2] are not inconsistent with $\Delta_{fus} H° = 18$ kcal·mol^{-1}.

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Strontium Oxide (SrO) $O_1Sr_1(l)$

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	45.409	80.846	80.846	0.000	−517.292	−494.209	86.583
300	45.480	81.128	80.847	0.084	−517.285	−494.066	86.025
400	48.480	94.650	82.671	4.792	−516.792	−486.396	63.517
500	50.534	105.701	86.205	9.748	−516.193	−478.865	50.027
600	52.049	115.053	90.254	14.880	−515.571	−471.458	41.044
700	53.262	123.170	94.389	20.147	−514.965	−464.154	34.636
800	54.300	130.351	98.444	25.526	−514.394	−456.935	29.835
900	55.220	136.800	102.353	31.002	−514.494	−449.713	26.101
1000	56.074	142.663	106.096	36.568	−513.693	−442.557	23.117
1100	56.873	148.045	109.668	42.215	−520.737	−435.119	20.662
1200	57.639	153.027	113.076	47.941	−520.731	−427.335	18.601
1300	58.379	157.670	116.330	53.742	−520.668	−419.555	16.858
1400	59.103	162.023	119.440	59.616	−520.547	−411.781	15.364
1500	59.810	166.125	122.417	65.562	−520.368	−404.018	14.069
1600	60.509	170.007	125.271	71.578	−520.132	−396.269	12.937
1700	61.199	173.696	128.012	77.664	−656.753	−387.356	11.902
1800	61.881	177.213	130.648	83.818	−654.543	−371.573	10.783
1900	62.559	180.577	133.188	90.040	−652.282	−355 914	9.785
2000	63.229	183.803	135.639	96.329	−649.973	−340.375	8.890
2000.010	63.229	183.804	135.639	96.330	GLASS <--> LIQUID TRANSITION		
2000.010	66.944	183.804	135.639	96.330			
2100	66.944	187.070	138.011	103.024	−647.283	−324.961	8.083
2200	66.944	190.184	140.312	109.718	−644.621	−309.675	7.353
2300	66.944	193.160	142.545	116.412	−641.992	−294.509	6.689
2400	66.944	196.009	144.714	123.107	−639.404	−279.457	6.082
2500	66.944	198.741	146.821	129.801	−636.862	−264.511	5.527
2600	66.944	201.367	148.869	136.496	−634.376	−249.667	5.016
2700	66.944	203.894	150.860	143.190	−631.953	−234.916	4.545
2800	66.944	206.328	152.798	149.884	−629.604	−220.254	4.109
2900	66.944	208.677	154.685	156.579	−627.337	−205.675	3.705
2938.000	66.944	209.549	155.389	159.123	--- CRYSTAL <--> LIQUID ---		
3000	66.944	210.947	156.522	163.273	−625.163	−191.172	3.329
3100	66.944	213.142	158.314	169.968	−623.092	−176.740	2.978
3200	66.944	215.267	160.060	176.662	−621.133	−162.374	2.650
3300	66.944	217.327	161.765	183.356	−619.295	−148.066	2.344
3400	66.944	219.326	163.428	190.051	−617.588	−133.813	2.056
3500	66.944	221.266	165.053	196.745	−616.019	−119.607	1.785
3600	66.944	223.152	166.641	203.440	−614.595	−105.444	1.530
3700	66.944	224.986	168.193	210.134	−613.323	−91.319	1.289
3800	66.944	226.772	169.711	216.828	−612.208	−77.226	1.062
3900	66.944	228.510	171.197	223.523	−611.253	−63.160	0.846
4000	66.944	230.205	172.651	230.217	−610.461	−49.117	0.641
4100	66.944	231.858	174.075	236.912	−609.835	−35.092	0.447
4200	66.944	233.472	175.470	243.606	−609.370	−21.080	0.262
4300	66.944	235.047	176.837	250.300	−609.071	−7.077	0.086
4400	66.944	236.586	178.178	256.995	−608.935	6.921	−0.082
4500	66.944	238.090	179.493	263.689	−608.957	20.918	−0.243
4600	66.944	239.562	180.783	270.384	−609.068	34.911	−0.396
4700	66.944	241.001	182.049	277.078	−609.376	48.914	−0.544
4800	66.944	242.411	183.291	283.772	−609.822	62.924	−0.685
4900	66.944	243.791	184.512	290.467	−610.402	76.946	−0.820
5000	66.944	245.143	185.711	297.161	−611.102	90.980	−0.950

PREVIOUS: CURRENT: December 1972

Strontium Oxide (SrO)　CRYSTAL-LIQUID　M_r = 103.6194 Strontium Oxide (SrO)　$O_1Sr_1(cr,l)$

0 to 2938 K crystal
above 2938 K liquid

Refer to the individual tables for details.

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−8.675	−589.801	−589.801	INFINITE
100	24.949	15.242	91.864	−7.662	−591.740	−581.794	303.898
200	40.409	38.334	59.542	−4.242	−592.263	−571.540	149.271
298.15	45.409	55.522	55.522	0.000	−592.036	−561.402	98.355
300	45.480	55.803	55.523	0.084	−592.029	−561.212	97.716
400	48.480	69.325	57.346	4.792	−591.536	−551.010	71.955
500	50.534	80.376	60.880	9.748	−590.937	−540.947	56.512
600	52.049	89.728	64.929	14.880	−590.315	−531.007	46.228
700	53.262	97.845	69.064	20.147	−589.709	−521.171	38.890
800	54.300	105.026	73.119	25.526	−589.138	−511.419	33.392
900	55.220	111.476	77.029	31.002	−589.238	−501.664	29.116
1000	56.074	117.338	80.771	36.568	−588.437	−491.977	25.698
1100	56.873	122.720	84.343	42.215	−595.481	−482.006	22.889
1200	57.639	127.702	87.751	47.941	−595.475	−471.690	20.532
1300	58.379	132.345	91.005	53.742	−595.412	−461.376	18.538
1400	59.103	136.698	94.115	59.616	−595.291	−451.070	16.830
1500	59.810	140.800	97.092	65.562	−595.112	−440.775	15.349
1600	60.509	144.682	99.946	71.578	−594.876	−430.493	14.054
1700	61.199	148.371	102.687	77.664	−731.497	−419.048	12.876
1800	61.881	151.889	105.323	83.818	−729.287	−400.732	11.629
1900	62.559	155.253	107.863	90.040	−727.026	−382.541	10.517
2000	63.229	158.479	110.314	96.329	−724.717	−364.469	9.519
2100	63.898	161.580	112.682	102.685	−722.365	−346.515	8.619
2200	64.563	164.568	114.973	109.109	−719.974	−328.672	7.804
2300	65.229	167.452	117.192	115.598	−717.551	−310.940	7.062
2400	65.890	170.242	119.345	122.154	−715.100	−293.314	6.384
2500	66.551	172.945	121.435	128.776	−712.631	−275.791	5.762
2600	67.208	175.568	123.467	135.464	−710.151	−258.366	5.191
2700	67.864	178.117	125.444	142.218	−707.669	−241.036	4.663
2800	68.517	180.597	127.370	149.037	−705.195	−223.799	4.175
2900	69.174	183.013	129.247	155.921	−702.739	−206.650	3.722
2938.000	69.425	183.915	129.948	158.555	CRYSTAL <−−> LIQUID TRANSITION		
2938.000	66.944	209.549	129.948	233.867			
3000	66.944	210.947	131.608	238.017	−625.163	−191.172	3.329
3100	66.944	213.142	134.203	244.712	−623.092	−176.740	2.978
3200	66.944	215.267	136.703	251 406	−621.133	−162.374	2.650
3300	66.944	217.327	139.115	258.100	−619.295	−148.066	2.344
3400	66.944	219.326	141.445	264.795	−617.588	−133.812	2.056
3500	66.944	221.266	143.698	271.489	−616.019	−119.607	1.785
3600	66.944	223.152	145.879	278.184	−614.595	−105.444	1.530
3700	66.944	224.986	147.992	284.878	−613.323	−91.319	1.289
3800	66.944	226.772	150.042	291.572	−612.208	−77.226	1.062
3900	66.944	228.510	152.032	298.267	−611.253	−63.160	0.846
4000	66.944	230.205	153.965	304.961	−610.461	−49.117	0.641
4100	66.944	231.858	155.845	311.656	−609.835	−35.092	0.447
4200	66.944	233.472	157.674	318.350	−609.370	−21.080	0.262
4300	66.944	235.047	159.455	325.044	−609.071	−7.077	0.086
4400	66.944	236.586	161.191	331.739	−608.935	6.921	−0.082
4500	66.944	238.090	162.883	338.433	−608.957	20.918	−0.243
4600	66.944	239.562	164.534	345.128	−609.068	34.911	−0.396
4700	66.944	241.001	166.146	351.822	−609.376	48.914	−0.544
4800	66.944	242.411	167.720	358.516	−609.822	62.924	−0.685
4900	66.944	243.791	169.258	365.211	−610.402	76.946	−0.820
5000	66.944	245.143	170.762	371.905	−611.102	90.980	−0.950

PREVIOUS:　CURRENT: December 1972

Strontium Oxide (SrO)　$O_1Sr_1(cr,l)$

Strontrium Oxide (SrO) IDEAL GAS $M_r = 103.6194$ Strontium Oxide (SrO) $O_1Sr_1(g)$

$S°(298.15\text{ K}) = 230.058 \pm 0.4\ \text{J·K}^{-1}\text{·mol}^{-1}$

$\Delta_fH°(0\text{ K}) = -11.52 \pm 16.7\ \text{kJ·mol}^{-1}$
$\Delta_fH°(298.15\text{ K}) = -13.39 \pm 16.7\ \text{kJ·mol}^{-1}$

Electronic States and Molecular Constants (σ–1)

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e°, cm^{-1}	α_e, cm^{-1}	r_e, A	Source
$X^1\Sigma^+$	0.0	1	653.2	3.92	0.33798	0.00219	1.9199	1–4
$a^3\Pi$	9055	6	463.5	1.61	0.2584	0.0020	2.195	1
$A'^1\Pi$	9794	2	460.3	1.61	0.2610	0.0023	2.184	1
$^3\Sigma^+$	[8000]	3	[619.6]	[0.9]	[0.3047]	[0.0011]	[2.021]	5
$A^1\Sigma^+$	10870	1	619.6	0.9	0.30471	0.00112	2.021	1 4
$^3\Sigma^+$	[22000]	3	[480]	[2.6]	[0.272]	[0.002]	[2.14]	5
$^3\Delta$	[22000]	6	[480]	[2.6]	[0.272]	[0.002]	[2.14]	5
$^1\Delta$	[24000]	2	[480]	[2.6]	[0.272]	[0.002]	[2.14]	5
$^3\Sigma^-$	[24000]	3	[480]	[2.6]	[0.272]	[0.002]	[2.14]	5
$^1\Sigma^-$	[24000]	1	[480]	[2.6]	[0.272]	[0.002]	[2.14]	5
$C^1\Sigma^+$	28546	1	480.2	2.6	0.2742	0.0021	2.132	4
$^3\Pi$	[23000]	6	[520]	[3.2]	[0.2936]	[0.0015]	[2.06]	5
$B^1\Pi$	24636	2	519.9	3.24	0.2936	0.0015	2.060	4

Enthalpy of Formation

We adopt $D° = 101.0 \pm 4$ and $\Delta_fH°(298.15\text{ K}) = -3.2 \pm 4$ kcal·mol^{-1} based on the equilibria analyzed below. Greatest weight is given to the conventional mass–spectrometric studies.[7,8] We give "<" or ">" for the resulting $D°$ values which we feel may be biased. The JANAF differences in $\Delta_fH°(298.15\text{ K})$ for MoO_3–MoO_2 and WO_3–WO_2 may be biased by ~4 and ~–3 kcal·mol^{-1}, respectively; this would cause bias of the opposite sign in $D°$ values derived from reactions C and D With these adjustments, our analyses would be comparable with those of Brewer and Rosenblatt[10] based on a $^1\Sigma$ ground state.

Less reliable data were reviewed by Drowart *et al.*[8] and Schofield.[11] Subsequent studies include two new techniques: nonisothermal Langmuir mass–spectrometry[9] and crossed–beam reaction threshold.[12] The former yields $D° = 98.3$ and >96 kcal·mol^{-1} (see reactions E and F below). JANAF data for the reaction SrO(cr) = Sr(g) + O(g) suggest that the P_0 assumed[9] for reaction F is too large. JANAF pressures for Sr(g) and O(g) may be combined with the estimated composition[3] of 5% SrO(g) to calculate K_p° for reaction F and $D° = 93.5 \pm 8$ kcal·mol^{-1}. $D°$ would increase to 97 kcal·mol^{-1} if the beam in the magnetic– deflection experiment[3] contained 10% SrO(g) rather than 5%. The crossed–beam reaction[12] was interpreted to give $D° = 112.5(+3.5$ to -0.71 kcal·mol^{-1}. We assume this value has a positive bias. Finally, Kalff[13] used spectrometry of CO–N_2O flames to derive $D° = 93.6 \pm 2.3$ kcal·mol^{-1}. This value becomes ~99 kcal·mol^{-1} when adjusted to be consistent with the JANAF free energy functions.

Source	Method	Reaction[a]	T/K	Data Points	δS cal·K^{-1}·mol^{-1}	$\Delta_rH°(298.15\text{ K})$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_fH°(298.15\text{K})$ kcal·mol^{-1}	$D°$
7	Knudsen mass spec.	A	1931–2170	5	9.5 ± 7.1	42 ± 15	22.6 ± 2.8	–3.3 ± 3	101.2
8	Knudsen mass spec.	B	2156–2321	4	–40.0 ± 10	–73 ± 22	16.3 ± 5.8	–4.1 ± 6	101.9
	Knudsen mass spec.	C	1987–2233	8	–2.5 ± 6.1	40 ± 13	45.4 ± 2.6	1.5 ± 6	>96.4
	Knudsen mass spec.	D	2326	1	–	–	44.9	–4.2 ± 5	<102.0
9	Langmuir mass spec.[b]	E	1747–1850	Eqn.	–3.8	134.2	141.0 ± 0.7	–0.5 ± 3	98.3
	Langmuir mass spec.	F[c]	1747–1850	Eqn.	3.3	102.9	97.0	1.8 ± 3	>96.0
3	Magnetic deflection	F	~2500	1	–	–	94.5	4.3 ± 8	93.5

[a] Reactions: A) $Sr(g) + SO(g) = SrO(g) + S(g)$ B) $Sr(g) + O_2(g) = SrO(g) + O(g)$ C) $Sr(g) + MoO_3(g) = SrO(g) + MoO_2(g)$ D) $Sr(g) + WO_3(g) = SrO(g) + WO_2(g)$ E) $SrO(cr) = SrO(g)$ F) $SrO(g) = Sr(g) + O(g)$

[b] Nonisothermal. [c] $P_0 = 0.4273P_{Sr}$ assumed.

Heat Capacity and Entropy

Electronic levels (T_0) and vibrational–rotational constants of the observed states are from Field[1] and Rosen.[4] The long–sought $a^3\Pi$ and $A'^1\Pi$ states of CaO, SrO and BaO were characterized by Field[1] using a new method for assignment of perturbations. This study resolved the long–standing controversy over low–lying electronic levels and confirmed[1] that $X^1\Sigma^+$ is the ground state.[3] We estimate the other potentially low–lying state ($^3\Sigma^+$) at 8000 cm^{-1} by assuming that it lies 3000 ± 2500 cm^{-1}[11,5] below the isoconfigurational A state. Other predicted states and thier vibrational–rotational constants are estimated in isoconfigurational groups by comparison with BeO, MgO, CaO and BaO.[5] Comparisons are facilitated by listing the states in the isoconfigurational order of MgO.[5,6] Our thermodynamic functions correspond to an "effective" ground state with $1<g<2$ instead of $g = 2$.[11] Our functions are calculated using first–order anharmonic corrections to Q_r^1 and Q_v^1 in the partition function $Q = Q_t\ \Sigma Q_r^1 Q_v^1 g_i \exp(-c_2\epsilon_i/T)$.

Continued on page 1813

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

T/K	C_p° (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_fH°$ (kJ·mol^{-1})	$\Delta_fG°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	–9.041	–11.519	–11.519	INFINITE
100	29.175	196.665	257.973	–6.131	–11.561	–19.758	9.320
200	30.890	217.295	233.018	–3.145	–12.519	–27.588	7.205
250	32.086	224.318	230.597	–1.570	–12.976	–31.307	6.541
298.15	33.092	230.058	230.058	0.	–13.389	–34.793	6.096
300	33.127	230.263	230.059	0.061	–13.404	–34.926	6.081
350	33.967	235.435	230.465	1.739	–13.817	–38.480	5.743
400	34.627	240.015	231.378	3.455	–14.225	–41.976	5.481
450	35.146	244.125	232.570	5.200	–14.640	–45.420	5.272
500	35.557	247.850	233.915	6.968	–15.070	–48.817	5.100
600	36.154	254.389	236.797	10.555	–15.992	–55.481	4.830
700	36.559	259.995	239.720	14.192	–17.016	–61.983	4.625
800	36.854	264.897	242.567	17.863	–18.153	–68.331	4.462
900	37.089	269.251	245.295	21.561	–20.032	–74.457	4.321
1000	37.309	273.170	247.890	25.281	–21.077	–80.448	4.202
1100	37.561	276.738	250.353	29.024	–30.025	–85.969	4.082
1200	37.894	280.020	252.690	32.796	–31.974	–90.969	3.960
1300	38.360	283.070	254.911	36.607	–33.900	–95.807	3.850
1400	39.004	285.935	257.025	40.474	–35.787	–100.498	3.750
1500	39.862	288.654	259.044	44.415	–37.612	–105.056	3.658
1600	40.957	291.260	260.977	48.454	–39.353	–109.495	3.575
1700	42.293	293.782	262.833	52.614	–177.899	–112.649	3.461
1800	43.859	296.243	264.621	56.920	–177.537	–108.820	3.158
1900	45.625	298.661	266.349	61.393	–177.025	–105.016	2.887
2000	47.549	301.049	268.024	66.051	–176.349	–101.243	2.644
2100	49.576	303.418	269.653	70.906	–175.497	–97.507	2.425
2200	51.648	305.772	271.242	75.967	–174.468	–93.817	2.227
2300	53.703	308.114	272.794	81.235	–173.266	–90.177	2.048
2400	55.681	310.441	274.314	86.705	–171.902	–86.594	1.885
2500	57.532	312.752	275.805	92.367	–170.393	–83 070	1.736
2600	59.211	315.042	277.271	98.206	–168.762	–79.608	1.599
2700	60.688	317.305	278.712	104.203	–167.037	–76.212	1.474
2800	61.941	319.536	280.130	110.336	–165.249	–72.880	1.360
2900	62.963	321.728	281.527	116.583	–163.429	–69.614	1.254
3000	63.752	323.876	282.903	122.921	–161.612	–66.410	1.156
3100	64.320	325.976	284.258	129.326	–159.830	–63.266	1.066
3200	64.681	328.025	285.594	135.778	–158.114	–60.179	0.982
3300	64.855	330.018	286.910	142.256	–156.492	–57.144	0.905
3400	64.865	331.955	288.207	148.743	–154.992	–54.156	0.832
3500	64.736	333.834	289.484	155.225	–153.636	–51.210	0.764
3600	64.489	335.654	290.741	161.687	–152.445	–48.301	0.701
3700	64.148	337.416	291.979	168.119	–151.434	–45.423	0.641
3800	63.734	339.122	293.197	174.514	–150.619	–42.568	0.585
3900	63.265	340.771	294.396	180.864	–150.008	–39.733	0.532
4000	62.758	342.367	295.575	187.166	–149.609	–36.911	0.482
4100	62.225	343.910	296.736	193.415	–149.428	–34.097	0.434
4200	61.680	345.403	297.877	199.610	–149.462	–31.284	0.389
4300	61.131	346.848	298.999	205.751	–149.717	–28.467	0.346
4400	60.586	348.247	300.102	211.837	–150.190	–25.643	0.304
4500	60.051	349.602	301.187	217.868	–150.874	–22.805	0.265
4600	59.531	350.917	302.254	223.847	–151.701	–19.955	0.227
4700	59.029	352.191	303.303	229.775	–152.775	–17.080	0.190
4800	58.547	353.429	304.335	235.654	–154.037	–14.179	0.154
4900	58.088	354.632	305.349	241.485	–155.480	–11.251	0.120
5000	57.651	355.801	306.346	247.272	–157.088	–8.292	0.087
5100	57.237	356.938	307.327	253.016	–158.837	–5.300	0.054
5200	56.846	358.046	308.292	258.720	–160.754	–2.272	0.023
5300	56.477	359.125	309.241	264.386	–162.809	0.796	–0.008
5400	56.130	360.177	310.174	270.016	–164.993	3.902	–0.038
5500	55.804	361.204	311.093	275.613	–167.295	7.051	–0.067
5600	55.498	362.207	311.997	281.178	–169.704	10.243	–0.096
5700	55.210	363.187	312.886	286.713	–172.211	13.478	–0.124
5800	54.940	364.145	313.762	292.220	–174.807	16.759	–0.151
5900	54.686	365.082	314.624	297.702	–177.271	20.060	–0.178
6000	54.448	365.999	315.472	303 158	–179.985	23.427	–0.204

PREVIOUS· June 1974 (1 atm) CURRENT· June 1974 (1 bar)

Strontium Oxide (SrO) $O_1Sr_1(g)$

$S°(298.15\ K) = 241.116 \pm 2.1\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = 193.72 \pm 62.8\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = 192.46 \pm 62.8\ kJ{\cdot}mol^{-1}$

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
$X^2\Delta_{3/2}$	0	2	$^2\phi_{7/2}$	22918.75	4	$^2\Delta_{5/2}$	27290.63	2
$^2\Delta_{5/2}$	3505.43	2	$^2\Pi_{1/2}$	23341.74	2	$^2\Delta_{3/2}$	32373.60	2
$^2\Delta_{3/2}$	10860.95	4	$^2\phi_{5/2}$	24058.42	2	$^2\Delta_{5/2}$	35785.83	4
$^2\Pi_{1/2}$	11062.00	4	$^2\Pi_{3/2}$	25593.13	2	$^2\Delta_{5/2}$	35886.20	2
$^2\phi_{5/2}$	12852.02	4	$^2\phi_{7/2}$	26121.50	2	$^2\Delta_{5/2}$	36615.00	4
$^2\Delta_{3/2}$	13569.27	4	$^2\Delta_{3/2}$	26673.04	2	$^2\Delta_{5/2}$	36785.00	4
$^2\phi_{5/2}$	15880.62	4						

$\omega_e = 1028.69\ cm^{-1}$ $\omega_ex_e = 3.51\ cm^{-1}$ $\sigma = 1$
$B_e = 0.402840\ cm^{-1}$ $\alpha_e = 0.00182\ cm^{-1}$ $r_e = 1.6872$ Å

Enthalpy of Formation

Based on the adopted ground state vibrational constants, a linear Birge–Sponer extrapolation yields $D_0° = 9.28$ eV (214.02 kcal·mol^{-1}). Applying a correction for the ionicity in the Ta–O bond,[1] we recalculate $D_0° = 8.57$ eV (199.94 kcal·mol^{-1}). This in turn leads to $\Delta_fH°$(TaO, g, 298.15 K) = 45.52 kcal·mol^{-1}, using auxiliary data.[2]

Inghram *et al.*[3] and Krikorian and Carpenter[4] have presented mass spectrometric evidence indicating that the predominant vapors in the vaporization of Ta–Ta_2O_5 mixtures in Ta Knudsen cells are TaO and TaO_2.

Source	Reaction	Data Points	T/K	$\Delta_rH°$(298.15 K), kcal·mol^{-1} 2nd law	$\Delta_rH°$(298.15 K), kcal·mol^{-1} 3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_fH°$(298.15 K), kcal·mol^{-1} 2nd law	$\Delta_fH°$(298.15 K), kcal·mol^{-1} 3rd law
3	A*	1	2022	—	147.31	-	-	+49.51
4	A	2	1927–2034	162.80	175.47	6.4	+65.00	+77.67
3	B*	5	2151–2278	193.95	144.81	−22.3 ± 14.1	+100.30	+51.26
4	B	3	2180–2271	166.53	172.90	2.8 ± 7.9	+72.98	+79.35
16	C	graph	1900–2900	54.15	93.33	17.5	54.15	93.33

*Recalculated pressures using Otvis and Stevenson method for estimating ionization cross sections.[4,5]
A: 0.6 Ta(cr) + 0.2 Ta_2O_5(cr) = TaO(g) B: 0.6 Ta(cr) + 0.2 Ta_2O_5(l) = TaO(g) C: Ta(cr) + 1/2 O_2(g) = TaO(g)

The discrepancies here are rather severe and indicate considerable uncertainty in the system studied. In addition to the standard difficulties in a Knudsen cell system and the subsequent assumptions used for a 2nd and 3rd law analysis, there is an additional problem of oxygen diffusing through the walls of the Ta Knudsen cell, followed by volatilization of TaO(g) from the outer surfaces.[4,6] Based on JANAF values for Ta_2O_5(cr) and Ta_2O_5(l), $\Delta_rH°$(298.15 K) for reaction (A) should be 4.25 kcal·mol^{-1} more positive than reaction (B). The 3rd law results of Krikorian and Carpetner[4] for reactions (A) and (B) differ by 2.57 kcal·mol^{-1} but the 2nd law results differ by 3.73 kcal·mol^{-1} in the wrong direction. The 3rd law results of Inghram *et al.*[3] differ by 2.50. It is interesting to note that if the pressures reported by Krikorian and Carpetner[4] are multiplied by a factor of 1000, a 3rd law analysis yields results in excellent agreement with the 3rd law results of Inghram *et al.*[3] 2nd law values would still be in disagreement, however, and serious 3rd law drifts would still be present. Drowart *et al.*[16] observed the vapors over a Ta wire at various oxygen pressures in the range 1900–2900 K. Our analysis of their graphically displayed results does not clarify the situation as there is again a large 3rd law drift. Inghram *et al.*[3] also measured the ion currents corresponding to ZrO(g) and TaO(g) over mixtures of ZrO_2(cr) and Ta(cr) in a Ta Knudsen cell. The reaction was stated as ZrO_2(cr) + Ta(cr) = ZrO(g) + TaO(g). A 2nd law analysis of seven data points yielded $\Delta_rH°$(2200 K) = 317 ± 7 kcal·mol^{-1} as reported by Inghram *et al.*[3] Using auxiliary data,[2] this leads to $\Delta_fH°$(TaO, g, 298.15 K) = 51 ± 12 kcal·mol^{-1}, where + 12 kcal·mol^{-1}reflects the additional uncertainty in $\Delta H°$(298.15 K) for ZrO(g). Goldstein *et al.*,[7] in studying the vaporization of $Nd_2O_3$from Ta Knudsen cells in the range 2040–2450 K, determined the enthalpy of reaction for Nd_2O_3(cr) + Ta(cr) = 2 NdO(g) + TaO(g). They reported $D_0° = 9.36 \pm 0.2$ eV for TaO(g). This leads to $\Delta_fH°$(TaO, g, 298.15 K) = 29.6 ± 5.0 kcal·mol^{-1}.

Brewer and Rosenblatt[17] have suggested Gibbs energy functions which are 1.38 to 2.14 cal·K^{-1}·mol^{-1} more positive than those adopted here. The reason for the difference is that Brewer and Rosenblatt[17] based their functions on low lying electronic states as observed in Ta^{++}(g). The $\Delta_fH°$(298.15 K) values derived from the 3rd law would increase by roughly 3.5–4.2 kcal·mol^{-1} with the drift becoming more positive by 2–3 cal·K^{-1}·mol^{-1} if we were to use Brewer and Rosenblatt's valves.

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

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_fH°$ (kJ·mol^{-1})	$\Delta_fG°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−8.766	193.721	193.721	INFINITE
100	29.105	208.958	267.528	−5.857	194.182	183.566	−95.885
200	29.398	229.177	243.870	−2.939	193.393	173.223	−45.241
250	29.921	235.789	241.615	−1.457	192.921	168.235	−35.151
298.15	30.600	241.116	241.116	0.	192.464	163.522	−28.648
300	30.628	241.305	241.116	0.057	192.447	163.343	−28.441
350	31.394	246.084	241.492	1.607	191.986	158.529	−23.659
400	32.136	250.325	242.336	3.196	191.541	153.780	−20.082
450	32.815	254.150	243.439	4.820	191.108	149.086	−17.305
500	33.424	257.639	244.687	6.476	190.683	144.439	−15.089
600	34.463	263.828	247.375	9.872	189.839	135.270	−11.776
700	35.344	269.208	250.118	13.363	188.999	126.242	−9.420
800	36.137	273.980	252.808	16.938	188.171	117.333	−7.661
900	36.875	278.280	255.403	20.589	187.363	108.527	−6.299
1000	37.564	282.201	257.890	24.311	186.575	99.810	−5.214
1100	38.201	285.812	260.266	28.100	185.799	91.171	−4.329
1200	38.779	289.161	262.536	31.950	185.027	82.603	−3.596
1300	39.297	292.286	264.706	35.854	184.256	74.099	−2.977
1400	39.759	295.215	266.781	39.807	183.492	65.654	−2.450
1500	40.173	297.973	268.770	43.804	182.742	57.263	−1.994
1600	40.549	300.577	270.677	47.840	182.007	48.922	−1.597
1700	40.900	303.046	272.509	51.913	181.279	40.626	−1.248
1800	41.237	305.394	274.272	56.020	180.539	32.373	−0.939
1900	41.572	307.632	275.969	60.160	179.770	24.163	−0.664
2000	41.915	309.773	277.606	64.335	178.971	15.994	−0.418
2100	42.272	311.827	279.187	68.544	178.142	7.865	−0.196
2200	42.650	313.802	280.716	72.790	177.286	−0.223	0.005
2300	43.050	315.707	282.196	77.075	176.402	−8.272	0.188
2400	43.475	317.548	283.631	81.401	175.487	−16.282	0.354
2500	43.923	319.332	285.023	85.771	174.539	−24.253	0.507
2600	44.393	321.063	286.376	90.186	173.551	−32.186	0.647
2700	44.882	322.748	287.692	94.650	172.514	−40.079	0.775
2800	45.385	324.389	288.974	99.163	171.417	−47.933	0.894
2900	45.898	325.991	290.223	103.727	170.249	−55.746	1.004
3000	46.417	327.555	291.441	108.343	168.993	−63.518	1.106
3100	46.937	329.086	292.631	113.011	167.630	−71.246	1.200
3200	47.454	330.584	293.794	117.730	166.142	−78.929	1.288
3300	47.962	332.052	294.931	122.501	128.049	−86.092	1.363
3400	48.459	333.492	296.044	127.322	126.662	−92.560	1.422
3500	48.940	334.903	297.134	132.192	125.316	−98.988	1.477
3600	49.402	336.288	298.202	137.110	124.010	−105.378	1.529
3700	49.843	337.648	299.250	142.072	122.741	−111.732	1.577
3800	50.260	338.983	300.278	147.077	121.509	−118.053	1.623
3900	50.652	340.294	301.288	152.123	120.309	−124.341	1.665
4000	51.018	341.581	302.279	157.207	119.141	−130.599	1.705
4100	51.356	342.845	303.253	162.326	118.002	−136.829	1.743
4200	51.667	344.086	304.210	167.477	116.889	−143.031	1.779
4300	51.950	345.305	305.152	172.658	115.799	−149.206	1.812
4400	52.205	346.502	306.078	177.866	114.730	−155.357	1.844
4500	52.433	347.678	306.990	183.098	113.679	−161.483	1.874
4600	52.635	348.833	307.887	188.352	112.644	−167.587	1.903
4700	52.811	349.967	308.770	193.624	111.621	−173.668	1.930
4800	52.963	351.080	309.640	198.913	110.608	−179.727	1.956
4900	53.091	352.174	310.497	204.216	109.603	−185.765	1.980
5000	53.197	353.247	311.341	209.531	108.603	−191.783	2.004
5100	53.282	354.302	312.173	214.855	107.606	−197.780	2.026
5200	53.348	355.337	312.993	220.187	106.610	−203.759	2.047
5300	53.395	356.354	313.802	225.524	105.612	−209.718	2.067
5400	53.425	357.352	314.599	230.865	104.610	−215.658	2.086
5500	53.440	358.332	315.385	236.208	103.602	−221.580	2.104
5600	53.440	359.295	316.161	241.553	102.586	−227.483	2.122
5700	53.427	360.241	316.926	246.896	101.561	−233.368	2.139
5800	53.401	361.170	317.681	252.238	−638.230	−236.433	2.129
5900	53.365	362.083	318.426	257.576	−639.492	−229.496	2.032
6000	53.318	362.979	319.161	262.910	−640.813	−222.535	1.937

PREVIOUS: December 1973 (1 atm) CURRENT. December 1973 (1 bar)

Continued on page 1813

Titanium Oxide, Alpha (α–TiO) CRYSTAL $M_r = 63.8794$ Titanium Oxide, Alpha (TiO) $O_1Ti_1(cr)$

$S°(298.15\ K) = 34.769 \pm 2.1\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs} = [1265]\ K$

$\Delta_fH°(0\ K) = -539.668 \pm 12.6\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -542.665 \pm 12.6\ kJ{\cdot}mol^{-1}$
$\Delta_{trs}H° = [4.2]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

Recent data tend to support our speculation[1] that previous calorimetric data refer to ill defined states of TiO(α, β) New combustion calorimetry[2] at 1100 K gave $\Delta_fH°(298.15\ K) = -129.9 \pm 1.1$ kcal mol^{-1} which is ~5 kcal·mol^{-1} more negative than two earlier combustion studies[3,4] near room temperature. The difference was attributed[2] to use of samples consisting of α–phase[2] or mainly β–phase.[3,4] This interpretation is reasonable but unproved, it is neither confirmed nor refuted by incomplete published descriptions of the samples. Previously, the samples[3,4] were assumed to be α phase since similar material gave a discontinuity in enthalpy data above 1200 K.

Lyon[5] proposed that $\Delta_fH°$ may be affected by vacancy concentration, which varies from ~14 to 15%[5] in samples of stoichiometric β–TiO obtained at normal pressure. Samples with vacancy concentrations dow to 0% have been prepared[6] at high pressure. PVT data[6] allowed calculation[5] of values of $\Delta_fH°$ for TiO(β, 0% vacancies) → TiO(β, 14% vacancies). These values, if valid, suggest that $\Delta_fH°$ should be quite different for vacancy free β–TiO and significantly different even for the normal range of vacancy concentrations. Ideal ordered α–TiO, containing 1/6 or 16.7% vacancies, should involve additional changes in volume[5] and $\Delta_fH°$. In summary, the discrepancy in $\Delta_fH°$ may arise from sample differences – phase, composition and vacancy concentration – or from bias in the reaction calorimetry.

Our choice of $\Delta_fH°$ is influenced by $\Delta_fG°$ values derived from oxygen potentials[7,8] over $TiO_x(0 < X < 1.5)$. We use solid state emf data[7] for many compositions in the range $0.6 < X < 1.6$; these are converted to $\Delta_fG(O_2)$ with the authors' results[7] for the reference couples Ta/Ta_2O_5 and "$TiO_{1.3}$", the integrated over appropriate ranges of x in order to obtain $\Delta_fG°$. For reaction C relating TiO(β) to Ti_2O_3 we obtain $\Delta_rG° = -38.20(1300\ K)$, $-37.49(1400\ K)$, $-36.82(1500\ K)$, $-36.180(1600\ K)$ and $-35.52(1700\ K)$ kcal·mol^{-1} with an estimated uncertainty of ±1 kcal·mol^{-1} (~3%). Combination with $\Delta_fG°$[9] of Ti_2O_3 yields $\Delta_fG°(TiO, \beta) = -131.5 + 23.5\ (T/1000)$, hopefully, the uncertainty does not exceed 1.5 kcal·mol^{-1}, based on a revised uncertainty of 1 kcal·mol^{-1} for Ti_2O_3.

Approximate values of $\Delta_fG°(TiO)$ may be derived from $TiO_{0.334}(cr)$ and Ti(cr). Calorimetric data[10] yield $\Delta_fG°(TiO_{0.334}) = -46.1 + 8.40\ (T/1000)$ for $1200 < T < 1700$; this equation excludes the added disordering entropy[10] which now is known to be included, at least partially, in order disorder transitions of the alloy near 800 K.[11] $\Delta_fG(O_2)$ in the range $0.334 < X < 0.5$ is approximated by limiting values, i.e., the mean from $X < 0.334$ and the univariant value[7] at $x = 0.6$, in order to get negative and positive limits for $\Delta_fG°(TiO)$. These limits differ by 1 to 2.5 kcal·mol^{-1} at 1300 to 1700 K; mean $\Delta_fG°$ values are $-102.0\ (1300\ K)$, $-96.8(1400\ K)$, $-92.6(1500\ K)$, $-89.3(1600\ K)$ and -86.0 kcal·mol^{-1}(1700 K). Equilibration with Ca/CaO and Mg/MgO[8] near 1200 K gave $\Delta_fG(O_2)$ for $X < 0.3$; we combine these by interpolation with values[7] at $X > 0.6$ to give $\Delta_fG°(TiO) = -107.3(1173\ K)$, $-106.6(1200\ K)$ and -103.8 kcal·mol^{-1}(1273 K). $\Delta_fG°$ values derived from Ti(cr) and $TiO_{0.334}(cr)$ are relatively uncertain, perhaps by 5 kcal·mol^{-1}, due to gaps in $\Delta_fG(O_2)$ and to greater uncertainty in emf and x.

$\Delta_fH°$ values from $\Delta_cH°$ and from 3rd law analyses of $\Delta_rG°$ are compared below. $\Delta_fH°$ from Ti_2O_3[7,9] is consistent with the new $\Delta_cH°$[2] but ~5 kcal·mol^{-1} more negative than the earlier value[3] which we assume to refer to β–TiO. $\Delta_fH°$ from Ti_2O_3[7,9] and from $\Delta_cH°$[3] could be made consistent if, as proposed by Charlu *et al.*,[2] $\Delta_tS°$ and S°(β) were increased by 3 cal·K^{-1}·mol^{-1}[see β TiO [9]]. If G. L. Humphrey[3] instead of T. V. Chartu *et al.*[2] were correct for α–TiO, $\Delta_fG(O_2)$ would have to be 14% larger than observed. The more uncertain $\Delta_fH°$ from $TiO_{0.334}$[7,9] is very temperature dependent (large δS); it agrees with T.V. Charlu *et al.*[2] at 1350 K and with[3] at 1700 K. $\Delta_fH°$ from Ti[7-9] is even more negative than.[2] We adopt $\Delta_fH° = -129.7$ kcal·mol^{-1} but increase the uncertainty to + 3 kcal·mol^{-1} to allow for possible uncertainties in the samples.

Source	Method	Reaction[a]	T/K	δS cal·K^{-1}·mol^{-1}	$\Delta_rH°(298.15\ K)$ kcal·mol^{-1}	$\Delta_fH°(298.15\ K)$,[b] kcal·mol^{-1} Authors	TiO(α)	TiO(β)
2	$\Delta_cH°$	A	1100–298	–	−96.05 ± 1.1	−129.86	−129.7	[−128.7]
3	$\Delta_cH°$	B	303–298	–	−101.61 ± 0.12	−123.9 ± 0.3	[−125.2]	−124.2
4	$\Delta_cH°$	B	293	–	−99.5	−124.5 ± 0.4	[−127.3]	−126.3
7,9 From Ti_2O_3	emf, $\Delta_rG°$	C	1300–1700	2.9	−52.77	–	[−130.0]	−129.0
7,9 From $TiO_{0.334}$	emf, $\Delta_fG°(O_2)$	D	1300–1700	−19.0	−127.5	–	[−128.5]	−127.5
7,9 From Ti(cr)	emf, $\Delta_fG(O_2)$	D	1273	–	−133.2	–	[−134.2]	−133.2
		E	1173–1200	−2.5	−135.4	–	−135.4	[−134.4]

[a] A) $TiO(\alpha?) + 1/2\ O_2(g) = TiO_2(rutile)$ B) $TiO(\beta?) + 1/2\ O_2 = TiO_2(rutile)$ C) $TiO(\beta) + 1/4\ O_2(g) = 1/2\ Ti_2O_3(cr)$
D) $Ti(\beta) + 1/2\ O_2(g) = TiO(\beta)$ E) $Ti(\beta) + 1/2\ O_2(g) = TiO(\alpha?)$.

[b] $\Delta_fH°$ in brackets calculated from $\Delta_{trs}H° = [1.0]$ kcal·mol^{-1}

Heat Capacity and Entropy

$C_p°$ is from data (52.6–296 K) of Shomate[12] and enthalpy data (357–1771 K) of Naylor.[13] $S°(298.15\ K) = 8.31$ cal·K^{-1}mol^{-1} is calculated from $C_p°$ based on $S°(50\ K) = 0.23$ cal·K^{-1}·mol^{-1}. Ideal, ordered α–TiO should have no configurational entropy at $T/K = 0$.[14] We assume that $C_p°(\alpha) = C_p°(\beta)$ and fit the enthalpy data (357–1200 K and 1273–1771 K) by a single curve after subtracting the apparent $\Delta_{trs}H° = 0.83$ kcal·mol^{-1} from points above T_{trs}. The single curve gives larger deviations than separate fits of the two regions, but the increases are of marginal significance.

Continued on page 1813

Enthalpy Reference Temperature = T_r = 298.15 K

Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	S°	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.000	0.000	INFINITE	−6.174	−539.668	−539.668	INFINITE
100	12.765	5.732	63.375	−5.764	−541.270	−532.352	278.072
200	30.681	20.585	38.164	−3.516	−542.394	−522.918	136.572
298.15	39.957	34.769	34.769	0.000	−542.665	−513.278	89.924
300	40.062	35.017	34.770	0.074	−542.665	−513.096	89.338
400	44.978	47.274	36 408	4.346	−542.491	−503.257	65.719
500	48.242	57.679	39.648	9.015	−542.092	−493.491	51.555
600	50.836	66.709	43.422	13.972	−541.541	−483.821	42.120
700	53.095	74.719	47.331	19.171	−540.857	−474.253	35.389
800	55.187	81.947	51.214	24.586	−540.035	−464.793	30.348
900	57.153	88.561	55.001	30.204	−539.111	−455.442	26.433
1000	59.078	94.682	58.667	36.016	−538.152	−446.197	23.307
1100	60.961	100.402	62.203	42.018	−537.219	−437.047	20.754
1200	62.802	105.785	65.613	48.206	−540.300	−427.861	18.624
1265.000	63.998	109.129	67.764	52.327	---- ALPHA <--> BETA ----		
1300	64.643	110.884	68.901	54.578	−538.700	−418.555	16.818
1400	66.442	115.741	72.075	61.133	−537.011	−409.376	15.274
1500	68.241	120.386	75.142	67.867	−535.248	−400.320	13.940
1600	70.040	124.848	78.110	74 781	−533.422	−391.384	12.777
1700	71.839	129.148	80.986	81.875	−531.546	−382.564	11.755
1800	73.597	133.304	83.778	89.147	−529.636	−373.856	10.849
1900	75.396	137.331	86.491	96.597	−527.704	−365.254	10.042
2000	77.153	141.243	89.131	104.224	−540.450	−356.300	9.306
2100	78.910	145.050	91.704	112.027	−539.263	−347.121	8.634
2200	80.668	148.762	94.214	120.006	−537.912	−338.002	8.025
2300	82.467	152.387	96.664	128.163	−536.394	−328.949	7.471
2400	84.224	155.934	99.060	136.497	−534.710	−319.965	6.964
2500	85.981	159.408	101.405	145.007	−532.861	−311.055	6.499

PREVIOUS: March 1967 CURRENT: December 1973

Titanium Oxide, Beta (β–TiO) CRYSTAL $M_r = 63.8794$ Titanium Oxide, Beta (TiO) $O_1Ti_1(cr)$

$S°(298.15\ K) = [38.077]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = [1265]\ K$
$T_{fus} = 2023 \pm 30\ K$

$\Delta_f H°(298.15\ K) = [-538.481]\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = [4.2]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [41.8]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of α–TiO by adding $\Delta_{trs} H°$ to the difference in $H°(1265\ K) - H°(298.15\ K)$ between α– and β–TiO. $\Delta_f G°$ data for β–TiO are reviewed on the table for α–TiO.[9] Values of $\Delta_f H°$ derived from $\Delta_f G°$ depend on the value of $S°$ (see Entropy). There are additional references on the $\Delta_f G°$ which deserve comment. Solid state emf data of Hoch *et al.*[18] are insufficient to yield $\Delta_f G°(\beta)$, especially in the direct way used by Drowart *et al.*[19] Their interpretation is inconsistent with phase diagrams[20,17] and extensive emf data[7] which show bivariant behavior in which $\Delta_f G(O_2)$ is a strong function of (O/Ti). It is not useful to reinterpret the emf data;[18] they show a temperature dependence of the wrong sign and we do not know the necessary electrode compositions. The often quoted $\Delta_f G°$ of Kubaschewski and Dench[21] is not an independent value since it assumes the correctness of the calorimetric data of the Bureau of Mines.[3,12,13] Kubaschewski's reassessment[22,8] of $\Delta_f G°(O_2)$ is superseded[9] due to new data.[7]

Heat Capacity and Entropy

We assume $C_p°(\beta) = C_p°(\alpha)$ as discussed on the table for α–TiO. $S°$ is calculated in a manner analogous to that of $\Delta_f H°$. $S°$ might be too low by as much as 3 or 4 $cal \cdot K^{-1} \cdot mol^{-1}$ [2] due to a possible uncertainty in $\Delta_{trs} H°$ (refer to Transition Data). The possibility exists because experimental samples[2–4,12,13] were not adequately characterized as to phase and vacancy concentration.

Phase Data

Stoichiometric TiO has been identified in two crystalline forms. High temperature β–TiO has a cubic NaCl–type structure,[23] while low temperature α–TiO has a closely related monoclinic structure.[24,25] Ideal α–TiO is an ordered array in which 1/6 of the lattice sites are vacant; half of the Ti and O atoms are missing alternately in every third (110) plane.[24] β–TiO obtained at normal pressures appears to have a lower and somewhat variable (~14–15%) vacancy concentration,[5] depending on conditions of preparation. Vacancy concentration can be reduced to arbitrary values (including zero) at high pressure by quenching from high temperature.[6] The process is reversed on reheating at normal pressure. Vacancy concentration[6,26] and vacancy disorder[20,25–27] in β–TiO appear to increase with increasing temperature, but definite conclusions are hampered since most data are for samples quenched to room temperature. Hilti[25] claimed two transitions: α→cubic (vacancy superlattice)→cubic (random vacancies). Jostsons and McDougall[20] designated the β– and α phases as γ and γ' in order to avoid confusion with other Ti–O alloys. The relatively wide homogeneity ranges of α– and β–TiO are summarized in recent phase diagrams[20, 17] and emf studies.[7] *Limits of stability of α–TiO and the identity of its adjacent phases are less well established*[20, 17] than for β phase. TiO is metallic, exhibiting weak paramagnetism[27] and superconductivity with T_c below 1 K.[26] Ordering of the vacancies by annealing had little effect on T_c.[26]

Transition Data

The nature and kinetics of α⇌β are crucial since we lack definite knowledge of the phases used in thermochemical studies. The transition α→β is more rapid than the reverse one. β–TiO is readily retained by quenching, but α can be obtained only by annealing[23 30] for several hours below T_{trs}. Moreover, there is disagreement as to whether the transition α→β proceeds directly[20] or via an intermediate peritectic decomposition, e.g. $Ti_2O + \beta\text{–}TiO_{1+x}$.[17] Emf data[7] seem more consistent with the latter, but none of the evidence is definitive.[17,20,24,27–30] Lyon[5] suggested that peritectic decomposition is an alternative to direct reduction of vacancy concentration on going from α to β (refer to Phase Data). The difference in vacancy concentration, if real, may preclude direct equilibrium between ideal α and normal β. This could invalidate calculation of $\Delta_{trs} S$ from $\Delta_{trs} H°$.[5]

Approximate ranges for T_{trs} include 1235–1270 K from enthalpy data;[13] 1235–1273 K from thermal analysis;[29] between 1223 and 1263 K,[20,24] between 1223 and 1288 K,[29] and between 1173 and 1223 K,[28,30] each based on the presence of α in samples quenched from various annealing temperatures. Later resistivity data[27] on Pearson's samples[28] suggest that T_{trs} is between 1233 and 1303 K. Hilti[25] reported 1253 K for the first transition and 1523 K for the second. The latter transition is not apparent in the enthalpy data.[13]

We adopt $T_{trs} = 1265$ K and arbitrarily take $\Delta_{trs} H° = 1.0\ kcal \cdot mol^{-1}$. The apparent enthalpy difference ($\Delta_f H° = 0.83\ kcal \cdot mol^{-1}$) at T_{trs} is equal to $\Delta_{trs} H°$ only if Naylor's sample[13] was originally α–TiO and returned to α form during drop calorimetry from above T_{trs}. Charlu *et al.*[2] proposed instead, based on the difference in $\Delta_c H°$ values, that $\Delta_{trs} H° = \sim 5\ kcal \cdot mol^{-1}$ and $\Delta_{trs} S° = \Delta_{trs} H°/T_{trs} = \sim 4\ cal \cdot K^{-1} \cdot mol^{-1}$. The resulting increase in $S°(\beta)$ would change our third law analysis of $\Delta_f G°$ for reactions C and D (see α–TiO). It would minimize the discrepancy between $\Delta_c H°$[3 4] and the third law $\Delta_f H°$ but would more than double the discrepancy (δS) in the temperature dependence of $\Delta_f G°(\beta)$ derived from Ti_2O_3.[7,9] We prefer to minimize δS even though the larger value is compatible with the estimated uncertainty in $\Delta_f G°(\beta)$.

Entropy calculations are available for processes somewhat related to α⇌β. The configurational entropy of TiO(β) with random vacancies was shown to be 2.0 $cal \cdot K^{-1} \cdot mol^{-1}$.[14] $\Delta_{fus} S°$ of 1.5 to 2.3 $cal \cdot K^{-1} \cdot mol^{-1}$ for TiO(β, 0% vacancies) → TiO(β, 14.4% vacancies) was calculated by Lyon[5] from compressibility, thermal expansion and a PV isotherm Taylor and Doyle[6] reported observing β TiO, presumably with much reduced vacancy concentration, at 56.4 kbar and 1153 K. This yields $\Delta_T \leq -80°$ assuming the $T_{trs} > 1233$ K at 1 atm. We estimate $\Delta V = -0.16\ cm^3 \cdot mol^{-1}$ from the densities[6,23] observed at 25°C and combine it with ΔP to calculate $\Delta_{trs} S° = \sim 2.6\ cal \cdot K^{-1} \cdot mol^{-1}$ for α→β. This calculation is highly uncertain; it is invalid if the transition is not an equilibrium one.

Fusion Data – Refer to the liquid table for details.

References - Refer to the liquid table

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	39.957	38.077	38.077	0.000	−538.481	−510.080	89.364
300	40.062	38.324	38.078	0.074	−538.480	−509.904	88.782
400	44.978	50.582	39.715	4.346	−538.307	−500.396	65.345
500	48.242	60.987	42.956	9.015	−537.908	−490.961	51.290
600	50.836	70.016	46.730	13.972	−537.356	−481.621	41.929
700	53.095	78.026	50.639	19.171	−536.673	−472.384	35.250
800	55.187	85.254	54.521	24.586	−535.851	−463.255	30.247
900	57.153	91.868	58.309	30.204	−534.927	−454.235	26.363
1000	59.078	97.990	61.974	36.016	−533.967	−445.321	23.261
1100	60.961	103.709	65.511	42.018	−533.035	−436.501	20.728
1200	62.802	109.093	68.921	48.206	−536.116	−427.646	18.615
1265.000	64.013	112.436	71.071	52.327	---- ALPHA <--> BETA ----		
1300	64.643	114.192	72.209	54.578	−534.515	−418.671	16.822
1400	66.442	119.048	75.382	61.133	−532.827	−409.822	15.291
1500	68.241	123.694	78.449	67.867	−531.063	−401.098	13.967
1600	70.040	128.155	81.417	74.781	−529.238	−392.492	12.814
1700	71.839	132.456	84.294	81.875	−527.362	−384.003	11.799
1800	73.597	136.612	87.086	89.147	−525.452	−375.625	10.900
1900	75.396	140.639	89.799	96.597	−523.520	−367.354	10.099
2000	77.153	144.551	92.439	104.224	−536.265	−358.732	9.369
2023.000	77.551	145.436	93.037	106.003	---- BETA <--> LIQUID ----		
2100	78.910	148.358	95.012	112.027	−535.079	−349.883	8.703
2200	80.668	152.069	97.521	120.006	−533.728	−341.095	8.099
2300	82.467	155.695	99.972	128.163	−532.210	−332.373	7.548
2400	84.224	159.242	102.368	136.497	−530.526	−323.720	7.046
2500	85.981	162.716	104.713	145.008	−528.677	−315.140	6.584

PREVIOUS: March 1967 CURRENT: December 1973

Titanium Oxide (TiO) LIQUID $M_r = 63.8794$

$S°(298.15\ K) = [60.140]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-493.939]\ kJ \cdot mol^{-1}$
$T_{fus} = 2023 \pm 30\ K$ $\Delta_{fus} H° = [41.8]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(TiO, l, 298.15\ K)$ is calculated from that of β–TiO by addition of $\Delta_{fus}H°$ and the enthalpy difference in enthalpy, $H°(2023\ K)$–$H°(298.15\ K)$, between β and liquid.

Heat Capacity and Entropy

$S°(298.15\ K)$ is calculated in a manner analogous to that used for $\Delta_f H°$. $C_p°$ is estimated as 8 $cal \cdot K^{-1}\ g \cdot atom^{-1}$. Below the assumed glass transition at 1200 K, $C_p°$ is taken to be the same as that of the crystal.

Fusion Data

T_{fus} was observed to be 1750°C,[31] 1760 ± 25°C[32] and >1750°C.[33] Incipient melting, partial melting and complete melting were observed[29] at approximately 1710°, 1730° and 1760°C, respectively. We adopt 1750 ± 30°C and estimate $\Delta_{fus}H°$ such that $\Delta_{fus}S°$ is 2.5 $cal \cdot K^{-1}$ $cal \cdot K^{-1} g \cdot atom$.[1] TiO does not melt congruently;[17,20,29,32,33] there are various interpretations of the liquidus curve.

Vaporization Data

The vapor over TiO(cr, l) is mainly TiO and Ti, so the residue increases in (O/Ti) ratio.[34]

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Titanium Oxide (TiO) $O_1Ti_1(l)$

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
0							
100							
200							
298.15	39.957	60.140	60.140	0.000	−493.939	−472.116	82.713
300	40.062	60.387	60.140	0.074	−493.938	−471.981	82.179
400	44.978	72.644	61.778	4.346	−493.765	−464.679	60.681
500	48.242	83.049	65.018	9.015	−493.366	−457.450	47.790
600	50.836	92.079	68.792	13.972	−492.814	−450.317	39.204
700	53.095	100.089	72.702	19.171	−492.131	−443.286	33.078
800	55.187	107.317	76.584	24.586	−491.309	−436.363	28.492
900	57.153	113.931	80.371	30.204	−490.385	−429.549	24.930
1000	59.078	120.053	84.037	36.016	−489.425	−422.841	22.087
1100	60.961	125.772	87.574	42.018	−488.493	−416.229	19.765
1200	62.802	131.156	90.984	48.206	−491.573	−409.579	17.829
1200.000	62.802	131.156	90.984	48.206	GLASS <−−> LIQUID TRANSITION		
1200.000	66.944	131.156	90.984	48.206			
1300	66.944	136.514	94.283	54.901	−489.651	−402.825	16.186
1400	66.944	141.475	97.479	61.595	−487.822	−396.215	14.783
1500	66.944	146.094	100.567	68.290	−486.098	−389.733	13.572
1600	66.944	150.414	103.549	74.984	−484.492	−383.361	12.515
1700	66.944	154.473	106.427	81.678	−483.016	−377.086	11.586
1800	66.944	158.299	109.203	88.373	−481.684	−370.895	10.763
1900	66.944	161.919	111.883	95.067	−480.507	−364.772	10.028
2000	66.944	165.352	114.472	101.762	−494.186	−358.254	9.357
2023.000	66.944	166.118	115.054	103.301	−−−− BETA <−−> LIQUID −−−−		
2100	66.944	168.619	116.973	108.456	−494.108	−351 460	8.742
2200	66.944	171.733	119.392	115.150	−494.041	−344.668	8.183
2300	66.944	174.709	121.733	121.845	−493.986	−337.880	7.673
2400	66.944	177.558	124.000	128.539	−493.942	−331.094	7.206
2500	66.944	180.291	126.197	135.234	−493.909	−324.309	6.776
2600	66.944	182.916	128.328	141.928	−493.886	−317.526	6.379
2700	66.944	185.443	130.397	148.622	−493.874	−310.743	6.012
2800	66.944	187.877	132.407	155.317	−493.872	−303.960	5.670
2900	66.944	190.226	134.360	162.011	−493.880	−297.178	5.353
3000	66.944	192.496	136.261	168.706	−493.898	−290.395	5.056
3100	66.944	194.691	138.110	175.400	−493.925	−283.611	4.779
3200	66.944	196.816	139.912	182.094	−493.962	−276.826	4.519
3300	66.944	198.876	141.668	188.789	−494.006	−270.040	4.274
3400	66.944	200.875	143.380	195.483	−494.060	−263.252	4.044
3500	66.944	202.815	145.050	202.178	−494.121	−256.463	3.828
3600	66.944	204.701	146.681	208.872	−494.190	−249.672	3.623
3700	66.944	206.535	148.274	215.566	−903.365	−235.090	3.319
3800	66.944	208.321	149.831	222.261	−902.214	−217.044	2.983
3900	66.944	210.060	151.353	228.955	−901.125	−199.027	2.666
4000	66.944	211.754	152.842	235.650	−900.098	−181.038	2.364
4100	66.944	213.407	154.299	242.344	−899 129	−163.074	2.078
4200	66.944	215.021	155.726	249.038	−898.218	−145.133	1.805
4300	66.944	216.596	157.123	255.733	−897.362	−127.212	1.545
4400	66.944	218.135	158.492	262.427	−896.559	−109.311	1.298
4500	66.944	219.639	159.835	269.122	−895.809	−91.428	1.061

PREVIOUS: March 1967 CURRENT: December 1973

Titanium Oxide (TiO) $O_1Ti_1(l)$

Titanium Oxide (TiO) CRYSTAL(α–β)-LIQUID $M_r = 63.8794$ Titanium Oxide (TiO) $O_1Ti_1(cr,l)$

0 to 1265 K crystal, alpha
126 to 2023 K crystal, beta
above 2023 K liquid

Refer to the individual tables for details.

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.000	0.000	INFINITE	−6.174	−539.668	−539.668	INFINITE
100	12.765	5.732	63.375	−5.764	−541.270	−532.352	278.072
200	30.681	20.585	38.164	−3.516	−542.394	−522.918	136.572
298.15	39.957	34.769	34.769	0.000	−542.665	−513.278	89.924
300	40.062	35.017	34.770	0.074	−542.665	−513.096	89.338
400	44.978	47.274	36.408	4.346	−542.491	−503.257	65.719
500	48.242	57.679	39.648	9.015	−542.092	−493.491	51.555
600	50.836	66.709	43.422	13.972	−541.541	−483.821	42.120
700	53.095	74.719	47.331	19.171	−540.857	−474.253	35.389
800	55.187	81.947	51.214	24.586	−540.035	−464.793	30.348
900	57.153	88.561	55.001	30.204	−539.111	−455.442	26.433
1000	59.078	94.682	58.667	36.016	−538.152	−446.197	23.307
1100	60.961	100.402	62.203	42.018	−537.219	−437.047	20.754
1200	62.802	105.785	65.613	48.206	−540.300	−427.861	18.624
1265.000	63.998	109.129	67.764	52.327	ALPHA <− −> BETA		
1265.000	64.013	112.436	67.764	56.511	TRANSITION		
1300	64 643	114.192	68.990	58.763	−534.515	−418.671	16.822
1400	66.442	119.048	72.394	65.317	−532.827	−409.822	15.291
1500	68.241	123.694	75.660	72.051	−531.063	−401.098	13.967
1600	70.040	128.155	78.802	78.965	−529.238	−392.492	12.814
1700	71.839	132.456	81.833	86.059	−527.362	−384.003	11.799
1800	73.597	136.612	84.761	93.331	−525.452	−375.625	10.900
1900	75.396	140.639	87.597	100.781	−523.520	−367.354	10.099
2000	77.153	144.551	90.347	108.409	−536.265	−358.731	9.369
2023.000	77.551	145.436	90.968	110.188	BETA <− −> LIQUID		
2023.000	66.944	166.118	90.968	152.028	TRANSITION		
2100	66.944	168.619	93.770	157.182	−494.108	−351.460	8.742
2200	66.944	171.733	97.243	163.877	−494.041	−344.668	8.183
2300	66.944	174.709	100.547	170.571	−493.986	−337.880	7.673
2400	66.944	177.558	103.697	177.266	−493.942	−331.094	7.206
2500	66.944	180.291	106.707	183.960	−493.909	−324.309	6.776
2600	66.944	182.916	109.588	190.654	−493.886	−317.526	6.379
2700	66.944	185.443	112.351	197.349	−493.874	−310.743	6.012
2800	66.944	187.877	115.005	204.043	−493.872	−303.960	5.670
2900	66.944	190.226	117.558	210.738	−493.880	−297.178	5.353
3000	66.944	192.496	120.019	217.432	−493.898	−290.395	5.056
3100	66.944	194.691	122.392	224.126	−493.925	−283.611	4.779
3200	66.944	196.816	124.685	230.821	−493.962	−276.826	4.519
3300	66.944	198.876	126.902	237.515	−494.006	−270.040	4.274
3400	66.944	200.875	129.048	244.210	−494.060	−263.252	4.044
3500	66.944	202.815	131.129	250.904	−494.121	−256.463	3.828
3600	66.944	204.701	133.146	257.598	−494.190	−249.672	3.623
3700	66.944	206.535	135.105	264.293	−903.365	−235.090	3.319
3800	66.944	208.321	137.008	270.987	−902.214	−217.044	2.983
3900	66.944	210.060	138.859	277.682	−901.125	−199.027	2.666
4000	66.944	211.754	140.661	284.376	−900.098	−181.038	2.364
4100	66.944	213.408	142.415	291.070	−899.129	−163.074	2.078
4200	66.944	215.021	144.124	297.765	−898.218	−145.133	1.805
4300	66.944	216.596	145.791	304.459	−897.362	−127.212	1.545
4400	66.944	218.135	147.418	311.154	−896.559	−109.311	1.298
4500	66.944	219.639	149.006	317.848	−895.809	−91.428	1.061

PREVIOUS: CURRENT: December 1973

Titanium Oxide (TiO) $O_1Ti_1(cr,l)$

Titanium Oxide (TiO) IDEAL GAS $M_r = 63.8794$ Titanium Oxide (TiO) $O_1Ti_1(g)$

$S°(298.15\ K) = 233.474 \pm 0.25\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = 53.93 \pm 8.4\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = 54.39 \pm 8.4\ kJ{\cdot}mol^{-1}$

Electronic States and Molecular Constants

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	ω_ex_e, cm^{-1}	α_e, cm^{-1}	B_e, cm^{-1}	r_e, Å	Source
$X^3\Delta$	0	2	1008.26	4.13	0.00303	0.5354	1.620	1,2
	96.4	2						
	197.5	2						
$E^3\Pi$	11800.0	6	919.	[3.8]	[0.0029]	[0.5134]	[1.654]	3,4
$A^3\phi$	14019.4	2	867.71	3.94	0.00318	0.50734	1.664	1,2
	14192.3	2						
	14360.7	2						
$B^3\Pi$	16226.4	2	873.	4.	[0.0032]	0.5079	1.663	2,4
	16248.0	2						
	16264.2	2						
$C^3\Delta$	19341.7	2	837.86	4.546	0.0029	0.4889	1.695	1,2
	19437.4	2						
	19531.6	2						
$a^1\Delta$	[1000.]	2	1016.3	3.93	[0.003]	0.5377	1.616	1,3-7
$d^1\Sigma^+$	[3219.]	1	1023.8	4.64	0.00337	0.5490	1.600	1,4
$b^1\Pi$	[12273.]	2	918.7	3.75	0.00286	0.5134	1.654	1,4
$c^1\phi$	[18841.]	2	916.7	4.33	[0.0032]	0.5228	1.639	1,4
$f^1\Delta$	[20069.]	2	[933.]	[4.2]	[0.003]	0.5037	1.670	8,5,4
$e^1\Sigma$	[27517.]	1	853.9	4.7	0.0025	0.4892	1.694	9,5,4

Enthalpy of Formation

$\Delta_fH°(298.15\ K) = 13.0 \pm 2\ kcal{\cdot}mol^{-1}$ and $D_0° = 158.5 \pm 2\ kcal{\cdot}mol^{-1}$ are selected from reactions A, B, C and E[16] which are summarized below. The first three are isomolecular exchange reactions studied by mass spectrometry.[13,14] Reaction E is obtained from univariant Ti_2O_3–Ti_3O_5 by combining Knudsen effusion with the pressure ratio (TiO_2/TiO) = 0.246 obtained from mass spectrometry.[16] We use the same analysis[16] for (E),[17] although the condensed phase may not be univariant. We presume that the smaller $D_0° = 145.4\ kcal{\cdot}mol^{-1}$ from reaction D is due to bias in the mass–spectrometric values[15] for the partial pressure of O(g). Larger values of $D°$ from sublimation[17,19] and vaporization[18] of TiO are subject to bias due to presence of species other than TiO in the vapor and to unknown liquid activities. Activities of TiO in $TiO_x(cr)$ are very close to unity at $x = 1.0$–1.1 and 1900 K according to emf data.[20]

The analysis of Drowart *et al.*[14] was the key to resolution of the discrepancy in $D_0°$;[21] later studies[13,16] confirmed their analysis. Our analysis uses $D_0°(GeO, g) = 156.4 \pm 1.5$, $D_0°(ScO, g) = 160.4 \pm 2.0$, and $D_0°(YO, g) = 170.4 \pm 2.5\ kcal{\cdot}mol^{-1}$ with other auxiliary data and newly calculated Gibbs–energy functions, all of which are essentially consistent with Drowart *et al.*[14,22] Our selected $D_0°(TiO) = 158.5 \pm 2\ kcal{\cdot}mol^{-1}$ may be compared with 174.5 and 156.3 kcal·mol^{-1} calculated by linear Birge–Sponer extrapolation of present[1] and older[23] vibrational constants of $X^3\Delta$. Kushawaha[24] used the older constants in construction of RKRV potential energy curves and thereby estimated $D_0° = 165.4\ kcal{\cdot}mol^{-1}$. He also derived $D_0° = 167.8 \pm 20\ kcal{\cdot}mol^{-1}$ from a chemiluminescent reaction,[10] but we dismiss this since auxiliary data for KO and TiCl were estimates.

Source	Method	Reaction[a]	T/K	Data Points	$\delta S°$ cal·K^{-1}·mol^{-1}	$\Delta_rH°$(298.15 K), kcal mol 2nd law	3rd law	$\Delta_fH°$(298.15 K) kcal·mol^{-1}	$D_0°$
13	Mass spec.	A	2145–2418	9	−6.4 ± 5.0	−11.5 ± 11.3	3.2 ± 2.8	11.7 ± 3.4	159.8
	Mass spec.	B	~2023–2417	24[b]	0.2 ± 1.5	−2.6 ± 3.3	−3.0 ± 1.5	14.0 ± 2.7	157.4
14	Mass spec.	B	1951–2463	Eqn.	0.0 ± 0.1	−3.0	−3.0	14.0 ± 2.4	157.4
	Mass spec.	C	2313	1	-	-	−12.0	13.0 ± 3.0	158.5
15	Mass spec.	D	2015–2240	12, 6	−0.2 ± 2.6	145.2 ± 5.4	146.5 ± 1.6	26.1 ± 2	145.4
16	Knudsen eff.	E	1937–2044	12	−2.0 ± 3.6	150.6 ± 7.1	154.7 ± 0.8	12.3 ± 3.5	159.1
17	Knudsen eff.	E	1971–2085	15	0.0 ± 12	152.0 ± 2.5	152.0 ± 2.8	9.7 ± 3.6	161.8
	Knudsen eff.	F	1847–1968	8	11 ± 3	157.1 ± 5	135.1 ± 3	6.4 ± 4	165.0
18	Mass spec.	G	2027–2072	2	48	225.	125.5 ± 4	7.5 ± 7	164.0

[a] A) $TiO(g) + Ge(g) = Ti(g) + GeO(g)$; B) $TiO(g) + Sc(g) = Ti(g) + ScO(g)$;
C) $TiO(g) + Y(g) = Ti(g) + YO(g)$; D) $TiO(g) = Ti(g) + O(g)$ from difference of two observed reactions $TiO_2(g) = O + TiO$ and $TiO_2 + Ti = 2\ TiO$;
E) $2\ Ti_2O_3(cr) = Ti_3O_5(\beta) + TiO(g)$; F) $TiO(high) = TiO(g)$
G) $TiO(l) \rightarrow TiO(g)$

[b] Extreme points selected from large data set.

Continued on page 1813

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−9.630	53.934	53.934	INFINITE
100	33.880	198 046	262.006	−6.396	55.155	44.842	−23.423
200	31.771	220.717	236.408	−3.138	55.040	34.491	−9.008
250	31.908	227.809	234.005	−1.549	54.737	29.387	−6.140
298.15	32.476	233.474	233.474	0.	54.392	24.535	−4.298
300	32.502	233.675	233.474	0.060	54.378	24.350	−4.240
350	33.263	238.741	233.873	1.704	53.997	19.375	−2.892
400	34.021	243.233	234.767	3.386	53.605	14.456	−1.888
450	34.702	247.280	235.937	5.105	53.208	9.586	−1.113
500	35.285	250.968	237.258	6.855	52.804	4.760	−0.497
600	36.176	257.485	240.100	10.431	51.975	−4.771	0.415
700	36 786	263.110	242.995	14.081	51.109	−14.161	1.057
800	37.212	268.051	245.824	17.782	50.217	−23.425	1.529
900	37.518	272.453	248.543	21.519	49.261	−32.573	1.891
1000	37.745	276.418	251.136	25.283	48.172	−41.609	2.173
1100	37.918	280.024	253.600	29.066	46.886	−50.527	2.399
1200	38.052	283.330	255.942	32.865	41.416	−59.198	2.577
1300	38.158	286.380	258.168	36.676	40.455	−67.545	2.714
1400	38.245	289.211	260.285	40.496	39.409	−75.814	2.829
1500	38.319	291.852	262.302	44.324	38.267	−84.005	2.925
1600	38.386	294.327	264.227	48.160	37.014	−92.116	3.007
1700	38.450	296.656	266.067	52.001	35.637	−100.145	3.077
1800	38.516	298.856	267.828	55.850	34.124	−108.089	3.137
1900	38.588	300.940	269.517	59.705	32.461	−115.945	3.188
2000	38.669	302.922	271.138	63.568	15.951	−123.256	3.219
2100	38.762	304.810	272.697	67.439	13.206	−130.149	3.237
2200	38.869	306.616	274.198	71.321	10.459	−136.911	3.251
2300	38.992	308.346	275.645	75.213	7.713	−143.548	3.260
2400	39.132	310.009	277.042	79.120	4.969	−150.066	3.266
2500	39.290	311.609	278.393	83.040	2.229	−156.469	3.269
2600	39.466	313.154	279.701	86.978	−0.505	−162.763	3.270
2700	39.661	314.647	280.967	90.934	−3.232	−168.952	3.269
2800	39.874	316.093	282.196	94.911	−5.948	−175.040	3.265
2900	40.105	317.496	283.389	98.910	−8.651	−181.032	3.261
3000	40.352	318.860	284.549	102.932	−11.341	−186.930	3.255
3100	40.614	320.187	285.677	106.981	−14.014	−192.738	3.248
3200	40.890	321.481	286.776	111.056	−16.670	−198.462	3.240
3300	41.179	322.744	287.847	115.159	−19.306	−204.102	3.231
3400	41.478	323.978	288.892	119.292	−21.921	−209.662	3.221
3500	41.787	325.184	289.911	123.455	−24.513	−215.146	3.211
3600	42.103	326.366	290.908	127.649	−27.082	−220.557	3.200
3700	42.425	327.524	291.882	131.876	−438.725	−218.108	3.079
3800	42.751	328.660	292.835	136.135	−440.010	−212.127	2.916
3900	43.080	329.774	293.768	140.426	−441.324	−206.113	2.761
4000	43.409	330.869	294.681	144.751	−442.666	−200.065	2.613
4100	43.738	331.945	295.577	149.108	−444 034	−193.983	2.471
4200	44.064	333.003	296.456	153.498	−445 427	−187.868	2.336
4300	44.386	334.044	297.318	157.921	−446.843	−181.719	2.207
4400	44.703	335.068	298.164	162.375	−448.281	−175.537	2.084
4500	45.015	336.076	298.996	166.861	−449.739	−169.322	1.965
4600	45.319	337.068	299.812	171.378	−451.216	−163.074	1.852
4700	45.614	338.046	300.616	175.925	−452.711	−156.794	1.743
4800	45.901	339.010	301.405	180.500	−454.222	−150.482	1.638
4900	46.178	339.959	302.183	185.104	−455.750	−144.138	1.537
5000	46.444	340.895	302.947	189.736	−457.293	−137.763	1.439
5100	46.699	341.817	303.701	194.393	−458.850	−131.357	1.345
5200	46.943	342.726	304.442	199.075	−460.421	−124.920	1.255
5300	47.174	343.622	305.173	203.781	−462.005	−118.453	1.167
5400	47.394	344.506	305.893	208.509	−463.602	−111.956	1.083
5500	47.602	345.378	306.603	213.259	−465.211	−105.430	1.001
5600	47.797	346.237	307.303	218.029	−466.833	−98.873	0.922
5700	47.980	347.085	307.994	222.818	−468.467	−92.288	0.846
5800	48.150	347.921	308.675	227.625	−470.113	−85.674	0.772
5900	48.309	348.745	309.347	232.448	−471.772	−79.032	0.700
6000	48.455	349.558	310.011	237.286	−473.442	−72.361	0.630

PREVIOUS· December 1973 (1 atm)   CURRENT· December 1973 (1 bar)

Titanium Oxide (TiO) $O_1Ti_1(g)$

Vanadium Oxide (VO) CRYSTAL $M_r = 66.9409$ Vanadium Oxide (VO) $O_1V_1(cr)$

$S°(298.15\ K) = 39.011 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2063 \pm 10\ K$

$\Delta_f H°(0\ K) = -429.715 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -431.789 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [54.4]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpies of formation for the vanadium oxides are based on the combustion studies by Mah and Kelley.[1] The adopted value is $\Delta_f H°(VO, cr, 298.15\ K) = -103.2\ kcal \cdot mol^{-1}$, as reported by Mah and Kelley.[1] For more details, refer to the V_2O_5(cr) table.[2] We increase their stated uncertainty limits of $+0.3\ kcal \cdot mol^{-1}$ to $\pm 1.5\ kcal \cdot mol^{-1}$ so as to more adequately include all uncertainties in the experimental procedure, rather than just the scatter in the final results.

Other enthalpy of formation results for VO(cr) derived from combustion studies are reported as $-102\ kcal \cdot mol^{-1}$ by Samsonov[3] and $-102 \pm 1\ kcal \cdot mol^{-1}$ by Vol'f and Ariya.[4] However, the latter study[4] also reported a corresponding result for V_2O_5(cr) which is 5.4 $kcal \cdot mol^{-1}$ more negative than the adopted JANAF value.[2] Older work by Kobayashi[5] involving water vapor equilibrium on vanadium and its oxides and by Mixter[6] involving sodium peroxide fusions are not considered.

Heat Capacity and Entropy

Todd and Bonnickson[7] measured the heat capacity of VO(cr) in the region 55–296 K. The sample, estimated to be 98.2% pure, was prepared by heating a mixture of V(cr) and V_2O_3(cr) in a hydrogen atmosphere. The heat capacity results showed an anomaly similar to that found by Anderson[8] for V_2O_3(cr). Todd and Bonnickson[7] concluded that the 20 $cal \cdot K^{-1} \cdot mol^{-1}$ in excess to that expected for a smooth $C_p°$ curve in the region 168–191 K was evidence of either an incomplete reaction in preparing VO(cr) or subsequent disproportionation. Experimental data in this region were not reported. Using the Debye function D(398/T) as suggested by Todd and Bonnickson,[7] we calculate $S°(50\ K) = 0.297\ cal \cdot K^{-1} \cdot mol^{-1}$ and $H°(50\ K) - H°(0\ K) = 11.051\ cal \cdot mol^{-1}$. The data are graphically curve fitted assuming a smooth sequence of "data points" in the region 168–191 K. Near 298.15 K the heat capacity data of Todd and Bonnickson[7] and the derivative of the smoothed enthalpy data of Orr[9] were constrained to join smoothly. Orr[9] used the same sample as did Todd and Bonnickson[7] and measured the enthalpy (fourteen data points) in the region 394–1698 K. The heat capacities derived from the Orr[9] data were extrapolated to T_{fus} and above.

The heat capacity, entropy and enthalpy values at 298 15 K reported by Chernyaev *et al.*[10] for VO_x, where $x = 0.86$, 0.99, 1.24 and 1.30, led to values for VO(cr) which are considerably lower than our adopted values. For example, the $S°(298.15\ K)$ value derived from the data of Chernyaev *et al.*[10,22] is roughly 1.3 $cal \cdot K^{-1} \cdot mol^{-1}$ lower than our adopted value.

Phase Data

Vanadium monoxide crystallizes in the cubic NaCl type structure and is stable over a wide range of composition, roughly between the limit $VO_{0.80}$ and $VO_{1.30}$. Details and many references may be found in Stringer[20] and Alexander and Carlson.[21]

Transition Data

There exists a large volume of literature dealing with transitions in the vanadium oxide condensed phases. These various oxides show widely varying electric and magnetic properties, as is discussed by Adler.[11] In the case of VO(cr), which has a wide homogeneity range, the reported data in the region of 120 K is conflicting. Sample purity, stoichiometry, and preparation undoubtedly play a major role in the appearance or lack of appearance of a possible transition. Much of the literature does not provide adquate sample characterization for an unequivical analysis of the data.

Conductivity measurements by Morin[12] on single crystals of VO(cr) and numerous measurements, including NMR, by Warren *et al.*[13] indicated a transition in the region 114–126 K and 88–125 K, respectively. The transition was described by Morin[12] as a *semiconductor metal* type. This is further discussed by Zhuze *et al.*[14] and Hyland.[15] However, Kawano *et al.*[16] and Takei and Koide[17] presented evidence on electric and magnetic properties and thermoelectric power for various vanadium monoxides within its homogeneity range which did not indicate any transition. Recent studies by Warren *et al.*[18] also indicated no evidence of a transition and, in addition, stated that the sample used in a previous study[13] was mainly V_2O_3(cr) as determined by x-ray analysis. Many more references on this subject may be found in the compilation by Neuberger[19] and in a review of the V–O system by Stringer.[20]

We conclude that there is no transition below T_{fus} for VO(cr) based primarily on the work cited above.[16-18]

Fusion Data – Refer to the liquid table for details.

Sublimation Data

At temperatures approaching T_{fus}, VO(cr) is reported to yield a vapor containing V(g), VO(g), and VO_2(g).[2]

References

[1] A. D. Mah and K. K. Kelley, U. S. Bur. Mines RI 5858, (1961).
[2] JANAF Thermochemical Tables: V_2O_5(cr), 6-30-73; VO(g), 12-31-73.
[3] G. V. Samsonov, Ukrain. Khim. Zhur. 23, 287 (1957); Chem. Abstr. 52, 1826g (1958).
[4] E. Vol'f and S. M. Ariya, J. Gen. Chem. USSR 29, 2433 (1959).
[5] M. Kobayashi, Bull. Chem. Soc. Japan 8, 231 (1933); Science Repts. Tohoku Imp. Univ., 1st Ser. 22, 1240 (1933).

Continued on page 1814

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−6.908	−429.715	−429.715	INFINITE
100	13.895	6.730	71.088	−6.436	−431.184	−422.473	220.677
200	34.100	23.035	42.859	−3.965	−432.005	−413.352	107.956
298.15	45.501	39.011	39.011	0.000	−431.789	−404.210	70.816
300	45.647	39.293	39.012	0.084	−431.778	−404.039	70.350
400	49.580	53.063	40.863	4.880	−431.032	−394.899	51.569
500	51.651	64.356	44.466	9.945	−430.157	−385.966	40.322
600	53.530	73.940	48.599	15.204	−429.199	−377.216	32.840
700	55.343	82.329	52.831	20.648	−428.158	−368.633	27.508
800	57.099	89.834	56.995	26.271	−427.037	−360.206	23.519
900	58.803	96.658	61.029	32.067	−425.846	−351.922	20.425
1000	60 463	102.940	64.910	38.030	−424.586	−343.776	17.957
1100	62.086	108.779	68.635	44 158	−423.259	−335.758	15.944
1200	63.677	114.250	72.211	50.446	−421.879	−327.864	14.272
1300	65 243	119.408	75.645	56.892	−420.450	−320.087	12.861
1400	66.791	124.300	78.947	63.494	−418.983	−312.422	11.657
1500	68.325	128.961	82.127	70.250	−417.478	−304.863	10.616
1600	69.842	133.419	85.195	77 159	−415.936	−297.405	9.709
1700	71.351	137.698	88.158	84.218	−414.366	−290.045	8.912
1800	72.851	141.819	91.025	91.429	−412.774	−282.778	8.206
1900	74.339	145.798	93.804	98.788	−411.171	−275.599	7.577
2000	75.847	149.649	96.500	106.297	−409.565	−268.506	7.013
2063.000	76.747	152.015	98.160	111.104	--- CRYSTAL <--> LIQUID ---		
2100	77.298	153.385	99.121	113.954	−407.967	−261.492	6.504
2200	78.781	157.015	101.670	121.758	−429.269	−254.449	6.041
2300	80.250	160.549	104.154	129.710	−427.853	−246.534	5.599
2400	81.718	163.996	106.576	137.808	−426.302	−238.684	5.195
2500	83.183	167.361	108.940	146.053	−424.615	−230.900	4.824
2600	84.646	170.652	111.250	154.445	−422.792	−223.187	4.484

PREVIOUS: CURRENT: December 1973

Vanadium Oxide (VO) LIQUID $M_r = 66.9409$

$S°(298.15\ K) = [69.137]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 2063 \pm 10\ K$

$\Delta_f H°(298.15\ K) = [-370.901]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = [54.4]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(VO, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the differences in enthalpy, $H°(2063\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is estimated as 7.5 $cal{\cdot}K^{-1}$ g atom.[1] Below the assumed transition temperature at 1200 K, $C_p°$ is assumed to be the same as in the crystal. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Alexander and Carlson[1] proposed a phase diagram for the V–VO system based on melting point determinations, differential thermal analysis, metallographic observations, and x-ray parametric measurements. These authors[1] reported that VO(cr) melts congruently at 2063 ± 10 K. We adopt this value for T_{fus}. In a phase diagram proposed by Stringer[2] a melting temperature of 1998 K was suggested but the melting was not congruent.

VO(cr) has a sodium chloride structure and is stable over a wide range of composition, as is discussed, for example by Stringer.[2] $\Delta_{fus}H°$ is estimated based on $\Delta_{fus}S° = 6.3\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ as in NaCl.[3] Since VO(cr) has a defect structure, a comparison with the $\Delta_{fus}S°$ value of NaCl is not entirely satisfactory. We make this comparison, however, pending further data.

Vaporization Data

There are no data available in the literature dealing with the vaporization of VO(l). We anticipate substantial decomposition to occur during heat treatment of VO(l). See VO(g) table for further information.[3]

References

[1] D. G. Alexander and O. N. Carlson, Met. Trans. 2, 2805 (1971).
[2] J. Stringer, J. Less Common Metals 8, 1 (1965).
[3] JANAF Thermochemical Tables: NaCl(cr), 9–30–64; VO(g), 12–31–73.

Vanadium Oxide (VO) $O_1V_1(l)$

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	45.501	69.137	69.137	0.000	−370.901	−352.304	61.722
300	45.647	69.419	69.138	0.084	−370.890	−352.189	61.322
400	49.580	83.188	70.988	4.880	−370.144	−346.062	45.191
500	51.651	94.481	74.592	9.945	−369.269	−340.141	35.534
600	53.530	104.066	78.725	15.204	−368.311	−334.403	29.112
700	55.343	112.454	82.956	20.648	−367.270	−328.833	24.538
800	57.099	119.959	87.121	26.271	−366.149	−323.418	21.117
900	58.803	126.783	91.154	32.067	−364.958	−318.147	18.465
1000	60.463	133.065	95.035	38.030	−363.698	−313.013	16.350
1100	62.086	138.904	98.761	44.158	−362.371	−308.008	14.626
1200	63.676	144.375	102.336	50.446	−360.991	−303.127	13.195
1200.000	63.676	144.375	102.336	50.446	GLASS <--> LIQUID TRANSITION		
1200.000	62.760	144.375	102.336	50.446			
1300	62.760	149.399	105.766	56.722	−359.733	−298.357	11.988
1400	62.760	154.050	109.051	62.998	−358.591	−293.679	10.957
1500	62.760	158.380	112.197	69.274	−357.566	−289.079	10.067
1600	62.760	162.430	115.211	75.550	−356.656	−284.543	9.289
1700	62.760	166.235	118.102	81.826	−355.870	−280.061	8.605
1800	62.760	169.822	120.876	88.102	−355.212	−275.621	7.998
1900	62.760	173.215	123.542	94.378	−354.693	−271.214	7.456
2000	62.760	176.434	126.107	100.654	−354.319	−266.831	6.969
2063.000	62.760	178.381	127.674	104.608	--- CRYSTAL <--> LIQUID ---		
2100	62.760	179.497	128.577	106.930	−354.103	−262.463	6.528
2200	62.760	182.416	130.959	113.206	−376.933	−257.996	6.126
2300	62.760	185.206	133.257	119.482	−377.193	−252.584	5.736
2400	62.760	187.877	135.478	125.758	−377.464	−247.161	5.379
2500	62.760	190.439	137.625	132.034	−377.745	−241.726	5.051
2600	62.760	192.900	139.704	138.310	−378.038	−236.279	4.747
2700	62.760	195.269	141.719	144.586	−378.341	−230.821	4.466
2800	62.760	197.551	143.672	150.862	−378.654	−225.352	4.204
2900	62.760	199.754	145.568	157.138	−378.977	−219.871	3.960
3000	62.760	201.881	147.410	163.414	−379.310	−214.379	3.733
3100	62.760	203.939	149.201	169.690	−379.652	−208.875	3.520
3200	62.760	205.932	150.942	175.966	−380.004	−203.361	3.320
3300	62.760	207.863	152.638	182.242	−380.364	−197.836	3.131
3400	62.760	209.737	154.290	188.518	−380.732	−192.299	2.954
3500	62.760	211.556	155.900	194.794	−381.108	−186.751	2.787

PREVIOUS: CURRENT: December 1973

Vanadium Oxide (VO) $O_1V_1(l)$

Vanadium Oxide (VO) CRYSTAL-LIQUID

0 to 2063 K crystal
above 2063 K liquid

Refer to the individual tables for details.

$M_r = 66.9409$ Vanadium Oxide (VO) $O_1V_1(cr,l)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
0	0.000	0.000	INFINITE	−6.908	−429.715	−429.715	INFINITE
100	13.895	6.730	71.088	−6.436	−431.184	−422.473	220.677
200	34.100	23.035	42.859	−3.965	−432.005	−413.352	107.956
298.15	45.501	39.011	39.011	0.000	−431.789	−404.210	70.816
300	45.647	39.293	39.012	0.084	−431.778	−404.039	70.350
400	49.580	53.063	40.863	4.880	−431.032	−394.899	51.569
500	51.651	64.356	44.466	9.945	−430.157	−385.966	40.322
600	53.530	73.940	48.599	15.204	−429.199	−377.216	32.840
700	55.343	82.329	52.831	20.648	−428.158	−368.633	27.508
800	57.099	89.834	56.995	26.271	−427.037	−360.206	23.519
900	58.803	96.658	61.029	32.067	−425.846	−351.922	20.425
1000	60.463	102.940	64.910	38.030	−424.586	−343.776	17.957
1100	62.086	108.779	68.635	44.158	−423.259	−335.758	15.944
1200	63.677	114.250	72.211	50.446	−421.879	−327.864	14.272
1300	65.243	119.408	75.645	56.892	−420.450	−320.087	12.861
1400	66.791	124.300	78.947	63.494	−418.983	−312.422	11.657
1500	68.325	128.961	82.127	70.250	−417.478	−304.863	10.616
1600	69.842	133.419	85.195	77.159	−415.936	−297.405	9.709
1700	71.351	137.698	88.158	84.218	−414.366	−290.045	8.912
1800	72.851	141.819	91.025	91.429	−412.774	−282.778	8.206
1900	74.339	145.798	93.804	98.788	−411.171	−275.599	7.577
2000	75.847	149.649	96.500	106.297	−409.565	−268.506	7.013
2063.000	76.747	152.015	98.160	111.104	CRYSTAL <--> LIQUID		
2063.000	62.760	178.381	98.160	165.496	TRANSITION		
2100	62.760	179.497	99.583	167.818	−354.103	−262.463	6.528
2200	62.760	182.416	103.282	174.094	−376.933	−257.996	6.126
2300	62.760	185.206	106.784	180.370	−377.193	−252.584	5.736
2400	62.760	187.877	110.108	186.646	−377.464	−247.161	5.379
2500	62.760	190.439	113.270	192.922	−377.745	−241.726	5.051
2600	62.760	192.900	116.286	199.198	−378.038	−236.279	4.747
2700	62.760	195.269	119.167	205.474	−378.341	−230.821	4.466
2800	62.760	197.551	121.926	211.750	−378.654	−225.352	4.204
2900	62.760	199.754	124.572	218.026	−378.977	−219.871	3.960
3000	62.760	201.881	127.114	224.302	−379.310	−214.379	3.733
3100	62.760	203.939	129.559	230.578	−379.652	−208.875	3.520
3200	62.760	205.932	131.915	236.854	−380.004	−203.361	3.320
3300	62.760	207.863	134.187	243.130	−380.364	−197.836	3.131
3400	62.760	209.737	136.382	249.406	−380.732	−192.299	2.954
3500	62.760	211.556	138.504	255.682	−381.108	−186.751	2.787

PREVIOUS: CURRENT: December 1973

$S^\circ(298\ 15\ K) = 230.901 \pm 2.1\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_fH^\circ(0\ K) = 127\ 82 \pm 20.9\ kJ\cdot mol^{-1}$
$\Delta_fH^\circ(298.15\ K) = 127.61 \pm 20.9\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^4\Sigma^-$	0	4
$B^4\Pi$	12706.8	8
$C^4\Sigma^-$	17420.3	4
	23890	[4]

$\omega_e = 1012.36\ cm^{-1}$ $\omega_ex_e = 5.26\ cm^{-1}$ $\sigma = 1$
$B_e = 0.54825\ cm^{-1}$ $\alpha_e = 0.00352\ cm^{-1}$ $r_e = 1.589$ Å

Enthalpy of Formation

Based on the adopted ground state vibrational constants, a linear Birge–Sponer extrapolation yields a dissociation energy of $D_0^\circ = 6.039$ eV (139.3 kcal·mol^{-1}) for VO(g). Applying a correction for the ionicity in the V–O bond[1], we recalculate $D_0^\circ = 6.495$ eV (149.8 kcal·mol^{-1}). This latter value leads to a $\Delta_fH^\circ(298.15\ K)$ value of 31.6 kcal·mol^{-1} using auxiliary data.[2]

Berkowitz *et al.*[3] determined the composition and partial pressures of the vapor over VO(cr) by employing a mass spectrometer to analyze the vapors effusing from a tungsten Knudsen cell containing VO(cr). The vapors detected mass spectrometrically at 1945 K were reported to be V(g), VO(g), and $VO_2(g)$. The VO^+ intensity was determined in two sets of experiments using the temperature variation method. Berkowitz *et al.*[3] analyzed these results using 2nd law methods and reported $\Delta_rH^\circ(T) = 125.2$ kcal·mol^{-1} (1690–1945 K) and 124.6 kcal·mol^{-1} (1680–1950 K) for the reaction VO(cr) = VO(g). Assigning these enthalpies of reaction to an intermediate temperature of 1800 K, we calculate $\Delta_fH^\circ(VO, g, 298.15\ K) = 30.1$ and 30.4 kcal·mol^{-1}, respectively, using auxiliary data.[2] Berkowitz *et al.*[3] also used the absolute pressure method and determined the partial pressure of VO(g) at two temperatures, 1875 K and 1876 K. The two absolute pressure data points differ in value by ~25%. A 3rd law analysis of these two data points leads to $\Delta_fH^\circ(VO, g, 298.15\ K)$ of 23.6 and 24 7 kcal·mol^{-1}. We prefer the 2nd law results of Berkowtiz *et al.*[3] since each result is based on multiple data points (~6) which cover a 260 K range.

Coppens *et al.*[4] used a combination of mass spectrometric and Knudsen cell techniques to determine the partial pressures necessary to define the equilibrium in the system VO(g) + Ge(g) = GeO(g) + V(g). The authors analyzed eight data points (1927– 2145 K) by the 3rd law method and reported $\Delta_rH^\circ(0\ K) = 7.60 \pm 0.38$ kcal·mol^{-1} which actually applies to the reverse reaction.[14] The Gibbs energy functions used by Coppens *et al.*[4] for VO are very similar to those adopted here. Using auxiliary data,[2,5] we calculate $\Delta_fH^\circ(298\ 15\ K) = 29.1$ kcal·mol^{-1} for VO(g).

An effusion–mass spectrometric investigation of the vapors in equilibrium with $V_2O_3(cr)$ was conducted by Farber *et al.*[6] Their study, using an aluminum cell, showed that the vapors at 2270 K contained V(g), VO(g), and $VO_2(g)$ as well as Al(g), AlO(g), and $Al_2O(g)$. A 3rd law analysis of the data at 2270 K yields $\Delta_rH^\circ(298.15\ K) = -26.5$ kcal·mol^{-1} for the reaction AlO(g) + V(g) = VO(g) + Al(g). Using auxiliary data[2] we calculate $\Delta_fH^\circ(298.15\ K) = 38.7$ kcal·mol^{-1} for VO(g). Farber *et al.*,[6] however, reported the use of a more recent determination of $\Delta_fH^\circ(298.15\ K)$ for AlO(g).[7] If this latter value (+16.57 kcal·mol^{-1}) is used, then the $\Delta_fH^\circ(298.15\ K)$ value for VO(g) is 35.3 kcal·mol^{-1}.

Frantseva and Semenov[8] studied the evaporation of $V_2O_3(cr)$ by a mass spectrometer used in conjunction with a double effusion chamber. They reported a D_0° value for VO(g) which is dependent, however, on their D_0° value for $VO_2(g)$.[2] The mass spectrometric study by Shchukarev *et al*[9] detected VO(g) above $V_2O_4(cr)$ and $V_2O_3(cr)$ but there was insufficient data reported to permit the calculation of a $\Delta_fH^\circ(298.15\ K)$ value for VO(g).

We adopt $\Delta_fH^\circ(298.15\ K) = 30.5$ kcal mol^{-1} for VO(g). This value is a rounded average of the two 2nd law treatments from Berkowitz *et al.*[3] and the results from Coppens *et al.*[4] Each of these three sets of experiments involve multiple data points. Most of the remaining studies each involved only one data point. However, it should be noted that the $\Delta_fH^\circ(298\ 15\ K)$ derived from the Hildenbrand correction to the linear Birge–Sponer extrapolation is within 1.1 kcal·mol^{-1} of the adopted value. The adopted enthalpy of formation leads to a dissociation energy of $D_0^\circ = 150.9$ kcal·mol^{-1} or 6.542 eV.

Heat Capacity and Entropy

Much of the spectroscopic work involving VO(g) has been reviewed and referenced by Rosen[10] and Weltner.[11] The adopted vibrational and rotational constants as well as the electronic levels are those tabulated by Rosen.[10] The EPR work of Kasai[12] and the optical absorption study by Richards and Barrow[13] established that the ground state was $^4\Sigma^-$. As reported in Rosen[10] there is evidence from matrix studies indicating a transition at 23890 cm^{-1}. We assume this level has a quantum weight of 4. the full weight of 8 is assigned to be B $^4\Pi$ state, rather than estimating the splitting. The Gibbs energy functions used here are approximately 3 cal·K^{-1}·mol^{-1} less than those proposed by Brewer and Rosenblatt.[14] The difference arises from the fact that Brewer and Rosenblatt approximated the VO electronic levels by using V^{++} electronic levels (which include many low lying levels) whereas we have used the observed VO electronic levels.

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K$_f$
0	0.	0.	INFINITE	−8.773	127.820	127.820	INFINITE
100	29.106	198.710	257.359	−5.865	128.787	118.300	−61.794
200	29.433	218.937	233.663	−2.945	128.415	107.888	−28.178
250	29.991	225.560	231.402	−1.461	128.027	102.800	−21.479
298.15	30.697	230.901	230.901	0.	127.612	97.978	−17.165
300	30.726	231.091	230.902	0.057	127.596	97.795	−17.028
350	31.510	235.886	231.278	1.613	127.147	92.863	−13.859
400	32.258	240.143	232.125	3.207	126.696	87.996	−11.491
450	32.931	243 982	233.233	4.837	126.246	83.186	−9.656
500	33.520	247.483	234.486	6.499	125.798	78.425	−8.193
600	34.459	253.682	237.182	9.900	124.898	69.035	−6.010
700	35.147	259.048	239.931	13.382	123.977	59.797	−4.462
800	35.656	263.777	242.622	16.924	123.016	50.694	−3.310
900	36 040	267.999	245.211	20.509	121.997	41.714	−2.421
1000	36.337	271.813	247.684	24.129	120 914	32.851	−1.716
1100	36.571	275.287	250.038	27.775	119.758	24.100	−1.144
1200	36.761	278.478	252.276	31.442	118.517	15.458	−0.673
1300	36.919	281.427	254.407	35.126	117.184	6.923	−0.278
1400	37.053	284.168	256 436	38.825	115.748	−1.505	0.056
1500	37.171	286.728	258.371	42.536	114.208	−9.827	0.342
1600	37.279	289.131	260.219	46.258	112.565	−18.043	0.589
1700	37.382	291.394	261.987	49.992	110.808	−26.153	0.804
1800	37.484	293.533	263.681	53.735	108.933	−34.156	0.991
1900	37.588	295.563	265.306	57.488	106.930	−42.052	1.156
2000	37.699	297.494	266.867	61.253	104.792	−49.838	1.302
2100	37.819	299.336	268.370	65.029	102.508	−57.514	1.431
2200	37.950	301.098	269.818	68.817	77.190	−64.973	1.543
2300	38.093	302.788	271.215	72.619	74.457	−71.374	1.621
2400	38.251	304.413	272.564	76.436	71.727	−77.656	1.690
2500	38.424	305.978	273.870	80.270	69.003	−83.824	1.751
2600	38.612	307 488	275.134	84.121	66.286	−89.884	1.806
2700	38.815	308.949	276.359	87.992	63.578	−95.839	1.854
2800	39.033	310.365	277.549	91.885	60.881	−101.693	1.897
2900	39.266	311.738	278.704	95.800	58.197	−107.453	1.935
3000	39.512	313.074	279.828	99.738	55.527	−113.119	1.970
3100	39.771	314.374	280.921	103.702	52.872	−118.696	2.000
3200	40.041	315.640	281.986	107.693	50.236	−124.189	2.027
3300	40.321	316.877	283.025	111.711	47.618	−129.599	2.051
3400	40.609	318.085	284.038	115.757	45.020	−134.930	2.073
3500	40.905	319.266	285.028	119.833	42.443	−140.186	2.092
3600	41.206	320.423	285.995	123.939	39.889	−145.367	2.109
3700	41.512	321.556	286.941	128.075	−409.450	−149.278	2.107
3800	41.820	322.667	287.867	132.241	−410.271	−142.235	1.955
3900	42.130	323.757	288.773	136.439	−411.119	−135.170	1.810
4000	42.440	324.828	289.661	140.667	−411.995	−128.084	1.673
4100	42.749	325.880	290.532	144.927	−412.900	−120.975	1.541
4200	43.055	326.913	291.386	149.217	−413.834	−113.843	1.416
4300	43.358	327.930	292.224	153.537	−414.799	−106.689	1.296
4400	43.656	328.930	293.047	157.888	−415.795	−99.513	1.181
4500	43.948	329.915	293.855	162.268	−416.823	−92.313	1.072
4600	44.234	330.884	294.650	166.678	−417.886	−85.090	0.966
4700	44.514	331.838	295.431	171.115	−418.982	−77.844	0.865
4800	44.785	332.778	296.199	175.580	−420.115	−70.573	0.768
4900	45.048	333.704	296.955	180.072	−421.286	−63.279	0.675
5000	45.301	334.617	297.699	184.589	−422.495	−55.960	0.585
5100	45.546	335.516	298.432	189.132	−423.745	−48.617	0.498
5200	45.781	336.403	299.153	193.698	−425.036	−41.250	0.414
5300	46.006	337.277	299.865	198.288	−426.371	−33.856	0.334
5400	46.220	338.139	300.565	202.899	−427.752	−26.438	0.256
5500	46.424	338.989	301.256	207.531	−429.180	−18.993	0.180
5600	46.618	339.828	301.938	212.183	−430.658	−11.521	0.107
5700	46.802	340.654	302.610	216.855	−432.187	−4 024	0.037
5800	46.975	341.470	303.273	221.543	−433.769	3.502	−0.032
5900	47.137	342.274	303.927	226.249	−435.406	11.054	−0.098
6000	47.290	343.068	304.573	230.971	−437.102	18.636	−0.162

PREVIOUS: December 1973 (1 atm) CURRENT December 1973 (1 bar)

Continued on page 1814

Tungsten Oxide (WO) IDEAL GAS $M_r = 199.8494$ Tungsten Oxide (WO) $O_1W_1(g)$

$S°(298.15\ K) = [248.198]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = 425.65 \pm 41.8\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = 425.09 \pm 41.8\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^3\Sigma^-]$	[0]	[3]
	[14160]	[1]
	[17211]	[2]
	[19189]	[6]

$\omega_e = 1065\ cm^{-1}$ $\omega_ex_e = [3.85]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.3498]\ cm^{-1}$ $\alpha_e = [0.0016]\ cm^{-1}$ $r_e = [1.81]$ Å

Enthalpy of Formation

The enthalpy of formation, $\Delta_fH°(WO, g, 298.15\ K) = 101.6\ kcal{\cdot}mol^{-1}$, is derived from the enthalpy of reaction, $\Delta_rH°(298.15\ K) = -42.0\ kcal{\cdot}mol^{-1}$ for $WO(g) \rightarrow W(cr) + O(g)$ with all JANAF auxiliary data. The value of $\Delta_rH°(298.15\ K)$ was calculated by the 3rd law method from the partial pressure data which were determined mass-spectrometrically in the temperature range from 2188 to 2475 K by DeMaria *et al.*[1] The drift in the 3rd law analysis was $-20 \pm 7\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

Heat Capacity and Entropy

The fundamental vibrational frequency, the ground state configuration, and the probable electronic levels for tungsten monoxide (g) were obtained from the infrared and ultraviolet spectroscopic investigations by matrix isolation by Weltner and McLeod.[2] The rotational constant B_e was calculated from the estimated bond distance of WO(g). The value x_e was calculated from the relation $x_e\mu^{1/2} = 0.014$ which was given by Barrow and Caunt.[3] The constant (0.014) was estimated based on ZrO(g) and VO(g). The value of α_e was calculated from the Morse potential function.

References

[1] G. DeMaria, R. P. Burns, J. Drowart and M. G. Inghram, J. Chem. Phys. 32, 1373 (1960).
[2] W. Weltner, Jr. and D. McLeod, Jr., J. Mol. Spectry. 17, 276 (1965).
[3] R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) 219A, 120 (1953).

Enthalpy Reference Temperature = T_r = 298.15 K						Standard State Pressure = $p°$ = 0.1 MPa	
	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	S°	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−8.757	425.652	425.652	INFINITE
100	29.104	216.077	274.560	−5.848	426.456	414.475	−216.500
200	29.360	236.289	250.944	−2.931	425.910	402.656	−105.163
250	29.843	242.888	248.696	−1.452	425.504	396.888	−82.925
298.15	30.490	248.198	248.198	0.	425.094	391.414	−68.574
300	30.517	248.386	248.198	0.056	425.079	391.205	−68.115
350	31.261	253.146	248.573	1.601	424.661	385.593	−57.547
400	31.990	257.369	249.413	3.182	424.255	380.039	−49.628
450	32.659	261.176	250.512	4.799	423.861	374.536	−43.475
500	33.251	264.648	251.754	6.447	423.476	369.076	−38.557
600	34.210	270.800	254.429	9.822	422.714	358.268	−31.190
700	34.919	276.129	257.157	13.280	421.944	347.587	−25.937
800	35.446	280.828	259.828	16.800	421.150	337.019	−22.005
900	35.844	285.027	262.399	20.365	420.324	326.552	−18.953
1000	36.150	288.820	264.854	23.966	419.460	316.178	−16.515
1100	36.391	292.277	267.192	27.593	418.554	305.894	−14.526
1200	36.585	295.452	269.417	31.242	417.604	295.694	−12.871
1300	36.744	298.387	271.534	34.909	416.609	285.574	−11.475
1400	36.878	301.115	273.551	38.590	415.567	275.534	−10.280
1500	36.995	303.663	275.474	42.284	414.478	265.569	−9.248
1600	37.100	306.054	277.311	45.989	413.339	255.678	−8.347
1700	37.199	308.307	279.069	49.704	412.151	245.861	−7.554
1800	37.296	310.436	280.753	53.429	410.914	236.114	−6.852
1900	37.396	312.455	282.369	57.163	409.626	226.438	−6.225
2000	37.502	314.376	283.922	60.908	408.289	216.831	−5.663
2100	37.616	316.208	285.416	64.664	406.902	207.292	−5.156
2200	37.740	317.961	286.856	68.432	405.467	197.821	−4.697
2300	37.878	319.641	288.245	72.212	403.983	188.415	−4.279
2400	38.029	321.257	289.587	76.008	402.454	179.075	−3.897
2500	38.195	322.812	290.885	79.819	400.879	169.800	−3.548
2600	38.376	324.314	292.142	83.647	399.264	160.588	−3.226
2700	38.572	325.766	293.360	87.494	397.583	151.440	−2.930
2800	38.783	327.172	294.543	91.362	395.804	142.356	−2.656
2900	39.009	328.537	295.692	95.252	393.888	133.337	−2.402
3000	39.248	329.864	296.809	99.164	391.810	124.388	−2.166
3100	39.499	331.155	297.896	103.101	389.529	115.511	−1.946
3200	39.761	332.413	298.955	107.064	387.015	106.711	−1.742
3300	40.033	333.640	299.988	111.054	384.244	97.994	−1.551
3400	40.314	334.840	300.995	115.071	381.182	89.365	−1.373
3500	40.602	336.012	301.979	119.117	377.765	80.830	−1.206
3600	40.896	337.160	302.940	123.192	373.899	72.400	−1.050
3700	41.193	338.285	303.880	127.296	334.719	64.275	−0.907
3800	41.494	339.387	304.800	131.431	333.242	56.986	−0.783
3900	41.796	340.469	305.701	135.595	331.789	49.735	−0.666
4000	42.098	341.531	306.584	139.790	330.360	42.521	−0.555
4100	42.398	342.574	307.449	144.015	328.954	35.343	−0.450
4200	42.696	343.600	308.297	148.269	327.572	28.198	−0.351
4300	42.991	344.608	309.130	152.554	326.213	21.086	−0.256
4400	43.281	345.599	309.948	156.868	324.877	14.006	−0.166
4500	43.566	346.575	310.751	161.210	323.564	6.955	−0.081
4600	43.844	347.536	311.540	165.580	322.273	−0.067	0.001
4700	44.115	348.482	312.316	169.978	321.004	−7.060	0.078
4800	44.378	349.413	313.079	174.403	319.754	−14.027	0.153
4900	44.633	350.331	313.830	178.854	318.525	−20.968	0.224
5000	44.878	351.235	314.569	183.329	317.313	−27.884	0.291
5100	45.115	352.126	315.297	187.829	316.120	−34.776	0.356
5200	45.341	353.004	316.014	192.352	314.942	−41.645	0.418
5300	45.558	353.870	316.720	196.897	313.779	−48.491	0.478
5400	45.764	354.724	317.416	201.463	312.630	−55.316	0.535
5500	45.960	355.565	318.102	206.050	311.492	−62.119	0.590
5600	46.146	356.395	318.778	210.655	310.366	−68.901	0.643
5700	46.321	357.213	319.445	215.278	309.248	−75.664	0.693
5800	46.486	358.020	320.103	219.919	308.139	−82.407	0.742
5900	46.640	358.816	320.753	224.575	307.035	−89.132	0.789
6000	46.784	359.601	321.394	229.246	305.936	−95.837	0.834

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

Zirconium Oxide (ZrO) IDEAL GAS $M_r = 107.2194$ Zirconium Oxide (ZrO) $O_1Zr_1(g)$

$S°(298.15\ K) = 227.627 \pm 8.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 59.63 \pm 50.2\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = 58.58 \pm 50.2\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	1	[18000]	2
[4000]	6	[22000]	6
[6000]	2	[25500]	2
15500	2	27300	1
[15700]	6	[28500]	6
[17500]	6		

$\omega_e = 978\ cm^{-1}$ $\omega_e x_e = 4\ cm^{-1}$ $\sigma = 1$
$B_e = 0.4142\ cm^{-1}$ $\alpha_e = 0.0023\ cm^{-1}$ $r_e = 1.711\ Å$

Enthalpy of Formation

$\Delta_f H°(298.15\ K) = 14.0 \pm 12\ kcal{\cdot}mol^{-1}$ is calculated from $\Delta_r H°(298.15\ K) = 290.342 \pm 12.8\ kcal{\cdot}mol^{-1}$ for the reaction $Zr(cr) + ZrO_2(cr) = 2\ ZrO(g)$. The value of $\Delta_r H°(298.15\ K)$ is obtained by the 3rd law analysis from the mass spectrometric studies of Chupka *et al.*[1] They observed the variation of the ZrO+ ion intensity over the system $Zr + ZrO_2$ and reported equilibrium constants for the reaction $Zr + ZrO_2 \rightarrow 2\ ZrO$ in the range 2124–2322 K. The 3rd law drift is $-58 \pm 28\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

Heat Capacity and Entropy

The ground state of ZrO(g) was assumed to be $^1\Sigma^+$ as determined from the matrix isolation spectra of Weltner *et al.*[2] Previously this had been described as the lower state in the A band system reported by Uhler and Akerlind.[3]

All molecular constants were obtained from Uhler and Akerlind[3] except $\omega_e = 978\ cm^{-1}$ and $\omega_e x_e = 4\ cm^{-1}$ which were calculated from ω and $\alpha_e = 0.0023\ cm^{-1}$ using the equations

$$\alpha_e = \frac{6\,(\omega_x \cdot B_e^3)^{1/2}}{\omega_e} - \frac{6\,B_e^2}{\omega_e} \text{ and } \omega = \omega_e - 2\,\omega_e x_e = 969.76\ cm^{-1}$$

The higher electronic levels were obtained or estimated from the correlation diagram given by Weltner and McLeon.[2]

References

[1] W. A. Chupka, J. Berkowitz and M. G. Inghram, J. Chem. Phys. 26, 1207 (1957).
[2] W. Weltner, Jr., and D. McLeod, Jr., J. Phys. Chem. 69, 3488 (1965).
[3] V. Uhler and L. Akerlind, Arkiv Fysik 10, 431 (1955).

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

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−8.786	59.629	59.629	INFINITE
100	29.106	195.385	254.156	−5.877	60.199	50.732	−26.500
200	29.489	215.622	230.400	−2.956	59.472	41.506	−10.840
250	30.099	222.263	228.131	−1.467	59.016	37.067	−7.745
298.15	30.845	227.627	227.627	0.	58.576	32.880	−5.760
300	30.875	227.818	227.628	0.057	58.559	32.721	−5.697
350	31.680	232.639	228.007	1.621	58.114	28.450	−4.246
400	32.439	236.919	228.858	3.224	57.681	24.241	−3.166
450	33.124	240.780	229.972	4.864	57.258	20.087	−2.332
500	33.745	244.303	231.231	6.536	56.838	15.979	−1.669
600	34.906	250.558	233.944	9.968	56.000	7.886	−0.687
700	36.165	256.031	236.716	13.520	55.158	−0.066	0.005
800	37.695	260.956	239.443	17.211	54.330	−7.899	0.516
900	39.539	265.500	242.089	21.070	53.539	−15.629	0.907
1000	41.624	269.772	244.645	25.126	52.809	−23.275	1.216
1100	43.811	273.841	247.116	29.398	52.155	−30.851	1.465
1200	45.942	277.746	249.507	33.887	47.867	−38.149	1.661
1300	47.875	281.501	251.824	38.580	47.900	−45.317	1.821
1400	49.510	285.111	254.074	43.452	48.055	−52.493	1.959
1500	50 791	288.573	256.259	48.470	48.289	−59.683	2.078
1600	51.705	291.882	258.383	53.598	48.556	−66.890	2.184
1700	52.273	295.035	260.447	58.799	48.811	−74.113	2.277
1800	52.538	298.032	262.453	64.042	49.011	−81.350	2.361
1900	52.552	300.874	264.401	69.299	49.116	−88.596	2.436
2000	52.372	303.565	266.292	74.546	49.096	−95.844	2.503
2100	52.049	306.113	268.128	79.768	48.922	−103.087	2.564
2200	51.629	308.525	269.910	84.953	27.249	−109.573	2.602
2300	51.152	310.810	271.639	90.092	26.289	−115.771	2.629
2400	50.648	312.976	273.317	95.182	25.269	−121.926	2.654
2500	50.140	315.034	274.945	100.222	24.187	−128.037	2.675
2600	49.646	316.990	276.525	105.211	23.044	−134.103	2.694
2700	49.179	318.855	278.058	110.152	21.842	−140.125	2.711
2800	48.747	320.636	279.547	115.048	20.585	−146.101	2.726
2900	48.354	322.339	280.994	119.902	19.277	−152.031	2.738
3000	48.004	323.973	282.399	124.720	17.922	−157.915	2.750
3100	47.697	325.542	283.766	129.505	16.525	−163.753	2.759
3200	47.433	327.052	285.095	134.261	15.090	−169.546	2.768
3300	47.209	328.508	286.389	138.993	13.622	−175.294	2.775
3400	47.025	329.914	287.648	143.704	12.126	−180.996	2.781
3500	46.876	331.275	288.875	148.399	10.605	−186.654	2.786
3600	46.762	332.594	290.072	153.080	9.063	−192.268	2.790
3700	46.677	333.874	291.238	157.752	7.504	−197.839	2.793
3800	46.621	335.118	292.377	162.417	5.930	−203.367	2.795
3900	46.589	336.328	293.488	167.077	4.345	−208.855	2.797
4000	46.579	337.508	294.574	171.735	2.752	−214.301	2.798
4100	46.588	338.658	295.635	176.394	1.152	−219.708	2.799
4200	46.614	339.781	296.673	181.054	−0.453	−225.075	2.799
4300	46.654	340.878	297.688	185.717	−2.061	−230.404	2.799
4400	46.707	341.951	298.682	190.385	−3.670	−235.696	2.798
4500	46.770	343.002	299.655	195.059	−5.279	−240.951	2.797
4600	46.841	344.030	300.609	199.739	−6.887	−246.171	2.795
4700	46.918	345.039	301.544	204.427	−8.495	−251.355	2.794
4800	47.001	346.027	302.460	209.123	−571.037	−244.888	2.665
4900	47.088	346.997	303.359	213.827	−572.292	−238.080	2.538
5000	47.176	347.950	304.241	218.540	−573.562	−231.247	2.416
5100	47.267	348.885	305.108	223.263	−574.846	−224.388	2.298
5200	47.357	349.803	305.958	227.994	−576.141	−217.504	2.185
5300	47.447	350.706	306.794	232.734	−577.448	−210.594	2.076
5400	47.536	351.594	307.616	237.483	−578.765	−203.660	1.970
5500	47.622	352.467	308.423	242.241	−580.092	−196.702	1.868
5600	47.707	353.326	309.217	247.008	−581.428	−189.719	1.770
5700	47.788	354.171	309.999	251.782	−582.772	−182.712	1.674
5800	47.865	355.003	310.767	256.565	−584.124	−175.681	1.582
5900	47.939	355.822	311.524	261.355	−585.483	−168.628	1.493
6000	48.008	356.628	312.269	266.153	−586.851	−161.551	1.406

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

Zirconium Oxide (ZrO) $O_1Zr_1(g)$

0 to 6000 K Ideal Diatomic Gas

$S°(298.15\ K) = 205.147 \pm 0.035$

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

Electronic and Molecular constants ($\sigma = 2$)

State	g_i	T, cm^{-1}	ω_e, cm^{-1}	Vibrational Anharmonicity, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	D_e, cm^{-1}	β_e, cm^{-1}
X $^3\Sigma_g^-$	3	0	1580.1932	$\omega_e x_e$ 11.980804	1.445622	0.01593268^{-5}		
				$\omega_e y_e$ 0.047474736	$6.406456\text{x}10^{-5}$			
				$\omega_e z_e$ $-1.272748\text{x}10^{-3}$	$-2.846158\text{x}10^{-6}$			
a $^1\Delta_g$	2	7882.39	[1509.3]	$\omega_e x_e$ [12.9]	1.4263	0.0171	[$4.97\text{x}10^{-6}$]	
b $^1\Delta_g^+$	1	13120.9085	1432.6661	$\omega_e x_e$ 13.9336	1.4004796	0.018169303	$5.356\text{x}10^{-6}$	$0.077\text{x}10^{-6}$
				$\omega_e y_e$ -0.0143	$-4.294192\text{x}10^{-5}$			
c$^1\Sigma_u^-$	1	32664.1	794.29	$\omega_e x_e$ 12.736	0.9155	0.01391	[$10.5\text{x}10^{-6}$]	
				$\omega_e y_e$ -0.2444		-0.000740		
				$\omega_e z_e$ 0.00055				
c$^3\Delta_u$	6	34319	[750]	$\omega_e x_e$ [14]	[0.91]	[0.014]		
A$^3\Sigma_u^+$	3	35007.15	799.08	$\omega_e x_e$ 12.16	0.91053	0.01416	$4.79\text{x}10^{-6}$	$-0.30\text{x}10^{-6}$
				$\omega_e y_e$ -0.550		-0.00097		$0.10\text{x}10^{-6}$
B$^3\Sigma_u^-$	3	49358.15	709.05770	$\omega_e x_e$ 10.614080	0.818975	0.0119225		
				$\omega_e y_e$ -0.059212435		$-6.30472\text{x}10^{-4}$		
				$\omega_e z_e$ -0.023974994				

Enthalpy of Formation

Zero by Definition.

Heat Capacity and Entropy

The thermal functions are calculated using the program of McBride and Gordon>[1] The contributions of vibrational anharmonicity, rotation–vibration interaction, and centrifugal stretching are calculated via the procedures given by Pennington and Kobe.[3] In this procedure the energy levels are calculated as follows: $\epsilon = T + G(v) - G(o) + B_v J(J+1) - D_v J^2(J+1)^2$where $G(v) = \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \omega_e y_e (v+1/2)^3 + \omega_e y_e (v+1/2)^4$ and $B_v = B_e - \alpha_1(v+1/2) + \alpha_2(v+1/2)^2 + \alpha_3(v+1/2)^3$ and $D_v = D_e + \beta_i(v+1/2)$. Where a value of D_e is not available it is calculated to be $D_e = 4B_e^3/\omega_e^2$.

Molecular constant data in the table above is from Krupenie[2] with the exception of B_e and α_1 for the C $^3\Delta_u$ state which we have estimated by analogy with neighboring states of the same electron configuration. Electronic levels above 50,000 cm^{-1}given by Krupenie are not included since they make negligible contributions to the thermodynamic properties at 6000 K.

The value of $S°(298.15\ K)$ agrees exactly with the CODATA recommended value.[4] It also agrees with the values of McBride *et al.*[5] and Gurvich *et al.*[6] within the stated uncertainty. The uncertainty in $S°(298.15\ K)$ is due to uncertainties in fundamental constants (particularly the gas constant), the atomic weight, and the ground state molecular constants. At high temperatures, further uncertainties arise from excited state molecular constants and approximate procedures used to account for higher vibrational–rotational levels of all states. Despite these increased uncertainties, our values of $S°$ are within 0.016 (6000 K) and 0.035 (5000 K) cal·K^{-1}·mol^{-1} of those calculated by superior methods[5,6] using older molecular constants.

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

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−8.683	0.	0.	0.
100	29.106	173.307	231.094	−5.779	0.	0.	0.
200	29.126	193.485	207.823	−2.868	0.	0.	0.
250	29.201	199.990	205.630	−1.410	0.	0.	0.
298.15	29.376	205.147	205.147	0.	0.	0.	0.
300	29.385	205.329	205.148	0.054	0.	0.	0.
350	29.694	209.880	205.506	1.531	0.	0.	0.
400	30.106	213.871	206.308	3.025	0.	0.	0.
450	30.584	217.445	207.350	4.543	0.	0.	0.
500	31.091	220.693	208.524	6.084	0.	0.	0.
600	32.090	226.451	211.044	9.244	0.	0.	0.
700	32.981	231.466	213.611	12.499	0.	0.	0.
800	33.733	235.921	216.126	15.835	0.	0.	0.
900	34.355	239.931	218.552	19.241	0.	0.	0.
1000	34.870	243.578	220.875	22.703	0.	0.	0.
1100	35.300	246.922	223.093	26.212	0.	0.	0.
1200	35.667	250.010	225.209	29.761	0.	0.	0.
1300	35.988	252.878	227.229	33.344	0.	0.	0.
1400	36.277	255.556	229.158	36.957	0.	0.	0.
1500	36.544	258.068	231.002	40.599	0.	0.	0.
1600	36.796	260.434	232.768	44.266	0.	0.	0.
1700	37.040	262.672	234.462	47.958	0.	0.	0.
1800	37.277	264.796	236.089	51.673	0.	0.	0.
1900	37.510	266.818	237.653	55.413	0.	0.	0.
2000	37.741	268.748	239.160	59.175	0.	0.	0.
2100	37.969	270.595	240.613	62.961	0.	0.	0.
2200	38.195	272.366	242.017	66.769	0.	0.	0.
2300	38.419	274.069	243.374	70.600	0.	0.	0.
2400	38.639	275.709	244.687	74.453	0.	0.	0.
2500	38.856	277.290	245.959	78.328	0.	0.	0.
2600	39.068	278.819	247.194	82.224	0.	0.	0.
2700	39.276	280.297	248.393	86.141	0.	0.	0.
2800	39 478	281.729	249.558	90.079	0.	0.	0.
2900	39.674	283.118	250.691	94.036	0.	0.	0.
3000	39.864	284.466	251.795	98.013	0.	0.	0.
3100	40.048	285.776	252.870	102.009	0.	0.	0.
3200	40.225	287.050	253.918	106.023	0.	0.	0.
3300	40.395	288.291	254.941	110.054	0.	0.	0.
3400	40.559	289.499	255.940	114.102	0.	0.	0.
3500	40.716	290.677	256.916	118.165	0.	0.	0.
3600	40.868	291.826	257.870	122.245	0.	0.	0.
3700	41.013	292.948	258.802	126.339	0.	0.	0.
3800	41.154	294.044	259.716	130.447	0.	0.	0.
3900	41.289	295.115	260.610	134.569	0.	0.	0.
4000	41.421	296.162	261.485	138.705	0.	0.	0.
4100	41.549	297.186	262.344	142.854	0.	0.	0.
4200	41.674	298.189	263.185	147.015	0.	0.	0.
4300	41.798	299.171	264.011	151.188	0.	0	0.
4400	41.920	300.133	264.821	155.374	0.	0.	0.
4500	42.042	301.076	265.616	159.572	0.	0.	0.
4600	42.164	302.002	266.397	163.783	0.	0.	0.
4700	42.287	302.910	267.164	168.005	0.	0.	0.
4800	42.413	303.801	267.918	172.240	0.	0.	0.
4900	42.542	304.677	268.660	176.488	0.	0.	0.
5000	42.675	305.538	269.389	180.749	0.	0.	0.
5100	42.813	306.385	270.106	185.023	0.	0.	0.
5200	42.956	307.217	270.811	189.311	0.	0.	0.
5300	43.105	308.037	271.506	193.614	0.	0.	0.
5400	43.262	308.844	272.190	197.933	0.	0.	0.
5500	43.426	309.639	272.864	202.267	0.	0.	0.
5600	43.599	310.424	273.527	206.618	0.	0.	0.
5700	43.781	311.197	274.181	210.987	0.	0.	0.
5800	43.973	311.960	274.826	215.375	0.	0.	0.
5900	44.175	312.713	275.462	219.782	0.	0.	0.
6000	44.387	313.457	276.089	224.210	0.	0.	0.

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

Oxygen, Ion (O_2^+) IDEAL GAS M_r = 31.99825 Oxygen, Ion (O_2^+) $O_2^+(g)$

$S°(298.15\ K) = 206.2 \pm 0.8\ J{\cdot}K{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = 1164.7 \pm 0.8\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [1170.888]\ kJ{\cdot}mol^{-1}$

Electronic and Molecular Constants ($\sigma = 2$)

State	g_i	T_o, cm^{-1}	ω_e, cm^{-1}	ω_ex_e, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Pi_g$	4	0	1905.13	16.2818	1.68912	0.0195769	1.116384
$a^4\Pi_{ui}$	8	32524	1035.534	10.32194	1.104320	0.01545646	1.31816042
$A^2\Pi_u$	4	40070	898.17	13.568	1.06297	0.02058	1.408220
$b^4\Sigma_g^-$	4	49191	119.913	17.13456	1.287297	0.02206747	1.2796516

Enthalpy of Formation

The adopted value for the enthalpy of formation of $O_2^+(g)$, $\Delta_fH°(0\ K) = 278.37 \pm 0.2\ kcal{\cdot}mol^{-1}$ is that recommended in a critical review on the energetics of gaseous ions by Rosenstock *et al.*[1] This value is derived from ionization potentials determined in the photoelectron spectrum of O_2 by Edqvist *et al.*,[2] the IP values are 12.071 ± 0.005 ev for the $X^2\Pi_{3/2g}$ state and 12.095 ± 0.005 ev for the $X^2\Pi_{1/2g}$ state.

$\Delta_fH°(O_2^+, g, 298.15\ K)$ is calculated from $\Delta_fH°(O_2, g, 0\ K)$ by using IP(O_2) with JANAF enthalpies, $H°(0\ K)-H°(298.15\ K)$, for $O_2(g)$ $O_2^+(g)$, and e^-(ref). $\Delta_fH°(O_2 \rightarrow O_2^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[1] $\Delta_fH°(298.15\ K)$ should be changed by $-6.197\ kJ{\cdot}mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The electronic and molecular constants are from the critical review of Krupenie.[3] Electronic levels above 50000 cm^{-1} given by Krupenie are not included since they make negligible contributions to the thermodynamic properties at 6000 K. The thermodynamic functions are calculated using first–order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_u\Sigma Q_r^iQ_v^ig_i\exp(-c_2\epsilon_i/T)$. Use of the program of McBride and Gordon[4] yields the same results.

The ground state is taken to be $^2\Pi_{3/2g}$ with a separation of the ground state doublet levels of ~200 cm^{-1}. The hypothetical $^2\Pi$ state without spin–orbit splitting would be 100 cm^{-1} higher.[3] Such a shift of the electronic energy levels does not significantly alter the thermal functions. The main source of error in the $S°(298.15\ K)$ value lies in the neglect of a more exact treatment of the splitting of the $X^2\Pi$ ground state.

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−8.674	1164.700		
100	29.105	174.406	232.113	−5.771			
200	29.111	194.582	208.881	−2.860			
250	29.132	201.079	206.695	−1.404			
298.15	29.195	206.215	206.215	0.	1170.888	1164.315	−203.983
300	29.199	206.396	206.216	0.054	1170.926	1164.274	−202.718
350	29.342	210.906	206.572	1.517	1171.952	1163.084	−173.581
400	29.573	214.839	207.364	2.990	1172.970	1161.748	−151.709
450	29.882	218.339	208.393	4.476	1173.978	1160.285	−134.682
500	30.250	221.506	209.548	5.979	1174.978	1158.710	−121.050
600	31.078	227.093	212.019	9.045	1176.963	1155.269	−100.575
700	31.916	231.947	214.526	12.195	1178.937	1151.497	−85.926
800	32.687	236.260	216.978	15.426	1180.910	1147.442	−74.920
900	33.364	240.150	219.340	18.729	1182.886	1143.140	−66.346
1000	33.945	243.697	221.601	22.095	1184.869	1138.618	−59.475
1100	34.440	246.956	223.760	25.515	1186.859	1133.897	−53.844
1200	34.859	249.971	225.820	28.981	1188.854	1128.994	−49.144
1300	35.216	252.776	227.787	32.485	1190.854	1123.924	−45.160
1400	35.521	255.397	229.667	36.022	1192.856	1118.701	−41.739
1500	35.784	257.857	231.465	39.588	1194.859	1113.334	−38.770
1600	36.011	260.174	233.187	43.178	1196.861	1107.834	−36.167
1700	36.210	262.363	234.840	46.789	1198.859	1102.208	−33.867
1800	36.384	264.438	236.427	50.419	1200.851	1096.465	−31.819
1900	36.538	266.409	237.954	54.065	1202.837	1090.612	−29.983
2000	36.675	268.287	239.424	57.726	1204.813	1084.654	−28.328
2100	36.798	270.079	240.841	61.399	1206.780	1078.598	−26.829
2200	36.908	271.793	242.209	65.085	1208.736	1072.449	−25.463
2300	37.009	273.436	243.532	68.781	1210.680	1066.210	−24.214
2400	37.101	275.013	244.811	72.486	1212.611	1059.887	−23.068
2500	37.185	276.530	246.049	76.201	1214.529	1053.484	−22.011
2600	37.263	277.990	247.250	79.923	1216.434	1047.004	−21.035
2700	37.336	279.397	248.415	83.653	1218.325	1040.452	−20.129
2800	37.403	280.756	249.546	87.390	1220.203	1033.830	−19.286
2900	37.466	282.070	250.645	91.134	1222.068	1027.140	−18.501
3000	37.526	283.341	251.713	94.883	1223.919	1020.387	−17.767
3100	37.583	284.573	252.754	98.639	1225.757	1013.573	−17.079
3200	37.637	285.767	253.767	102.400	1227.583	1006.699	−16.433
3300	37.689	286.926	254.754	106.166	1229.397	999.768	−15.825
3400	37.740	288.051	255.717	109.938	1231.200	992.783	−15.252
3500	37.790	289.146	256.656	113.714	1232.991	985.744	−14.711
3600	37.838	290.211	257.574	117.496	1234.772	978.655	−14.200
3700	37.887	291.249	258.470	121.282	1236.542	971.515	−13.715
3800	37.936	292.260	259.346	125.073	1238.304	964.330	−13.256
3900	37.985	293.246	260.203	128.869	1240.056	957.097	−12.819
4000	38.035	294.208	261.041	132.670	1241.800	949.819	−12.403
4100	38.088	295.148	261.861	136.476	1243.536	942.498	−12.008
4200	38.142	296.067	262.665	140.288	1245.265	935.135	−11.630
4300	38.199	296.965	263.452	144.105	1246.987	927.731	−11.270
4400	38.258	297.844	264.224	147.927	1248.702	920.286	−10.925
4500	38.322	298.704	264.980	151.756	1250.412	912.802	−10.596
4600	38.389	299.547	265.723	155.592	1252.116	905.281	−10.280
4700	38.462	300.373	266.451	159.434	1253.815	897.723	−9.977
4800	38.539	301.184	267.166	163.284	1255.508	890.129	−9.687
4900	38.622	301.979	267.869	167.142	1257.197	882.500	−9.408
5000	38.711	302.761	268.559	171.009	1258.881	874.836	−9.139
5100	38.807	303.528	269.237	174.885	1260.561	867.139	−8.881
5200	38.910	304.283	269.904	178.771	1262.237	859.407	−8.633
5300	39.020	305.025	270.559	182.667	1263.910	851.645	−8.393
5400	39.138	305.755	271.204	186.575	1265.578	843.850	−8.163
5500	39.265	306.475	271.839	190.495	1267.242	836.025	−7.940
5600	39.400	307.183	272.464	194.428	1268.903	828.170	−7.725
5700	39.545	307.882	273.079	198.375	1270.559	820.285	−7.517
5800	39.699	308.571	273.685	202.338	1272.213	812.372	−7.316
5900	39.863	309.251	274.282	206.316	1273.862	804.428	−7.122
6000	40.036	309.922	274.871	210.310	1275.507	796.458	−6.934

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

Oxygen, Ion (O_2^-) IDEAL GAS $M_r = 31.99935$ Oxygen, Ion (O_2^-) $O_2^-(g)$

$\Delta_f H°(0\ K) = -42.46 \pm 0.75\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = 209.591 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-48.593]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i,cm^{-1}	g_i
$^2\Pi_g$	0	4

$\omega_e = 1089 \pm 40\ cm^{-1}$ $\omega_e x_e = 12.1 \pm 1.6\ cm^{-1}$ $\sigma = 2$
$B_e = 1.17 \pm 0.02\ cm^{-1}$ $\alpha_e = [0.017]\ cm^{-1}$ $r_e = 1.341 \pm 0.010$ Å

Enthalpy of Formation

The enthalpy of formation at 0 K for $O_2^-(g)$ is based n the electron affinity value derived from a thorough analysis of the laser photodetachment measurements of Celotta *et al.*[1] This study let to EA(O_2) = 0.440 ± 0.008 eV. Using auxiliary data,[2] we calculate $\Delta_f H°(O_2^-$, g, 0 K) = 10.15 ± 0.18 kcal·mol^{-1} and $D_0^°(O_2^-) = 94.4 \pm 0.3$ kcal·mol^{-1}; the latter value assumes dissociation into ground state O(g) and O^-(g). The adopted EA(O_2) value is also recommended by Rosenstock *et al.*[3] and Massey.[4] Both of these latter studies have reviewed and summarized earlier work from which EA values could be derived.

$\Delta_f H°(O_2^-$, g, 298.15 K) is obtained from $\Delta_f H°(O_2$, g, 0 K) by using EA(O_2) with JANAF[2] enthalpies, $H°(0\ K)$–$H°(298.15\ K)$, for $O_2^-(g)$, $O_2(g)$, and $e^-(g)$. $\Delta_r H°(O_2^- \rightarrow O_2 + e^-$, 298.15 K) differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3] $\Delta_f H°$(298.15 K) should be changed by + 6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The laser photodetachment study of Celotta *et al.*[1] which yielded a precise value for EA(O_2) also yielded precise values for r_e and B_e as well as values for ω_e and $\omega_e x_e$. We adopt these values and calculate α_e assuming a Morse function for the ground state. Support for these values comes from recent studies based on total scattering cross section[5] and differential eleastic cross section.[6,7] Other (earlier) studies yielding vibrational information are discussed by Krupenie.[8] The recent ab initio study by Das *et al.*[11] suggests slightly different vibrational–rotational constants ($\omega_e = 1098$, $\omega_e x_e = 9.04$, $B_e = 1.135$, and $\alpha_e = 0.0151$ cm^{-1}).

The ground and excited electronic states are discussed by Krupenie,[8] Massey,[4] and Das *et al.*[11] The approximate theoretical potential energy diagram given by Krupenie[8] suggests a $^2\Pi_g$ ground state with three rather low lying excited states: $^4\Sigma_u^-$ at ~21000 cm^{-1}, $^2\Pi_u$ at ~28500 cm^{-1}, and $^2\Sigma_u^-$ at ~32300 cm^{-1}. The ab initio study by Das *et al.*[11] suggests the same ordering of the levels at 19833 cm^{-1}, 27213 cm^{-1}, and 30076 cm^{-1}. The fluorescence observed by Rolfe[9] was assigned as $^2\Pi_{ui} \rightarrow X^2\Pi_{gi}$, but an upper state assignment of $^2\Sigma_u^-$ cannot be ruled out.[8] This study indicated that the presumed $^2\Pi_{ui}$ state lies at 29400 cm^{-1} (which we adopt), in good agreement with the calculated potential energy diagram. Hurst and Bortner[10] obtained evidence of excitation to an electronic state of O_2^- (presumable $^4\Sigma_u^-$) which lies approximately 1 eV above the ground state. The potential energy diagrams given by Krupenie[8] and Das *et al.*[11] suggest this level is significantly higher. The position of this level will not significantly affect the entropy values.

The three excited states are predicted to be quite shallow (binding energies ~1 eV) as compared to the ground state. The inclusion in our calcualtion of such states, with the use of appropriate vibrational–rotational constants as given by Das *et al.*[11] would lead to erroneous heat capacity values above 3000 K. The proper inclusion of these three excited states would require a direct summation technique with rotational cutoff.

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.752	−42.464		
100	29.110	177.477	235.940	−5.846			
200	29.353	197.692	212.335	−2.929			
250	29.818	204.287	210.089	−1.451			
298.15	30.453	209.591	209.591	0.	−48.593	−43.663	7.650
300	30.480	209.780	209.592	0.056	−48.629	−43.633	7.597
350	31.224	214.534	209.966	1.599	−49.603	−42.723	6.376
400	31.962	218.752	210.805	3.179	−50.557	−41.674	5.442
450	32.648	222.557	211.903	4.794	−51.498	−40.507	4.702
500	33.262	226.029	213.144	6.442	−52.431	−39.236	4.099
600	34.271	232.187	215.818	9.821	−54.290	−36.422	3.171
700	35.032	237.530	218.546	13.288	−56.156	−33.297	2.485
800	35.609	242.247	221.220	16.821	−58.038	−29.904	1.953
900	36.055	246.468	223.795	20.406	−59.938	−26.273	1.525
1000	36.407	250.285	226.256	24.029	−61.855	−22.430	1.172
1100	36.691	253.769	228.601	27.685	−63.787	−18.393	0.873
1200	36.926	256.972	230.834	31.366	−65.734	−14.181	0.617
1300	37.123	259.936	232.960	35.069	−67.693	−9.805	0.394
1400	37.293	262.693	234.986	38.790	−69.664	−5.279	0.197
1500	37.441	265.271	236.920	42.527	−71.647	−0.611	0.021
1600	37.572	267.692	238.769	46.277	−73.642	4.190	−0.137
1700	37.690	269.973	240.538	50.041	−75.649	9.116	−0.280
1800	37.798	272.131	242.234	53.815	−77.669	14.160	−0.411
1900	37.897	274.177	243.861	57.600	−79.702	19.317	−0.531
2000	37.989	276.123	245.426	61.394	−81.749	24.582	−0.642
2100	38.075	277.979	246.933	65.197	−83.810	29.949	−0.745
2200	38.157	279.752	248.384	69.009	−85.885	35.415	−0.841
2300	38.234	281.450	249.785	72.829	−87.975	40.975	−0.931
2400	38.308	283.079	251.139	76.656	−90.079	46.626	−1.015
2500	38.380	284.644	252.448	80.490	−92.198	52.366	−1.094
2600	38.448	286.151	253.715	84.332	−94.332	58.190	−1.169
2700	38.515	287.603	254.944	88.180	−96.479	64.098	−1.240
2800	38.580	289.005	256.135	92.035	−98.641	70.085	−1.307
2900	38.644	290.360	257.292	95.896	−100.816	76.148	−1.372
3000	38.706	291.671	258.416	99.763	−103.004	82.288	−1.433
3100	38.767	292.941	259.510	103.637	−105.204	88.501	−1.491
3200	38.826	294.173	260.574	107.517	−107.417	94.784	−1.547
3300	38.885	295.368	261.610	111.402	−109.641	101.137	−1.601
3400	38.943	296.530	262.620	115.294	−111.876	107.558	−1.652
3500	39.001	297.660	263.605	119.191	−114.121	114.045	−1.702
3600	39.057	298.759	264.567	123.094	−116.376	120.596	−1.750
3700	39.113	299.830	265.505	127.002	−118.641	127.209	−1.796
3800	39.169	300.874	266.422	130.916	−120.914	133.885	−1.840
3900	39.224	301.892	267.319	134.836	−123.195	140.620	−1.883
4000	39.279	302.886	268.196	138.761	−125.484	147.413	−1.925
4100	39.333	303.857	269.054	142.692	−127.780	154.264	−1.965
4200	39.387	304.805	269.894	146.628	−130.084	161.171	−2.004
4300	39.440	305.732	270.716	150.569	−132.395	168.133	−2.042
4400	39.494	306.640	271.523	154.516	−134.713	175.149	−2.079
4500	39.547	307.528	272.313	158.468	−137.037	182.217	−2.115
4600	39.599	308.398	273.088	162.425	−139.369	189.337	−2.150
4700	39.652	309.250	273.848	166.387	−141.708	196.508	−2.184
4800	39.704	310.085	274.594	170.355	−144.053	203.729	−2.217
4900	39.756	310.904	275.327	174.328	−146.407	210.999	−2.249
5000	39.808	311.708	276.047	178.307	−148.768	218.317	−2.281
5100	39.860	312.497	276.754	182.290	−151.138	225.683	−2.311
5200	39.912	313.271	277.449	186.279	−153.516	233.094	−2.341
5300	39.963	314.032	278.132	190.272	−155.904	240.552	−2.371
5400	40.015	314.780	278.803	194.271	−158.302	248.054	−2.399
5500	40.066	315.514	279.464	198.275	−160.711	255.601	−2.427
5600	40.117	316.237	280.114	202.285	−163.131	263.193	−2.455
5700	40.168	316.947	280.754	206.299	−165.565	270.827	−2.482
5800	40.219	317.646	281.385	210.318	−168.011	278.505	−2.508
5900	40.270	318.334	282.005	214.343	−170.473	286.223	−2.534
6000	40.321	319.011	282.616	218.372	−172.950	293.986	−2.559

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

Phosphorus Oxide (PO$_2$) IDEAL GAS $M_r = 62.97256$ Phosphorus Oxide (PO$_2$) O$_2$P$_1$(g)

$S°(298.15\ K) = [253.685]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [-311.142]\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [-314.524]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[980](1)
[515](1)
[1044](1)

Ground State Quantum Weight: 2 $\sigma = 2$
Point Group: C_{2v}
Bond Distance: P–O = [1.485] Å
Bond Angle: O–P–O = [134°4']
Product of the Moments of Inertia: $I_A I_B I_C = [94.2392 \times 10^{-117}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from an estimated enthalpy of dissociation (270 ± 25 kcal·mol^{-1}) reported by Brewer and Rosenblatt.[1]

Heat Capacity and Entropy

The molecular constants selected for this table were estimated by Gordon.[2] The molecular constants for PO$_2$(g) have been estimated by Gordon[2], Potter *et al.*[3] and Henderson and Scheffee.[4] The entropies at 3000 K calculated from these three estimates differ by less than 0.8 cal·K^{-1}·mol^{-1}. The principal moments of inertia are: $I_A = [0.8775 \times 10^{-39}]$, $I_B = [9\ 9337 \times 10^{-39}]$, and $I_C = [10.8112 \times 10^{-39}]\ g^3{\cdot}cm^6$

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.662	−311.142	−311.142	INFINITE
100	33.536	214.043	287.365	−7.332	−311.604	−313.909	163.969
200	36.825	238.134	257.323	−3.838	−313.285	−315.789	82.476
250	39.137	246.597	254.354	−1.939	−313.936	−316.339	66.095
298.15	41.407	253.685	253.685	0.	−314.524	−316.748	55.493
300	41.493	253.942	253.686	0.077	−314.546	−316.762	55.153
350	43.699	260.506	254.199	2.207	−315.827	−317.015	47.312
400	45.659	266.472	255.366	4.442	−316.403	−317.145	41.415
450	47.347	271.950	256.909	6.769	−316.910	−317.206	36.820
500	48.779	277.015	258.669	9.173	−317.364	−317.214	33.139
600	50.998	286.116	262.503	14.168	−318.161	−317.107	27.607
700	52.574	294.103	266.458	19.351	−318.865	−316.875	23.646
800	53.710	301.201	270.366	24.668	−319.517	−316.546	20.668
900	54.548	307.578	274.152	30.083	−320.140	−316.137	18.348
1000	55.178	313.359	277.788	35.571	−320.747	−315.660	16.488
1100	55.663	318.642	281.266	41.114	−321.346	−315.122	14.964
1200	56.042	323.502	284.586	46.700	−385.513	−313.451	13.644
1300	56.344	328.001	287.754	52.320	−385.334	−307.453	12.354
1400	56.587	332.185	290.780	57.967	−385.164	−301.469	11.248
1500	56.786	336.096	293.672	63.636	−385.003	−295.497	10.290
1600	56.951	339.767	296.440	69.323	−384.853	−289.535	9.452
1700	57.089	343.224	299.091	75.025	−384.716	−283.581	8.713
1800	57.206	346.490	301.635	80.740	−384.593	−277.636	8.057
1900	57.305	349.586	304.078	86.466	−384.486	−271.697	7.469
2000	57.390	352.527	306.427	92.201	−384.395	−265.763	6.941
2100	57.464	355.329	308.690	97.944	−384.321	−259.833	6.463
2200	57.528	358.004	310.871	103.693	−384.265	−253.906	6.028
2300	57.584	360.563	312.976	109.449	−384.227	−247.982	5.632
2400	57.634	363.014	315.010	115.210	−384.208	−242.059	5.268
2500	57.678	365.368	316.978	120.976	−384.209	−236.136	4.934
2600	57.717	367.631	318.883	126.745	−384.228	−230.213	4.625
2700	57.751	369.810	320.729	132.519	−384.266	−224.289	4.339
2800	57.782	371.911	322.520	138.295	−384.322	−218.362	4.074
2900	57.810	373.939	324.258	144.075	−384.398	−212.435	3.826
3000	57.836	375.899	325.947	149.857	−384.491	−206.503	3.596
3100	57.859	377.796	327.589	155.642	−384.602	−200.568	3.380
3200	57.880	379.633	329.187	161.429	−384.730	−194.630	3.177
3300	57.899	381.415	330.743	167.218	−384.875	−188.687	2.987
3400	57.916	383.143	332.258	173.009	−385.037	−182.739	2.807
3500	57.932	384.822	333.736	178.801	−385.214	−176.787	2.638
3600	57.947	386.455	335.178	184.595	−385.406	−170.829	2.479
3700	57.960	388.043	336.586	190.390	−385.613	−164.866	2.327
3800	57.972	389.588	337.960	196.187	−385.834	−158.896	2.184
3900	57.984	391.094	339.303	201.985	−386.070	−152.921	2.048
4000	57.995	392.563	340.617	207.784	−386.318	−146.940	1.919
4100	58.004	393.995	341.901	213.584	−386.580	−140.953	1.796
4200	58.014	395.393	343.158	219.385	−386.855	−134.958	1.678
4300	58.022	396.758	344.389	225.187	−387.143	−128.957	1.567
4400	58.030	398.092	345.594	230.989	−387.443	−122.950	1.460
4500	58.038	399.396	346.775	236.793	−387.756	−116.936	1.357
4600	58.045	400.672	347.933	242.597	−388.082	−110.914	1.259
4700	58.051	401.920	349.069	248.401	−388.420	−104.885	1.166
4800	58.057	403.142	350.183	254.207	−388.771	−98.848	1.076
4900	58.063	404.339	351.276	260.013	−389.136	−92.804	0.989
5000	58.069	405.513	352.349	265.819	−389.515	−86.752	0.906
5100	58.074	406.662	353.402	271.627	−389.908	−80.693	0.826
5200	58.078	407.790	354.437	277.434	−390.315	−74.627	0.750
5300	58.083	408.897	355.455	283.242	−390.737	−68.551	0.676
5400	58.087	409.982	356.454	289.051	−391.176	−62.469	0.604
5500	58.091	411.048	357.437	294.860	−391.632	−56.378	0.535
5600	58.095	412.095	358.404	300.669	−392.105	−50.277	0.469
5700	58.099	413.123	359.355	306.479	−392.597	−44.169	0.405
5800	58.102	414.134	360.291	312.289	−393.108	−38.051	0.343
5900	58.106	415 127	361.212	318.099	−393.640	−31.927	0.283
6000	58.109	416.104	362.119	323.910	−394.193	−25.790	0.225

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

Phosphorus Oxide (PO$_2$) O$_2$P$_1$(g)

Lead Oxide (PbO_2) CRYSTAL $M_r = 239.1988$ Lead Oxide (PbO_2) $O_2Pb_1(cr)$

$S°(298.15\ K) = 71.797 \pm 0.42\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -269.874 \pm 2.9\ kJ{\cdot}mol^{-1}$

$\Delta_fH°(298.15\ K) = -274.470 \pm 2.9\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

Espada *et al.*[1] have calorimetrically determined the heat of the reaction $PbO_2(cr) + 2\ H_2(g) \rightarrow Pb(cr) + 2\ H_2O(l)$ as -71.02 ± 0.16 kcal·mol^{-1} from which they derive $\Delta_fH°(PbO_2, cr, 298.15\ K) = -65.61 \pm 0.32$ kcal·mol^{-1}. This value assumes that the PbO_2 was 100% pure, in fact it is virtually impossible[2] to prepare a sample free of water and fully oxidized. Thus, Espada *et al.*[1] have increased their uncertainty to ± 0.7 kcal·mol^{-1} to cover the likely spread of values assuming typical compositions.

Millar[3] has recalculated the data of Glasstone for the Gibbs energy of the cell reaction $PbO_2(cr) + H_2(g) \rightarrow PbO(red) + H_2O(l)$ as $\Delta_rG°(298.15\ K) = -49.600$ kcal·mol^{-1}. With auxiliary Gibbs energy data[4,5] we calculate $\Delta_fG°(PbO_2, cr, 298.15\ K) = -52.33$ kcal·mol^{-1} which corresponds to $\Delta_fH°(PbO_2, cr, 298.15\ K) = -66.45$ kcal·mol^{-1} in reasonable agreement with the value reported by Espada *et al.*[1]

We adopt the value $\Delta_fH°(PbO_2, cr, 298.15\ K) = -65.6 \pm 0.7$ kcal·mol^{-1}.

Heat Capacity and Entropy

Duisman and Giauque[2] have reported the heat capacity of PbO_2 from 15 to 318 K and have calculated the entropy at 298.15 K based on $S°(15\ K) = 0.079$ cal·K^{-1}·mol^{-1}. They had considerable difficulty in preparing a suitable sample of PbO and finally used a sample containing PbO and H_2O, as impurities, for which significant corrections were made to the measured data. Millar[3] also has measured the heat capacity from 70 to 298 K but is 7% higher than the adopted values.

High temperature enthalpy data have been reported by Palmaer[6] and Bousquet *et al.*[7] but these data suffer from unknown amounts of impurity, for which the correction is probably substantial, and decomposition to intermediate oxides. Thus, the heat capacity above room temperature was estimated by a graphical extrapolation of the low temperature heat capacity.

Decomposition Data

Numerous investigators have reported the decomposition of PbO_2 at elevated temperatures, however, the exact processes are still not well defined. Otto[8] indicates a three step process to Pb_3O_4, but the intermediate compositions are not established. The temperature at which the decomposition pressure of oxygen reaches 0.2 atm was reported as 260°C by Otto while White and Roy[9] indicate 293°C. The enthalpies and entropies reported are in serious disagreement with adopted values and indicate failure to attain equilibrium.

References

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.000	0.000	INFINITE	−10.965	−269.874	−269.874	INFINITE
100	29.878	21.983	117.951	−9.597	−273.176	−254.361	132.865
200	49.957	49.530	77.063	−5.507	−274.522	−234.876	61.343
298.15	61.170	71.797	71.797	0.000	−274.470	−215.397	37.737
300	61.318	72.176	71.799	0.113	−274.461	−215.030	37.440
400	67.613	90.754	74.289	6.586	−273.688	−195.323	25.507
500	71.698	106.314	79.180	13.567	−272.580	−175.855	18.371
600	74.517	119.649	84.841	20.885	−271.311	−156.628	13.636
700	76.210	131.267	90.661	28.424	−274.848	−136.820	10.210
800	77.571	141.536	96.391	36.116	−273.510	−117.192	7.652
900	78.602	150.736	101.927	43.927	−272.090	−97.737	5.673
1000	79.301	159.056	107.231	51.825	−270.609	−78.443	4.097
1100	79.669	166.634	112.292	59.777	−269.091	−59.300	2.816
1200	79.705	173.570	117.114	67.748	−267.562	−40.296	1.754

PREVIOUS: March 1962   CURRENT: December 1971

Lead Oxide (PbO_2) $O_2Pb_1(cr)$

Sulfur Dioxide (SO_2) IDEAL GAS $M_r = 64.0588$ Sulfur Dioxide (SO_2) $O_2S_1(g)$

$S°(298.15\ K) = 248.212 \pm 0.08\ J·K^{-1}·mol^{-1}$

$\Delta_fH°(0\ K) = -294.299 \pm 0.21\ kJ·mol^{-1}$

$\Delta_fH°(298.15\ K) = -296.842 \pm 0.21\ kJ·mol^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}
1151.38(1)
517.69(1)
1361.76(1)

Ground State Quantum Weight: 1
Point Group: C_{2v} $\sigma = 2$
Bond Distance: S–O = 1.432 ± 0.003 Å
Bond Angle: O–S–O = 119.53° ± 0.40°
Product of the Moments of Inertia: $I_AI_BI_C = 1.070 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

Eckman and Rossini[1] measured the enthalpy of combustion of rhombic sulfur to SO_2. Changes due to different atomic weights and electrical constants, though negligible, have been made.

Heat Capacity and Entropy

The functions were calculated by Gordon[2] using the method of Pennington and Kobe.[3] Structural parameters are given by Sirvetz,[4] obtained from microwave measurements Frequencies were measured by Shelton *et al.*[5] A 3rd law value of $S°(298.15\ K) = 59.24\ cal·K^{-1}·mol^{-1}$ was obtained by Giauque and Stevenson.[6] The principal moments of inertia are (all in $g·cm^2$): $I_A = 1.380 \times 10^{-39}$, $I_B = 8.131 \times 10^{-39}$, and $I_C = 9.534 \times 10^{-39}$.

References

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0 000	0.000	INFINITE	−10.552	−294.299	−294.299	INFINITE
100	33.526	209.025	281.199	−7.217	−294.559	−296.878	155.073
200	36.372	233.033	251.714	−3.736	−295.631	−298.813	78.042
298.15	39.878	248.212	248.212	0.000	−296.842	−300.125	52.581
300	39.945	248.459	248.213	0.074	−296.865	−300.145	52.260
400	43.493	260 448	249.824	4.250	−300.257	−300.971	39.303
500	46.576	270.495	252.979	8.758	−302.736	−300.871	31.432
600	49.049	279.214	256.641	13.544	−304.694	−300.305	26.144
700	50.961	286.924	260.427	18.548	−306.291	−299.444	22.345
800	52.434	293.829	264.178	23.721	−307.667	−298.370	19.482
900	53.580	300.073	267.825	29.023	−362.026	−296.051	17.182
1000	54.484	305.767	271.339	34.428	−361.940	−288.725	15.081
1100	55.204	310.995	274.710	39.914	−361.835	−281.409	13.363
1200	55.794	315.824	277.937	45.464	−361.720	−274.102	11.931
1300	56.279	320.310	281.026	51.069	−361.601	−266.806	10.720
1400	56.689	324.496	283.983	56.718	−361.484	−259.518	9.683
1500	57.036	328.419	286.816	62.404	−361.372	−252.239	8.784
1600	57.338	332.110	289.533	68.123	−361.268	−244.967	7.997
1700	57.601	335.594	292.141	73.870	−361.176	−237.701	7.304
1800	57.831	338.893	294.647	79.642	−361.096	−230.440	6.687
1900	58.040	342.026	297.059	85.436	−361.031	−223.183	6.136
2000	58.229	345.007	299.383	91.250	−360.981	−215.929	5.639
2100	58.400	347.853	301.624	97.081	−360.948	−208.678	5.191
2200	58.555	350.573	303.787	102.929	−360.931	−201.427	4 782
2300	58.702	353.179	305.878	108.792	−360.930	−194.177	4 410
2400	58.840	355.680	307.902	114.669	−360.947	−186.927	4.068
2500	58.965	358.085	309.861	120.559	−360.980	−179.675	3.754
2600	59.086	360.400	311 761	126.462	−361.030	−172.422	3.464
2700	59.199	362.632	313.604	132.376	−361.095	−165.166	3.195
2800	59.308	364 787	315.394	138.302	−361 175	−157.908	2.946
2900	59.413	366.870	317.133	144.238	−361.270	−150.648	2.713
3000	59.513	368.886	318.825	150.184	−361.379	−143.383	2.497
3100	59.609	370.839	320.471	156 140	−361.502	−136.114	2.294
3200	59.706	372.733	322.075	162.106	−361.638	−128.842	2.103
3300	59.794	374.572	323.638	168.081	−361.786	−121.565	1.924
3400	59.881	376.358	325.162	174.065	−361.946	−114.283	1.756
3500	59.969	378.095	326.650	180.057	−362.118	−106.996	1.597
3600	60.053	379.786	328.103	186.058	−362.300	−99.704	1.447
3700	60.137	381.432	329.522	192.068	−362.493	−92.408	1.305
3800	60.216	383.037	330.909	198.086	−362.697	−85.105	1.170
3900	60.296	384.602	332.266	204.111	−362.911	−77.796	1.042
4000	60.375	386.130	333.593	210.145	−363.134	−70.484	0.920
4100	60.450	387.621	334.893	216.186	−363.368	−63.164	0.805
4200	60.530	389 079	336.166	222.235	−363.611	−55.840	0.694
4300	60.605	390.504	337.413	228.292	−363.864	−48.508	0.589
4400	60.676	391.898	338.636	234.356	−364.128	−41.172	0 489
4500	60.752	393.263	339.834	240.427	−364.401	−33.829	0.393
4600	60.823	394.599	341.010	246.506	−364.686	−26.480	0.301
4700	60.894	395.908	342.165	252.592	−364.981	−19.125	0.213
4800	60.969	397.190	343.298	258.685	−365.288	−11.763	0.128
4900	61.036	398.448	344.410	264.785	−365.607	−4.394	0.047
5000	61.107	399.682	345.504	270.893	−365.938	2.981	−0.031
5100	61.178	400.893	346.578	277.007	−366.283	10.364	−0.106
5200	61.250	402.082	347.634	283.128	−366.641	17.751	−0.178
5300	61.317	403.249	348.672	289.257	−367.014	25.148	−0.248
5400	61.388	404.396	349.693	295.392	−367.403	32.550	−0.315
5500	61.455	405.523	350.698	301.534	−367.807	39.960	−0.380
5600	61.522	406.631	351.687	307.683	−368.230	47.379	−0.442
5700	61.588	407.720	352.661	313.838	−368.671	54.804	−0.502
5800	61.655	408.792	353.619	320.000	−369.131	62.238	−0.561
5900	61.727	409.846	354.563	326.169	−369.611	69.677	−0.617
6000	61.793	410.884	355.493	332.346	−370.113	77.128	−0.671

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

Cristobalite, High (SiO_2) CRYSTAL $M_r = 60.0843$ Silicon Oxide, Cristobalite, High (SiO_2) $O_2Si_1(cr)$

$S°(298.15\ K) = 50.053\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs1} = 543 \pm 3$ K(low cristobalite → high cristobalite)
$T_{trs2} = 1079 \pm 250$ K(high quartz → high cristobalite)
$T_{fus} = 1996 \pm 5$ K(high cristobalite → liquid)

$\Delta_f H°(298.15\ K) = -905.489\ kJ{\cdot}mol^{-1}$
$\Delta_{trs1}H° = 1.343 \pm 0.25\ kJ{\cdot}mol^{-1}$
$\Delta_{trs2}H° = 2.008 \pm 0.63\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 9.581 \pm 2.1\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of low cristobalite by addition of $\Delta_{trs}H° = 0\ 321\ kcal{\cdot}mol^{-1}$ and the difference between $H°(543\ K)–H°(298.15\ K)$ for low and high forms.

Heat Capacity and Entropy

$C_p°$ 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 siica. Data of Wietzel[3] for his sample prepared at 1600°C deviate by + 3% at 673 K and + 1.6% at 1973 K. $C_p°$ 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 enthalpy 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 pressures 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 T_{fus}. 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 $\Delta_r G° = 0$ for high quartz → high cristobalite; $\Delta_{trs}H° = 0.48 \pm 0.15\ kcal{\cdot}mol^{-1}$ is the corresponding enthalpy difference. The uncertainty in T_{trs} is derived from that in $\Delta_{trs}H°$ which, in turn, is taken from $\Delta_r H°(970\ K) = 0.45 \pm 0.15\ kcal{\cdot}mol^{-1}$ obtained by Holm[7] from $\Delta_{sol}H°$ measurements in an oxide melt. It is apparent that T_{trs} 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.

Fusion 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] $\Delta_{fus}H°$ *is calculated as the difference in* $\Delta_f H°$ for liquid and crystal at T_{fus}. Mackenzie *et al.*[11] showed that cristobalite may be superheated by as much as 40° above T_{fus} due to its slow rate of fusion.

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	26.581	50.053	50.053	0.000	−905.489	−853.636	149.554
300	27.154	50.219	50.054	0.050	−905.530	−853.315	148.575
400	47 413	61.218	51.416	3.921	−906.752	−835.678	109.128
500	56.856	72.923	54.555	9.184	−906.826	−817.885	85.444
600	62.049	83.788	58.536	15.151	−906.394	−800.132	69.658
700	65.229	93.609	62.857	21.526	−905.721	−782.473	58.389
800	67.337	102.466	67.264	28.161	−904.932	−764.919	49.944
900	68.823	110.487	71.628	34.973	−904.088	−747.468	43.382
1000	69.923	117.798	75.885	41.913	−903.221	−730.112	38.137
1100	70.772	124.504	80.004	48.949	−902.350	−712.843	33.850
1200	71.446	130.691	83.974	56.061	−901.485	−695.653	30.281
1300	71.998	136.432	87.791	63.234	−900.636	−678.535	27.264
1400	72.467	141.786	91.459	70.458	−899.808	−661.482	24.680
1500	72.869	146.799	94.983	77.725	−899.006	−644.487	22.443
1600	73.220	151.514	98.370	85.030	−898.235	−627.544	20.487
1700	73.534	155.962	101.628	92.368	−947.674	−610.202	18.749
1800	73.814	160.173	104.765	99 735	−946 742	−590.378	17.132
1900	74.074	164.171	107.787	107.130	−945.806	−570.605	15.687
2000	74.316	167.977	110.702	114.549	−944.869	−550.882	14.388
2100	74.542	171.608	113.517	121.992	−943.931	−531.206	13.213
2200	74.751	175.081	116.237	129.457	−942.994	−511.573	12.146
2300	74.952	178.408	118.868	136.942	−942.059	−491.985	11.173
2400	75.145	181.602	121.416	144.447	−941.126	−472.437	10.282
2500	75.333	184.674	123.885	151.971	−940.197	−452.927	9.463
2600	75.509	187.632	126.280	159.513	−939.271	−433.454	8.708
2700	75.684	190.485	128.606	167.073	−938.348	−414.017	8.010
2800	75.852	193.240	130.865	174.650	−937.428	−394.614	7.362
2900	76.015	195.905	133.062	182.243	−936.512	−375.245	6.759
3000	76.178	198.485	135.200	189.853	−935.599	−355.906	6.197

PREVIOUS: CURRENT: June 1967

Cristobalite, Low (SiO_2) CRYSTAL $M_r = 60.0843$ Silicon Oxide, Cristobalite, Low (SiO_2) $O_2Si_1(cr)$

$S°(298.15\ K) = 43.396 \pm 0.13\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{tr} = 543 \pm 3\ K$ (low cristobalite → high cristobalite)

$\Delta_f H°(0\ K) = -903.482 \pm 2.1\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -908.346 \pm 2.1\ kJ{\cdot}mol^{-1}$
$\Delta_{trs} H° = 1.343 \pm 0.25\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of quartz using $\Delta_r H°(970\ K) = 0.45 \pm 0.15\ kcal{\cdot}mol^{-1}$ for high quartz → high cristobalite, as determined by Holm[1] from $\Delta_{sol} H°$ is an oxide melt. This value reduces to $\Delta_r H°(298.15\ K) = 0.60\ kcal{\cdot}mol^{-1}$ for low quartz → low cristobalite. Kracek[2] obtained essentially the same value, $\Delta_r H°(298.15\ K) = 0.63\ kcal{\cdot}mol^{-1}$, from $\Delta_{sol} H°$ in HF(aq, 74.7 °C), while Hummel[3] found $\Delta_r H°(298\ 15\ K) = 1.80\ kcal{\cdot}mol^{-1}$ from $\Delta_{sol} H°$ in HF(aq, 26.5 °C). The larger $\Delta_r H°$ corresponds to a less negative $\Delta_f H°$ (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 $\Delta_f H°$ 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	T/K	Data Points	$\Delta_r H(T)$ kcal·mol⁻¹	$\Delta_r H°(298.15\ K)$ kcal·mol⁻¹	Drift cal·K⁻¹·mol⁻¹	$\Delta_f H°(298.15\ K)$ kcal·mol⁻¹
1	$\Delta_{sol} H°$ in oxide melt	A	970	3	0.45 ± 0.15	0.6	–	−217.10
2	$\Delta_{sol} H°$ in HF(aq, 26.5°C)	A	299.65	8	1.80 ± 0.2	1.80	–	−215.90 [3]
	$\Delta_{sol} H°$ in HF(aq, 74.7°C)	A	298 348	–	–	0.63 ± 0.05	–	−217.07
4	$\Delta_{sol} H°$ in HF(aq, 73.7°C)	A	298 347	6	–	0.93 ± 0.1	–	−216.77
5	Keq + γ(Si)	B	1843–1953	3	104.5 ± 0.6*	−112.48*	0.8	−217.17
6	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	$K°_p$	E	1703–1829	14	145.9 ± 1.3*	146.92*	−2.3 ± 0.7	−217.94
8	$K°_p$	E	1673–1853	5	145.5 ± 3.5*	147.43*	−1.9 ± 1.9	−218.45

*Values at T are from 2nd law analysis while those at 298.15 K are from 3rd law.

Reactions:
A) SiO_2(quartz, low or high) = SiO_2(cristobalite, low or high)
B) SiO_2(high cristobalite) + 2 H_2(g) = Si(l) + 2 H_2O(g)
C) SiO_2(high cristobalite) + 2 C(graph) = Si(l) + 2 CO(g)
D) SiO_2(high cristobalite) + 2 SiC(β) = 3 Si(l) + 2 CO(g)
E) SiO_2(high cristobalite) + 3 C(graph) = SiC(β) + 2 CO(g)

Heat Capacity and Entropy

$C°_p$ below 300 K is based on data of Westrum.[11] Earlier data of Anderson[12] are in satisfactory agreement. The entropy is obtained from $C°_p$ using $S°(5\ K) = 0.0007\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. $C°_p$ 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 T_{tr}. T_{tr} is taken as the temperature at the peak in the heating curve for well ordered cristobalite, however, see[15] [16] for detaled discussions of temperatures about 25 lower which were found from cooling curves. $\Delta_{trs} H°$ 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 T_{tr}, which suggests that the sample was less well-ordered than desirable. $\Delta_{trs} H°$ is confirmed, however, by other data which are summarized below. Additional polymorphism is discussed on the table for high cristobalite.

Source	Method	$\Delta_{trs} H°$, kcal·mol⁻¹
13	Enthalpy data	0.321
17	Microcalorimetric thermal analysis	0.318 ± 0.018
18	ΔV and dT/DP	0.27
19	Differential thermal analysis	0.26 ± 0.01

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Continued on page 1814

Enthalpy Reference Temperature = T_r = 298.15 K						Standard State Pressure = $p°$ = 0.1 MPa	
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C°_p$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−7.037	−903.482	−903 482	INFINITE
100	16.000	11.247	74.760	−6.351	−905.967	−889.378	464.563
200	32.995	27.878	47.145	−3.853	−907.559	−872.105	227.770
298.15	44.953	43.396	43.396	0.000	−908.346	−854.509	149.706
300	45.145	43.675	43.397	0.083	−908.355	−854.175	148.725
400	53.145	57.848	45.275	5.029	−908.501	−836.079	109.181
500	58.672	70.326	49.064	10.631	−908.236	−817.997	85.456
600	62.969	81.426	53.549	16.726	−907.677	−799.998	69.646
700	65.689	91.348	58.254	23.166	−906.940	−782.108	58.362
800	67.572	100.247	62.956	29.832	−906.119	−764.330	49.906
900	69.036	108.292	67.554	36.664	−905.254	−746.658	43.335
1000	70.291	115.633	72.000	43.632	−904.359	−729.084	38.083

PREVIOUS: CURRENT: June 1967

Silicon Oxide, Quartz (SiO_2) CRYSTAL $M_r = 60.0843$ Silicon Oxide, Quartz (SiO_2) $O_2Si_1(cr)$

$\Delta_fH°(0\ K) = -905.872 \pm 1.7\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 41.463 \pm 0.13\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = -910.857 \pm 1.7\ kJ{\cdot}mol^{-1}$

$T_{trs1} = 847 \pm 1.5$ K (low quartz → high quartz) $\Delta_{trs1}H° = 0.728 \pm 0.17\ kJ{\cdot}mol^{-1}$

$T_{trs2} = 1079 \pm 250$ K (high quartz → high cristobalite) $\Delta_{trs2}H° = 2.008 \pm 0.63\ kJ{\cdot}mol^{-1}$

$T_{fus} = 1696 \pm 50$ K (high quartz → liquid) $\Delta_{fus}H° = 7.699 \pm 0.8\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is based on data of Wise[1] for combustion of SiO_2(low quartz) and Si(cr) in F_2 to form SiF_4(g). Good[2] burned a mixture of Si(cr) 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 $\Delta_fH°(298.15\ K) = -217.5 \pm 0.5\ kcal{\cdot}mol^{-1}$. Agreement with the adopted value is excellent, considering the complexity of the latter scheme. Both schemes are independent of $\Delta_fH°$(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 $kcal{\cdot}mol^{-1}$. Pertinent equilibrium data are analyzed on the table of SiO_2(low cristobalite), while the calorimetric results are summarized below.

Source	Reaction	$\Delta_rH°(298.15\ K)$, $kcal{\cdot}mol^{-1}$	$\Delta_fH°(298.15\ K)$, $kcal{\cdot}mol^{-1}$
1	SiO_2(low quartz) + 2 F_2(g) → SiF_4(g) + O_2(g)	−168.26 ± 0.28	−217.72 ± 0.34
2	See text.	—	−217.5 ± 0.5
3	Si(cr) + 2 O_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 $C_p°$ using $S°(2\ K) = 0.00001\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ from 300 to 847 K is derived from adiabatic calorimetric data of Moser[8] and Sinel'nikov.[9] The adopted $C_p°$ is discontinuous at 847 K and $\Delta C_p° = -2.17\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. 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] $C_p°$ 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 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ at 900 K. The higher value, due to use of a larger $\Delta_{trs1}H°$, was presumably based on Roth,[12] Wietze[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 $kcal{\cdot}mol^{-1}$, respectively; however, a recent enthalpy datum[15] obtained by transposed temperature drop calorimetry deviates +75 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ at 968 K.

Transition Data

$T_{trs1} = 847 \pm 1.5$ K is based on thermal analysis of many specimens by Keith and Tuttle.[16] Wide variations in T_{trs1} 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 enthalpy of transition is derived as $(1011-854+17) = 174\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, where *1011 ± 6 is* $H°(873.15\ K)-H°(823.15\ K)$ measured by Moser,[8] 854 is the corresponding increment calculated from the JANAF $C_p°$ and 17 is an endpoint correction for the difference between the observed and adopted curves below 823.15 K. Some recent data which confirm the adopted $\Delta_{trs1}H°$ are summarized below.

Source	Method	$\Delta_{trs1}H°$, $kcal{\cdot}mol^{-1}$
8	H and $C_p°$ from adiabatic calorimetry	0.174
9	Integration of $C_p°$ from adiabatic calorimetry	0.143
10	Thermal analysis	0.198
17	ΔV with $dT/dP = 0.026$ K/atm	0.12
18	Microcalorimetric thermal analysis, Single crystal	0.156, 0.165, 0.178 ± − .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. $\Delta_{trs2}H°$ and $\Delta_{fus}H°$ are calculated from the differences in the $\Delta_fH°$ values of the appropriate phases at T_{trs2} and T_{fus}.

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.000	0.000	INFINITE	−6.916	−905.872	−905.872	INFINITE
100	15.686	9.694	72.496	−6.280	−908.406	−891.662	465.756
200	32.639	26.087	45.187	−3.820	−910.036	−874.223	228.324
298.15	44.589	41.463	41.463	0.000	−910.857	−856.443	150.045
300	44.769	41.740	41.464	0.083	−910.866	−856.106	149.061
400	53.430	55.874	43.333	5.017	−911.024	−837.812	109.407
500	59.643	68.499	47.127	10.686	−910.692	−819.539	85.617
600	64.417	79.808	51.648	16.896	−910.017	−801.368	69.765
700	68.768	90.063	56.414	23.554	−909.062	−783.331	58.453
800	73.701	99.555	61.220	30.668	−907.794	−765.452	49.979
847.000	76.509	103.840	63.467	34.196	I <− −> II		
847.000	67.417	104.700	63.467	34.924	TRANSITION		
900	67.948	108.807	66.017	38.512	−905.918	−747.785	43.400
1000	68.952	116.018	70.662	45.357	−905.145	−730.256	38.145
1100	69.956	122.637	75.090	52.302	−904.365	−712.805	33.848
1200	70.961	128.767	79.311	59.348	−903.567	−695.426	30.271
1300	71.965	134.487	83.338	66.494	−902.744	−678.114	27.247
1400	72.969	139.857	87.185	73.741	−901.893	−660.866	24.657
1500	73.973	144.925	90.867	81.088	−901.011	−643.681	22.415
1600	74.977	149.731	94.397	88.535	−900.097	−626.555	20.455
1696.000	75.940	154.128	97.654	95.779	− − − − − − II <− −> LIQUID − − − − −		
1700	75.981	154.307	97.787	96.083	−949.326	−609.041	18.714
1800	76.986	158.678	101.050	103.732	−948.113	−589.059	17.094
1900	77.990	162.868	104.194	111.480	−946.823	−569.146	15.647
2000	78.994	166.894	107.229	119.330	−945.456	−549.303	14.346

PREVIOUS: December 1962 CURRENT: June 1967

Continued on page 1814

$S°(298.15\ K) = 47.928 \pm 1.3\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$T_{fus} = 1996 \pm 5\ K$(high cristobalite → liquid)

$\Delta_fH°(0\ K) = 897.756\ kJ{\cdot}mol^{-1}$

$\Delta_fH°(298.15\ K) = -902.661\ kJ{\cdot}mol^{-1}$

$\Delta_{fus}H° = 9.581 \pm 2.1\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_fH°$(l, supercooled, 298.15 K) is calculated from that of quartz using $\Delta_rH°(970\ K) = 1.45 \pm 0.15\ kcal{\cdot}mol^{-1}$ for high quartz Å $SiO_2(l)$, as determined by Holm[1] from $\Delta_{sol}H°$ in an oxide melt. This value reduces to $\Delta_rH°(298.15\ K) = 1.96\ kcal{\cdot}mol^{-1}$ for low quartz → $SiO_2(l)$ and is consistent within ± 0.3 $kcal{\cdot}mol^{-1}$ with other calorimetric data summarized below. Earlier results were reviewed by Hummel.[4]

Source	Method	Reaction	T/K	$\Delta_rH°(T)$ kcal·mol⁻¹	$\Delta_rH°(298.15\ K)$ kcal·mol⁻¹	$\Delta_fH°(298.15\ K)$ kcal·mol⁻¹
1	$\Delta_{sol}H°$ in oxide melt	A	970	1.45 ± 0.15	1.96	−215.74
2	$\Delta_cH°$ in flourine	B	298	1.78 ± 0.46	1.78	−215.92
3	$\Delta_{sol}H°$ in HF(aq, 74.7 C)	A	298–348	–	2.18 ± 0.05	−215.52
4	$\Delta_{sol}H°$ in HF(aq, 26.5 C)	A	300	2.27 ± 0.2	2.27	−215.43

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

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

Heat Capacity and Entropy

$C_p°$ 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% in the range 60–160 K and at 300 K but are in agreement elsewhere. The entropy is calculated from $C_p°$ using $S°(2.34\ K)–S°(0\ K) = 0.0001\ cal{\cdot}K^{-1}mol^{-1}$ and $S°(0\ K) = 1.098\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. $C_p°$ data[6] for a different sample annealed at 1300°C yield an entropy larger by <0.04 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$. Earlier data were reviewed by Kelley.[8] The residual entropy is calculated from $S°(0\ K) = S°(1996\ K)–S°(1996;0\ K) = 41.258–40.160 = 1\ 098\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, where 40.160 is obtained from the adopted functions, while 41.258 is the sum of $\Delta_{fus}S° = 1.14\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ and $S°(1996\ K) = 40.111\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ for high cristobalite. We estimate the uncertainty as ±0.3 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$, primarily from the uncertainty in $\Delta_{fus}H°$.

$C_p°$ 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. $C_p°$ 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%. Enthalpy data of Egan[13] and Kelley[14] deviate from the adopted values by less than 1% in the range 1000–1500 K, although large positive deviations appear at lower temperatures.

In the region 1500–1700 K, the adopted $C_p°$ 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 $C_p°$ rises to that of the stable liquid. $C_p°$ above 1700 K is estimated as 20.5 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ or 6.83 $cal{\cdot}K^{-1}$ g $atom^{-1}$. 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.

Fusion Data

The melting point of high cristobalite is 1996 ± 5 K, while the metastable melting point of high quartz is 1696 ± 50 K. $\Delta_{fus}H°$ is the difference between $\Delta_fH°$ for liquid and high cristobalite at T_{fus}. Values ranging from 1.8 to 3.6 $kcal{\cdot}mol^{-1}$ have been derived from various interpretations of phase diagrams.[1]

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.000	4.594	INFINITE	−6.996	−897.756	−897.756	INFINITE
100	16.154	15.983	78.952	−6.297	−900.228	−884.112	461.813
200	32.736	32.602	51.618	−3.803	−901.824	−867.314	226.519
298.15	44.183	47.928	47.928	0.000	−902.661	−850.175	148.947
300	44.367	48.202	47.929	0.082	−902.671	−849.850	147.972
400	52.518	62.156	49.776	4.952	−902.893	−832.194	108.673
500	58.082	74.510	53.513	10.499	−902.684	−814.537	85.094
600	62.045	85.468	57.943	16.515	−902.203	−796.949	69.381
700	64.973	95.263	62.587	22.873	−901.548	−779.457	58.164
800	67.208	104.091	67.233	29.486	−900.780	−762.067	49.758
900	68.956	112.112	71.780	36.298	−899.936	−744.777	43.226
1000	70.350	119.452	76.186	43.266	−899.041	−727.585	38.005
1100	71.475	126.211	80.430	50.359	−898.113	−710.484	33.738
1200	72.396	132.471	84.509	57.554	−897.165	−693.469	30.186
1300	73.157	138.296	88.425	64.832	−896.211	−676.533	27.183
1400	73.848	143.743	92.184	72.183	−895.256	−659.670	24.613
1500	74.475	148.852	95.794	79.587	−894.317	−642.876	22.387
1600	80.040	153.767	99.263	87.206	−893.232	−626.146	20.442
1696.000	85.772	158.655	102.487	95.261	----- II <--> LIQUID -----		
1700	85.772	158.857	102.619	95.604	−941.610	−609.059	18.714
1800	85.772	163.759	105.881	104.181	−939.468	−589.559	17.109
1900	85.772	168.397	109.050	112.759	−937.350	−570.178	15.675
2000	85.772	172.796	112.128	121.336	−935.255	−550.907	14.388
2100	85.772	176.981	115.118	129.913	−933.183	−531.741	13.226
2200	85.772	180.971	118.021	138.490	−931.133	−512.672	12.172
2300	85.772	184.784	120.842	147.067	−929.106	−493.697	11.212
2400	85.772	188.434	123.582	155.645	−927.102	−474.809	10.334
2500	85.772	191.936	126.247	164.222	−925.119	−456.004	9.528
2600	85.772	195.300	128.839	172.799	−923.158	−437.279	8.785
2700	85.772	198.537	131.360	181.376	−921.217	−418.628	8.099
2800	85.772	201.656	133.816	189.953	−919.297	−400.048	7.463
2900	85.772	204.666	136.207	198.531	−917.397	−381.538	6.872
3000	85.772	207.574	138.538	207.108	−915.517	−363.092	6.322
3100	85.772	210.386	140.810	215.685	−913.655	−344 708	5.808
3200	85.772	213.109	143.027	224.262	−911.811	−326.385	5.328
3300	85.772	215.749	145.191	232.839	−909.985	−308.119	4.877
3400	85.772	218.309	147.304	241.417	−908.175	−289.907	4.454
3500	85.772	220.796	149.369	249.994	−906.381	−271.749	4.056
3600	85.772	223.212	151.387	258.571	−1288.754	−243.181	3.528
3700	85.772	225.562	153.360	267.148	−1286.577	−214.168	3.024
3800	85.772	227.849	155.290	275.725	−1284.416	−185.212	2.546
3900	85.772	230.077	157.179	284.303	−1282.269	−156.313	2.094
4000	85.772	232.249	159.029	292.880	−1280.137	−127.470	1.665
4100	85.772	234.367	160.841	301.457	−1278.019	−98.680	1.257
4200	85.772	236.434	162.616	310.034	−1275.914	−69.941	0.870
4300	85.772	238.452	164.356	318.611	−1273.822	−41.252	0.501
4400	85.772	240.424	166.063	327.189	−1271.742	−12.612	0.150
4500	85.772	242.351	167.737	335.766	−1269.674	15.981	−0.186

PREVIOUS: December 1962   CURRENT: June 1967

CRYSTAL–LIQUID

0	to	847	K	crystal, low quartz (trigonal)
847	to	1079	K	crystal, high quartz (hexagonal)
1079	to	1996	K	crystal, high cristobalite
above		1996	K	liquid

Refer to the individual tables for details.

M_r = 60.0843 Silicon Oxide (SiO_2)

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−6.916	−905.872	−905.872	INFINITE
100	15.686	9.694	72.496	−6.280	−908.406	−891.662	465.756
200	32.639	26.087	45.187	−3.820	−910.036	−874.223	228.324
298.15	44.589	41.463	41.463	0.000	−910.857	−856.443	150.045
300	44.769	41.740	41.464	0.083	−910.866	−856.106	149.061
400	53.430	55.874	43.333	5.017	−911.024	−837.812	109.407
500	59.643	68.499	47.127	10.686	−910.692	−819.539	85.617
600	64.417	79.808	51.648	16.896	−910.017	−801.368	69.765
700	68.768	90.063	56.414	23.554	−909.062	−783.331	58.453
800	73.701	99.555	61.220	30.668	−907.794	−765.452	49.979
847.000	76.509	103.840	63.467	34.196	I <--> II TRANSITION		
847.000	67.417	104.700	63.467	34.924			
900	67.948	108.807	66.017	38.512	−905.918	−747.785	43.400
1000	68.952	116.018	70.662	45.357	−905.145	−730.256	38.145
1100	69.956	122.637	75.090	52.302	−904.365	−712.805	33.848
1200	70.961	128.767	79.311	59.348	−903.567	−695.426	30.271
1300	71.965	134.487	83.338	66.494	−902.744	−678.114	27.247
1400	72.969	139.857	87.185	73.741	−901.893	−660.866	24.657
1500	73.973	144.925	90.867	81.088	−901.011	−643.681	22.415
1600	74.977	149.731	94.397	88.535	−900.097	−626.555	20.455
1696.000	75.940	154.128	97.654	95.779	II <--> LIQUID TRANSITION		
1696.000	85.772	158.655	97.654	103.456			
1700	85.772	158.857	97.798	103.799	−941.610	−609.059	18.714
1800	85.772	163.759	101.328	112.377	−939.468	−589.559	17.109
1900	85.772	168.397	104.737	120.954	−937.350	−570.178	15.675
2000	85.772	172.796	108.031	129.531	−935.255	−550.907	14.388
2100	85.772	176.981	111.215	138.108	−933.183	−531.741	13.226
2200	85.772	180.971	114.296	146.685	−931.133	−512.672	12.172
2300	85.772	184.784	117.278	155.263	−929.106	−493.697	11.212
2400	85.772	188.434	120.168	163.840	−927.102	−474.809	10.334
2500	85.772	191.936	122.969	172.417	−925.119	−456.004	9.528
2600	85.772	195.300	125.687	180.994	−923.158	−437.279	8.785
2700	85.772	198.537	128.325	189.571	−921.217	−418.628	8.099
2800	85.772	201.656	130.889	198.149	−919.297	−400.048	7.463
2900	85.772	204.666	133.381	206.726	−917.397	−381.538	6.872
3000	85.772	207.574	135.806	215.303	−915.517	−363.092	6.322
3100	85.772	210.386	138.167	223.880	−913.655	−344.708	5.808
3200	85.772	213.109	140.466	232.457	−911.811	−326.385	5.328
3300	85.772	215.749	142.708	241.035	−909.985	−308.119	4.877
3400	85.772	218.309	144.894	249.612	−908.175	−289.907	4.454
3500	85.772	220.796	147.027	258.189	−906.381	−271.749	4.056
3600	85.772	223.212	149.110	266.766	−1288.754	−243.181	3.528
3700	85.772	225.562	151.145	275.343	−1286.577	−214.168	3.024
3800	85.772	227.849	153.133	283.921	−1284.416	−185.212	2.546
3900	85.772	230.077	155.078	292.498	−1282.269	−156.313	2.094
4000	85.772	232.249	156.980	301.075	−1280.137	−127.470	1.665
4100	85.772	234.367	158.842	309.652	−1278.019	−98.680	1.257
4200	85.772	236.434	160.665	318.229	−1275.914	−69.941	0.870
4300	85.772	238.452	162.450	326.807	−1273.822	−41.252	0.501
4400	85.772	240.424	164.200	335.384	−1271.742	−12.612	0.150
4500	85.772	242.351	165.916	343.961	−1269.674	15.981	−0.186

PREVIOUS: CURRENT: June 1967

Silicon Oxide (SiO_2) IDEAL GAS $M_r = 60.0843$ Silicon Oxide (SiO_2) $O_2Si_1(g)$

$S°(298.15\ K) = [228.976]\ J·K^{-1}·mol^{-1}$

$\Delta_fH°(0\ K) = -304.11 \pm 33.5\ kJ·mol^{-1}$
$\Delta_fH°(298.15\ K) = -305.43 \pm 33.5\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[980] (1)
[370] (2)
[1430] (1)

Ground State Quantum Weight: [1] $\sigma = [2]$
Point Group: $[D_{\infty h}]$
Bond Angle: O–Si–O = [180]°
Bond Distance: Si–O = [1.55] Å
Rotational Constant: $B_0 = [0.219280]\ cm^{-1}$

Enthalpy of Formation

The adopted value is based on the data summarized below. Margrave[1] has reported a value of $\Delta_{sub}H°(298.15\ K) = 140.9 \pm 1\ kcal·mol^{-1}$ but details are not yet available. Assuming that this corresponds to reaction A below, we calculate $\Delta_fH°(298.15\ K) = -75.5\ kcal·mol^{-1}$. 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 $\Delta_{sub}H°$ from ion intensities. The resulting range for $\Delta_{sub}H°(298.15\ K)$, *136 to 141 kcal·mol*$^{-1}$, *is consistent* with the lower limit of 130 $kcal·mol^{-1}$, 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 $\Delta_{sub}H°$ of 148 $kcal·mol^{-1}$. The adopted $\Delta_fH°$ corresponds to $\Delta_{sub}H°(298.15\ K) = 143.4 \pm 8\ kcal·mol^{-1}$ and to $\Delta_{at}H(0\ K) = 297.3 \pm 8\ kJ·mol^{-1}$.

Source	Reaction	Method	T/K	$\Delta_fH°(298.15\ K)\ kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta H°(298.15\ K)$, $kcal·mol^{-1}$
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 × 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 $k\delta/l^2 = 0.3 \times 10^5$ dyne/cm, which are obtained from those of SiO, CO_2 and CO.

References

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[4] R. F. Porter, W. A. Chupka and M. G. Inghram, J. Chem. Phys. 23, 216 (1955).
[5] J. W. Linnett, "The Electronic Structure of Molecules," pp. 43–55, Methuen and Co. Ltd., London, (1964).

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

T/K	$C_p°$ ($J·K^{-1}mol^{-1}$)	$S°$ ($J·K^{-1}mol^{-1}$)	$-[G°-H°(T_r)]/T$ ($J·K^{-1}mol^{-1}$)	$H°-H°(T_r)$ ($kJ·mol^{-1}$)	$\Delta_fH°$ ($kJ·mol^{-1}$)	$\Delta_fG°$ ($kJ·mol^{-1}$)	log K_f
0	0.	0.	INFINITE	−10.581	−304.112	−304.112	INFINITE
100	31.422	188.175	264.459	−7.628	−304.330	−305.433	159.542
200	38.997	212.419	232.851	−4.086	−304.878	−306.331	80.006
250	41.746	221.426	229.688	−2.066	−305.165	−306.662	64.074
298.15	44.007	228.976	228.976	0.	−305.432	−306.926	53.772
300	44.089	229.249	228.977	0.081	−305.442	−306.935	53.442
350	46.161	236.204	229.522	2.339	−305.696	−307.163	45.842
400	48.007	242.491	230.756	4.694	−305.922	−307.357	40.137
450	49.641	248.241	232.384	7.136	−306.121	−307.524	35.696
500	51.076	253.547	234.238	9.655	−306.298	−307.670	32.142
600	53.416	263.076	238.269	14.885	−306.604	−307.915	26.806
700	55.180	271.449	242.423	20.319	−306.872	−308.112	22.992
800	56.513	278.909	246.526	25.906	−307.130	−308.272	20.128
900	57.531	285.627	250.503	31.611	−307.394	−308.399	17.899
1000	58.317	291.730	254.326	37.405	−307.672	−308.496	16.114
1100	58.934	297.319	257.984	43.269	−307.974	−308.563	14.652
1200	59.425	302.468	261.479	49.187	−308.302	−308.603	13.433
1300	59.820	307.241	264.818	55.150	−308.663	−308.613	12.400
1400	60.143	311.687	268.009	61.149	−309.060	−308.595	11.514
1500	60.409	315.845	271.061	67.177	−309.497	−308.547	10.745
1600	60.631	319.751	273.983	73.229	−309.978	−308.468	10.070
1700	60.817	323.433	276.785	79.302	−360.682	−307.911	9.461
1800	60.976	326.914	279.474	85.392	−361.028	−304.797	8.845
1900	61.111	330.214	282.058	91.497	−361.383	−301.663	8.293
2000	61.228	333.352	284.545	97.614	−361.747	−298.511	7.796
2100	61.330	336.342	286.941	103.742	−362.125	−295.340	7.346
2200	61 418	339.197	289.252	109.879	−362.515	−292.150	6.937
2300	61.496	341.929	291.483	116.025	−362.919	−288.943	6.562
2400	61.564	344.547	293.640	122.178	−363.339	−285.718	6.218
2500	61.625	347.062	295.727	128.337	−363.774	−282.475	5.902
2600	61.679	349.480	297.748	134.503	−364.225	−279.214	5.609
2700	61 727	351.809	299.707	140.673	−364.691	−275.935	5.338
2800	61.770	354.054	301.609	146.848	−365.173	−272.639	5.086
2900	61.809	356.223	303.455	153.027	−365.672	−269.326	4.851
3000	61.845	358.319	305.249	159.210	−366.186	−265.995	4.631
3100	61.877	360.347	306.993	165.396	−366.715	−262.646	4.426
3200	61.906	362.312	308.692	171.585	−367.259	−259.281	4.232
3300	61.933	364.217	310.346	177.777	−367.818	−255.898	4.051
3400	61.957	366 067	311.957	183.971	−368.390	−252.497	3.879
3500	61.979	367.863	313.529	190.168	−368.977	−249.081	3.717
3600	62.000	369.609	315.063	196.367	−753.729	−235.186	3.412
3700	62.019	371.308	316.560	202.568	−753.928	−220.779	3.117
3800	62.036	372.962	318.023	208.771	−754.141	−206.366	2.837
3900	62.052	374.574	319.452	214.975	−754.367	−191.948	2.571
4000	62.067	376.145	320.850	221.181	−754.606	−177.524	2.318
4100	62.081	377 678	322.217	227.389	−754.858	−163.094	2.078
4200	62.094	379.174	323.556	233.597	−755.122	−148.658	1.849
4300	62.106	380.635	324.866	239.807	−755.396	−134.215	1.630
4400	62.117	382.063	326.150	246.018	−755.683	−119.766	1.422
4500	62.128	383.459	327.408	252.231	−755.979	−105.310	1.222
4600	62.137	384.825	328.641	258.444	−756.287	−90.848	1.032
4700	62.147	386.161	329.851	264.658	−756.606	−76.378	0.849
4800	62.155	387.470	331.038	270.873	−756.936	−61.902	0.674
4900	62.163	388.752	332.203	277.089	−757.278	−47.418	0.505
5000	62.171	390.007	333.346	283.306	−757.632	−32.927	0.344
5100	62.178	391.239	334.469	289.523	−757.997	−18.429	0.189
5200	62.185	392.446	335.573	295.742	−758.376	−3.925	0.039
5300	62.192	393.631	336.657	301.960	−758.769	10.588	−0.104
5400	62.198	394.793	337.723	308.180	−759.177	25.108	−0.243
5500	62.203	395.935	338.771	314.400	−759.599	39.635	−0.376
5600	62.209	397.055	339.802	320.621	−760.038	54.171	−0.505
5700	62.214	398.157	340.816	326.842	−760.495	68.714	−0.630
5800	62.219	399.239	341.814	333.063	−760.972	83.267	−0.750
5900	62.224	400.302	342.796	339.286	−761.468	97.825	−0.866
6000	62.228	401.348	343.763	345.508	−761.985	112.395	−0.978

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

$S°(298.15\ K) = [280.306 \pm 11.72]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -197.73 \pm 62.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -200.83 \pm 62.8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
X^2B_1	0	2
$^2A_1$	11618	2
$^2A_2$	16236	2

Vibrational Frequencies and Degeneracies ν, cm^{-1}
971 (1)
[300] (1)
912 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Ta–O = [1.69] Å
Bond Angle: O–Ta–O = [110]°
Product of the Moments of Inertia: $I_AI_BI_C = [6.232542 \times 10^{-115}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Inghram, *et al.*[1] and Krikorian and Carpenter[2] have presented mass spectrometric evidence indicating that the predominant vapors in the vaporization of Ta–Ta_2O_5 mixtures in Ta Knudsen cells are TaO and TaO_2. As in the case with TaO(g),[5] the absolute pressures of $TaO_2(g)$ calculated from both studies differ by a factor of roughly 1000 in the range 2022–2278 K (IPTS–68). Results of our 2nd and 3rd law analysis of these and other data are presented below.

Source	Reaction	Data Points	T/K	$\Delta_r H°$(298.15 K), kcal·mol⁻¹ 2nd law	$\Delta_r H°$(298.15 K), kcal·mol⁻¹ 3rd law	Drift cal·K⁻¹·mol⁻¹	$\Delta_f H°$(298.15 K), kcal·mol⁻¹ 2nd law	$\Delta_f H°$(298.15 K), kcal·mol⁻¹ 3rd law
1	A*	2	2022–2023	–	156.13	–	–	−39.47
1	B*	4	2151–2209	51.67	150.86	45 ± 41	–	−36.25
2	B	1	2271	–	184.67	–	–	−2.44
1	C*	4	2022–2179	70.72	70.05	−0.3 ± 4.5	−49.44	−48.10
2	C	1	2271	–	81.03	–	–	−70.06
3	D	graph	1900–2860	−19.83	26.38	20.6 ± 2.8	−19.83	26.38

*Recalculated pressures using Otvis and Stevenson method for estimating ionization cross sections;[2,4] procedure increases $\Delta_r H°$ by ~3 kcal·mol⁻¹.

A: $0.2\ Ta(cr) + 0.4\ Ta_2O_5(cr) = TaO_2(g)$ C: $0.5\ Ta(cr) + 0.5\ TaO_2(g) = TaO(g)$
B: $0.2\ Ta(cr) + 0.4\ Ta_2O_5(l) = TaO_2(g)$ D: $Ta(cr) + O_2(g) = TaO_2(g)$

As was observed in the TaO(g) table,[5] the results of the 2nd and 3rd law analysis show considerable scatter. We adopt $\Delta_f H°(TaO_2$, g, 298.15 K) = −48.0 kcal·mol⁻¹ based primarily on our analysis of the data from Inghram *et al.*[1] for the reaction $0.5\ Ta(cr) + 0.5\ TaO_2(g) = TaO(g)$. For this reaction we adopt a rounded result of $\Delta_r H°$(298.15 K) = 70.0 kcal·mol⁻¹. The adopted $\Delta_f H°$(298.15 K) value leads to a dissocation energy D_0° = 15.3 eV (3520 kcal·mol⁻¹) for the process $TaO_2(g) = Ta(g) + 2\ O(g)$. This value is 1.8 times the dissociation energy of TaO(g).[5]

Heat Capacity and Entropy

The electronic levels and vibrational frequencies are those reported by Weltner and McLeod.[7] The results were based on a matrix isolation study of TaO_2 trapped in argon and neon matrices at 20 K and 4 K, respectively. The infrared spectrum was interpreted to favor a bent molecule in the ground state. Kaufman *et al.*[8] reported that $TaO_2(g)$ is bent based on the deflection of molecular beams of TaO_2 by an electronic quadrupole. This latter result is dependent, however, on there being no low lying electronic states. The bending frequency for the ground state has not been observed but is estiamted to be 300 cm⁻¹ based on the observed ν_2 = 285 cm⁻¹ value for the $^2A_1$ state.[7] The Ta–O bond distance is estimated to be the same as in TaO(g)[5] whereas the bond angle is estimated to be 110°.

It should be noted that the Gibbs energy functions used here are roughly 2–4 cal·K⁻¹ g·atom⁻¹ more positive those of Brewer and Rosenblatt[6] for linear TaO_2; the 3rd law $\Delta_f H°$(298.15 K) values in the above table would change by ~4.5 kcal·mol⁻¹.

Continued on page 1814

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−11.262	−197.730	−197.730	INFINITE
100	35.386	237.647	316.528	−7.888	−198.255	−203.075	106.076
200	39.861	263.617	284.196	−4.116	−199.646	−207.356	54.156
250	41.977	272.738	281.019	−2.070	−200.283	−209.208	43.712
298.15	44.000	280.306	280.306	0.	−200.832	−210.876	36.945
300	44.076	280.578	280.306	0.081	−200.852	−210.938	36.728
350	46.019	287.521	280.850	2.335	−201.348	−212.579	31.726
400	47.726	293.780	282.082	4.679	−201.784	−214.153	27.966
450	49.181	299.488	283.703	7.103	−202.176	−215.675	25.035
500	50.404	304.735	285.548	9.594	−202.538	−217.155	22.686
600	52.279	314.100	289.545	14.733	−203.218	−220.015	19.154
700	53.596	322.264	293.648	20.031	−203.879	−222.762	16.623
800	54.538	329.486	297.685	25.440	−204.540	−225.414	14.718
900	55.229	335.951	301.584	30.930	−205.212	−227.983	13.232
1000	55.746	341.798	305.318	36.480	−205.903	−230.477	12.039
1100	56.143	347.131	308.880	42.076	−206.627	−232.899	11.059
1200	56.453	352.030	312.275	47.706	−207.393	−235.254	10.240
1300	56.701	356.559	315.509	53.364	−208.202	−237.543	9.545
1400	56.903	360.768	318.593	59.045	−209.045	−239.769	8.946
1500	57.073	364.700	321.538	64.744	−209.914	−241.933	8.425
1600	57.218	368.388	324.352	70.458	−210.804	−244.039	7.967
1700	57.348	371.861	327.045	76.187	−211.722	−246.088	7.561
1800	57.467	375.142	329.627	81.928	−212.686	−248.083	7.199
1900	57.581	378.253	332.105	87.680	−213.712	−250.021	6.874
2000	57.692	381.209	334.487	93.444	−214.804	−251.904	6.579
2100	57.805	384.026	336.779	99.219	−215.960	−253.731	6.311
2200	57.922	386.718	338.989	105.005	−217.180	−255.501	6.066
2300	58.043	389.296	341.120	110.803	−218.466	−257.215	5.842
2400	58.170	391.768	343.179	116.614	−219.822	−258.871	5.634
2500	58.305	394.146	345.171	122.437	−221.254	−260.469	5.442
2600	58.447	396.435	347.099	128.275	−222.768	−262.008	5.264
2700	58.596	398.644	348.967	134.127	−224.376	−263.486	5.097
2800	58.753	400.778	350.780	139.994	−226.087	−264.904	4.942
2900	58.917	402.842	352.540	145.878	−227.914	−266.259	4.796
3000	59 088	404.843	354.250	151.778	−229.875	−267.548	4.658
3100	59.264	406.783	355.913	157.696	−231.985	−268.769	4.529
3200	59.445	408.667	357.533	163.631	−234.265	−269.920	4.406
3300	59.631	410.499	359.110	169.585	−273.190	−270.526	4.282
3400	59.820	412.282	360.648	175.557	−275.449	−270.411	4.154
3500	60.011	414.019	362.148	181.549	−277.706	−270.230	4.033
3600	60.205	415.712	363.612	187.560	−279.958	−269.985	3.917
3700	60.398	417.365	365.043	193.590	−282.206	−269.677	3.807
3800	60.592	418.978	366.441	199.639	−284.449	−269.308	3.702
3900	60.785	420.554	367.809	205.708	−286.686	−268.880	3.601
4000	60.976	422.096	369.147	211.796	−288.918	−268.395	3.505
4100	61.165	423.604	370.456	217.903	−291.143	−267.854	3.413
4200	61.350	425.080	371.739	224.029	−293.363	−267.260	3.324
4300	61.532	426.525	372.997	230.173	−295.576	−266.612	3.239
4400	61.710	427.942	374.230	236.335	−297.784	−265.913	3.157
4500	61.882	429.331	375.439	242.515	−299.986	−265.164	3.078
4600	62.050	430.693	376.625	248.712	−302.184	−264.367	3.002
4700	62.212	432.029	377.790	254.925	−304.377	−263.520	2.929
4800	62.368	433.340	378.933	261.154	−306.567	−262.628	2.858
4900	62.518	434.628	380.057	267.398	−308.755	−261.689	2.790
5000	62.662	435.892	381.161	273.657	−310.940	−260.706	2.724
5100	62.799	437.135	382.246	279.931	−313.126	−259.680	2.660
5200	62.930	438.355	383.314	286.217	−315.312	−258.612	2.598
5300	63.053	439.555	384.364	292.516	−317.499	−257.499	2.538
5400	63.170	440.735	385.397	298.827	−319.691	−256.347	2.480
5500	63.280	441.895	386.413	305.150	−321.886	−255.155	2.423
5600	63.384	443.036	387.414	311 483	−324.088	−253.920	2.368
5700	63.480	444.159	388.400	317.826	−326.298	−252.648	2.315
5800	63.570	445.264	389.371	324.179	−1067.272	−248.535	2.238
5900	63.653	446.351	390.327	330.540	−1069.715	−234.400	2.075
6000	63.730	447 422	391.270	336.910	−1072.215	−220.220	1.917

PREVIOUS December 1973 (1 atm) CURRENT. December 1973 (1 bar)

Titanium Oxide, Anatase (TiO_2) CRYSTAL $M_r = 79.8788$ Titanium Oxide, Anatase (TiO_2) $O_2Ti_1(cr)$

$S°(298.15\ K) = 49.907 \pm 0.33\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus}(anatase \rightarrow liquid) = [1949 \pm 60\ K]$

$\Delta_f H°(0\ K) = -933.837 \pm 2.1\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -938.722 \pm 2.1\ kJ{\cdot}mol^{-1}$
$\Delta_{fus} H° = [57.990]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of TiO_2(rutile) using $\Delta_r H°(968\ K) = -1.57 \pm 0.19\ kcal{\cdot}mol^{-1}$ for anatase → rutile. Navrotsky and Kleppa,[1] using oxide melt calorimetry, derived $\Delta_r H°$ from the difference in $\Delta_{sol} H°$ between anatase and rutile. Reduction of their value using JANAF enthalpies yields $\Delta_r H°(298.15\ K) = -1.44 \pm 0.3$ and $\Delta_f H°(\text{anatase}, 298.15\ K) = -224.36 \pm 0.5\ kcal{\cdot}mol^{-1}$. Uncertainties in the enthalpies and in $\Delta_f H°$(rutile) contribute significantly to the overall uncertainty. Kybett and Margrave[2] derived $\Delta_f H°(298.15\ K) = -223 \pm 1\ kcal{\cdot}mol^{-1}$ from fluorine calorimetry. Their reaction was $TiO_2(anatase) + 2\ F_2(g) \rightarrow TiF_4(cr) + O_2(g)$, but they gave no experimental data. Kybett's results for anatase and rutile may be combined to yield $\Delta_r H°(298.15\ K) = -2 \pm 1.4\ kcal{\cdot}mol^{-1}$ for anatase → rutile; this is consistent with the adopted value. Values for $\Delta_r G° = \Delta_r H°$ of -0.2 to $-0.3\ kcal{\cdot}mol^{-1}$ for anatase → rutile were derived by Schuiling and Vink[12] from relative solubilities in aqueous NaCl at 200° and 300°C. We suspect that this less negative result arises from saturating solid phases which differ in physical form and chemical composition from standard state macrocrystalline anatase (refer to Phase Data).

Heat Capacity and Entropy

$C_p°$ below 300 K is based on data of Shomate,[3] (52–296 K) and his Debye Einstein extrapolation to absolute zero. The entropy is calculated by polynomial integration of $C_p°$ based on $S°(50\ K) = 0.45\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

$C_p°$ above 300 K is from constrained fitting of enthalpy data (739–1305 K) of Naylor.[4] Naylor's points at 416 and 546 K are omitted due to positive bias in this temperature range. Enthalpy data (580–1001 K) of Lietz[5] deviate by $-3.7 \pm 1.2\%$ at all temperatures. Similar discrepancies exist in Lietz' data for TiO_2(rutile). These discrepancies and the bias in Naylor's data near room temperature are discussed on the table for rutile.[6] The choice between Naylor[4] and Lietz[5] is not clearcut, but we feel that Naylor's data lead to more reasonable values of $C_p°$. New data on a well characterized sample are needed.

The two discrepant studies[4,5] do agree that the enthalpy of anatase is slightly larger than that of rutile at all temperatures in the observed region. Our adopted $C_p°$ reproduces the approximate enthalpy difference between anatase and rutile as observed by each author.[4,5]

Phase Data

Both anatase and rutile have tetragonal crystal structures, but in anatase the elongated unit cell contains four molecules compared with two in the unit cell of rutile. Anatase transforms exothermally and irreversibly to rutile at temperatures above κ1200 K.[7-9] The rate of transformation is relatively slow and is governed by the nature and amount of impurities.[7] Certain impurities markedly decrease the transformation temperature which can be as low as 700 K in the presence of an alkali flux.[10] These observations led to the conclusion that anatase is a metastable phase which persists up to a temperature sufficient to activate the crystal rearrangement. This was confirmed by the calorimetric data of Navrotsky and Kleppa,[1] who concluded that anatase is metastable with respect to rutile at all temperatures.

Lietz[5] reported a transition in anatase at κ918 K based on his enthalpy data and on changes in prism angles measured by Schroder.[11] We reject Lietz' T_{trs}, since his $\Delta_{trs} H°$ is not distinguishable from his experimental scatter. Lietz' data for rutile and anatase exhibit remarkably similar deviations in this temperature region. Schroder's data have the same deficiency. Lattice parameter data[13] show scatter but no obvious change in this temperature range.

Characterization of anatase samples is particularly important for interpreting physical and chemical properties. Anatase precipitated from acidic sulfate solutions consists of agglomerates of very small crystals with large amounts of water and SO_3.[14] X–ray and electron diffraction show the major lines of anatase but fail to show the impurities, suggesting that the latter are present in noncrystalline form. These precipitates[14] lose water near 150°C and SO_3 near 650°C; crystal growth starts near 600°C. Precipitates from other media give anatase at lower temperatures,[15] but calcination temperatures of at least 650°C are needed fror complete conversion of these precipitates into pure, macrocrystalline anatase. This suggests an alternative explanation for reports[5] [11] of T_{trs} ~645°C.

Fusion Data

T_{fus} is hypothetical in the sense that metastable anatase probably will convert to rutile (see Phase Data) before it can be superheated to the melting point. T_{fus} is calculated as the temperature at which $\Delta_r G° = 0$ for $TiO_2(anatase) \rightarrow TiO_2(l)$. $\Delta_{fus} H°$ is the calculated difference in $\Delta_f H°$ at T_{fus}.

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Continued on page 1814

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−8.627	−933.837	−933.837	INFINITE
100	19.159	9.623	89.203	−7.958	−936.632	−919.438	480.265
200	41.865	30.501	54.580	−4.816	−938.318	−901.476	235.441
298.15	55.271	49.907	49.907	0.000	−938.722	−883.266	154.745
300	55.471	50.249	49.908	0.102	−938.721	−882.922	153.730
400	63.593	67.433	52.195	6.095	−938.313	−864.368	112.875
500	68.145	82.156	56.753	12.702	−937.506	−845.970	88.378
600	70.890	94.842	62.069	19.664	−936.529	−827.753	72.062
700	72.655	105.911	67.559	26.846	−935.488	−809.706	60.421
800	73.860	115.696	72.976	34.176	−934.421	−791.810	51.700
900	74.726	124.448	78.218	41.607	−933.386	−774.046	44.924
1000	75.354	132.355	83.242	49.112	−932.464	−756.393	39.510
1100	75.814	139.559	88.039	56.672	−931.729	−738.823	35.084
1200	76.191	146.172	92.612	64.272	−935.171	−721.191	31.393
1300	76.484	152.283	96.970	71.907	−934.101	−703.403	28.263
1400	76.735	157.960	101.126	79.568	−933.112	−685.695	25.584
1500	76.944	163.262	105.094	87.252	−932.219	−668.054	23.264
1600	77.111	168.233	108.886	94.955	−931.438	−650.470	21.236
1700	77.237	172.912	112.516	102.673	−930.785	−632.930	19.448
1800	77.362	177.330	115.995	110.403	−930.274	−615.425	17.859
1900	77.446	181.515	119.335	118.143	−929.921	−597.943	16.439
2000	77.530	185.490	122.544	125.892	−944.427	−580.022	15.149

PREVIOUS September 1966   CURRENT December 1973

Titanium Oxide, Rutile (TiO_2) CRYSTAL $M_r = 79.8788$

$S^\circ(298.15\ K) = 50.292 \pm 0.17\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2130 \pm 20\ K$ (rutile → liquid)

$\Delta_f H^\circ(0\ K) = -939.870 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_f H^\circ(298.15\ K) = -944.747 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H^\circ = [66.944 \pm 16.7]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H^\circ$ is the value obtained by Mah *et al.*[1] a study by oxygen calorimetry. Eighteen combustions[1] of three well–characterized samples of titanium metal led to a selected value of -225.8 ± 0.1 kcal·mol^{-1}. This is comparable with other oxygen–combustion values of -225.5 ± 0.2,[2] -224.9 ± 0.4[3] and -225.3 ± 0.3[4] and a fluorine combustion value of -225 ± 1[5] derived from the reaction $TiO_2(rutile) + 2\ F_2(g) \rightarrow TiF_4(cr) + O_2(g)$. No experimental data were given in the latter study.[5]

The 1967 JANAF Table[6] assigned an uncertainty of ± 1 kcal·mol^{-1} to $\Delta_f H^\circ$ due to possible uncertainty in corrections for oxygen deficiency in the rutile produced by combustion.[1,3] The atomic ratio O/Ti in the combustion product was determined by ignition to constant weight in air[1,2] or in wet oxygen[3] at 1000°C. Ratios obtained were 1.985 to 1.994,[1] 2.00[2] and about 1.95.[3] Mah's corrections to the stoichiometric composition correspond to about -0.8 to -1.7 kcal·mol^{-1} in $\Delta_f H^\circ$. Our opinion of the reliability of these corrections has changed due to new information on the crystal structure, $\Delta_f G^\circ$ and $\Delta_f S^\circ$ of oxygen deficient compositions.[7,8] Mah's O/Ti ratios are at compositions where there appears to be hysteresis in measurements of the oxygen potential near 1300 K.[7] The full range of the hysteresis corresponds to less than 20% of the oxygen potential. We assume that this percentage is an upper limit for error which might be introduced in the corrections of $\Delta_f G^\circ$ and $\Delta_f H^\circ$ from the observed O/Ti ratios to the stoichiometric composition. Thus, we assign an uncertainty of ± 0.3 kcal·mol^{-1} to $\Delta_f H^\circ = -225.8$, but note that the less negative value of -224.9 ± 0.4 kcal·mol^{-1} [3] is one of several alternatives for minimizing the deviation from integral values of $\Delta_f G^\circ$[7] relating rutile to Ti_3O_5 at 1304 K.

Heat Capacity and Entropy

C_p° below 300 K is based on data of Sandin and Keesom,[9] (0.3–20 K), Dugdale *et al.*,[10] (12–270 K) and Shomate,[11] (52–298 K). Smoothed values rather than data points were reported in the first two studies[9,10] and only in the range 20–50 K by Dugdale.[10] Dugdale's deviation plot indicates that the smooth curves[10,11] agree within about ±0.3% above 77 K, but at lower temperatures the data of Shomate show a positive bias increasing to over 2% at 52 K. We adopt Dugdale's curve below 80 K and calculate S° by polynomial integrations of C_p°. The extrapolation below 0.3 K is insignificant. C_p° data (69–295 K) of McDonald and Seltz[12] are omitted since they are roughly 3% higher than the adopted curve.

C_p° above 300 K is from constrained fitting of enthalpy data (763–1746 K) of Naylor.[13] The point at 394 K is omitted due to positive bias (~6%) in the drop calorimeter at the lowest temperature; a similar bias is observed in Naylor's data for the four other titanium oxides and in materials such as MgF_2 studied at nearly the same time. This bias and the low purity (97.9%) of Naylor's sample are unfortunate; they favor the selection of two more recent enthalpy studies[14,15] which conflict with that of Naylor. The adopted curve is favored, however, by four enthalpy points observed at 965 K by Navrotsky *et al.*[16] and by comparisons with C_p° for GeO_2, MnO_2, and V_2O_4, which have the same tetragonal–SnO_2 crystal structure as rutile.

Enthalpy data of Lietz,[15] (578–1283 K) deviate from the adopted curve by ~−3% at all temperatures; similar deviations occur in his data for TiO_2(anatase). Data of Slyusar *et al.*,[14] (645–1990 K) deviate by ~−4% below 1136 K and by −1.7 to +3.4% at higher temperatures. The discontinuity of almost 3% in the data near 1100 K seems to correspond to the temperature at which the authors switched container materials and temperature sensors.[14] Data for Ti_2O_3, Ti_3O_5 and Ti_4O_7[14] also have discontinuities in this region; the data below the discontinuity for Ti_2O_3 show a negative bias like rutile. Moreoever, the authors[14] report $T_{fus} = 2014$ K, which is ~100 too low for rutile. Other data are too scattered[17] and too uncertain[18,19] to help resolve the difference with Naylor.[13]

These discrepancies cause us to reject the data of Slyusar *et al.*[14] and to consider as coincidence the agreement with Lietz.[15] These two data sets yield C_p° values deviating from the adopted curve by −0.8 cal·K^{-1}·mol^{-1} at 700 K, 0.0 at 1100 K, and +3 at 2000 K. New data on a pure sample of rutile are needed to resolve the disagreement. We note that use of the rejected C_p° curve is one of several alternatives for minimizing the deviation from equilibria[7] relating rutile to Ti_3O_5 at 1304 K.

Fusion Data – Refer to the liquid table for details.

Sublimation Data

$\Delta_{sub} H^\circ(298.15\ K) = 152.8 \pm 3$ kcal·mol^{-1} is calculated from $\Delta_f H^\circ(TiO_2, g)$. Sublimation makes TiO_2(cr) deficient in oxygen.

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Continued on page 1815

Titanium Oxide, Rutile (TiO_2) $O_2Ti_1(cr)$

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.000	0.000	INFINITE	−8.636	−939.870	−939.870	INFINITE
100	18.502	10.142	89.638	−7.950	−942.649	−925.506	483.435
200	42.012	30.807	54.969	−4.833	−944.360	−907.579	237.035
298.15	55.103	50.292	50.292	0.000	−944.747	−889.406	155.820
300	55.287	50.633	50.293	0.102	−944.746	−889.063	154.800
400	62.835	67.671	52.564	6.043	−944.390	−870.541	113.681
500	67.203	82.201	57.077	12.562	−943.670	−852.157	89.024
600	69.931	94.712	62.331	19.429	−942.789	−833.936	72.601
700	71.764	105.638	67.754	26.519	−941.841	−815.868	60.881
800	73.078	115.311	73.106	33.764	−940.857	−797.939	52.100
900	74.057	123.977	78.285	41.122	−939.896	−780.132	45.278
1000	74.852	131.822	83.253	48.569	−939.032	−762.428	39.825
1100	75.479	138.986	87.999	56.086	−938.339	−744.803	35.368
1200	76.023	145.577	92.526	63.662	−941.807	−727.113	31.650
1300	76.525	151.683	96.844	71.290	−940.742	−709.265	28.499
1400	76.944	157.370	100.967	78.964	−939.741	−691.497	25.800
1500	77.320	162.691	104.906	86.677	−938.819	−673.798	23.464
1600	77.655	167.692	108.676	94.426	−937.992	−656.158	21.421
1700	77.990	172.410	112.287	102.209	−937.274	−638.566	19.621
1800	78.283	176.876	115.753	110.022	−936.679	−621.013	18.021
1900	78.576	181.117	119.082	117.865	−936.224	−603.489	16.591
2000	78.868	185.155	122.286	125.738	−950 606	−585.531	15.293
2100	79.161	189.010	125.372	133.640	−951.213	−567.263	14.110
2130.000	79.228	190.133	126.276	136.016	--- CRYSTAL <--> LIQUID ---		
2200	79.412	192.698	128.349	141.568	−951.817	−548.964	13.034
2300	79.663	196.234	131.224	149.522	−952.417	−530.640	12.051
2400	79.914	199.630	134.004	157.501	−953.015	−512.289	11.150
2500	80.165	202.897	136.695	165.505	−953.610	−493.913	10.320

PREVIOUS: September 1966 — CURRENT: December 1973

Titanium Oxide (TiO_2) LIQUID M_r = 79.8788

$S°(298.15 K) = [72.345] J \cdot K^{-1} \cdot mol^{-1}$

$T_{fus} = 2130 \pm 20 K$ (rutile → liquid)

$\Delta_f H°(298.15 K) = [-894.055] kJ \cdot mol^{-1}$

$\Delta_{fus} H° = [66.944 \pm 16.7] kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(TiO_2, l, 298.15 K)$ is calculated from that of TiO_2(rutile) by adding $\Delta_{fus} H°$ to the difference in enthalpy, $H°(2130 K)-H°(298.15 K)$, between rutile and liquid.

Heat Capacity and Entropy

$C_p°$ is estimated as 8 cal $K^{-1} \cdot g\text{–}atom^{-1}$ by comparison with MgF_2, $CaCl_2$, V_2O_4 and WO_3. Below the assumed glass transition at 1400 K, $C_p°$ is taken to be the same as that of TiO_2(rutile). $S°(298.15 K)$ is calculated in a manner analogous to that used for $\Delta_f H°$.

Fusion Data

Schneider[1] reviewed eleven melting point studies and converted the values to IPTS–48. Eight of the results fall in the range 2113 ± 10 K for measurements in air. Brauer and Littke,[2] using an atmosphere of oxygen–argon mixtures, found 2103 ± 15 K in air, 2113 ± 15 K with oxygen at 300 torr, 2133 ± 15 K at 500 torr and 2143 ± 15 K at higher oxygen pressures. The authors[2] interpreted the sharp increase in T_{fus} with increased oxygen pressure as being due to suppression of the oxygen deficiency in TiO_2. The residue of the sample melted in air gave an oxygen stoichiometry of 1.996 compared with 2.000 at higher oxygen pressures; the color showed a corresponding change from dark blue to bright yellow. The oxygen deficiency may have been even greater if there was significant reoxidation during cooling to room temperature. Schneider[1] questioned the attainment of black–body conditions in the temperature measurements; in fact, Brauer and Littke[2] tried to compensate for the change in sample color by use of similarly colored compounds in calibrations of the pyrometer. We wonder if this *eliminated all relative bias in the melting temperatures.*

$T_{fus} = 2130 \pm 20 K$ is adopted. This is intermediate between the data in air and those at highest oxygen pressures. $\Delta_{fus} H°$ is estimated such that $\Delta_{fus} S° = 7.5$ cal $K^{-1} \cdot mol^{-1}$, or 2.5 cal $K^{-1} \cdot g \cdot atom^{-1}$, based on observed data for isostructural V_2O_4. The resulting $\Delta_{fus} H°$ of 16 ± 4 $kcal \cdot mol^{-1}$ may be compared with approximate values of $\Delta_{fus} H°$ derived from binary phase data. We obtain 12 $kcal \cdot mol^{-1}$ from the binary with Al_2O_3,[3] 14 $kcal \cdot mol^{-1}$ from BaO[4] and ZrO_2,[5] 16 $kcal \cdot mol^{-1}$ from Ta_2O_5[6] and 21 $kcal \cdot mol^{-1}$ from WO3.[7] These values are derived by calculating apparent $\Delta_{fus} H°$ values assuming activity coefficients of unity and then extrapolating the apparent values to $(T_{fus}-T) = 0$ in order to minimize activity effects. We omit other binary systems which deviate grossly from ideality. Uncertainties in the binary results are estimated to be about ±5 $kcal \cdot mol^{-1}$.

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Titanium Oxide (TiO_2) $O_2Ti_1(l)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	55.103	72.345	72.345	0.000	−894.055	−845.289	148.091
300	55.287	72.686	72.346	0.102	−894.054	−844.987	147.125
400	62.835	89.724	74.617	6.043	−893.698	−828.670	108.213
500	67.203	104.254	79.130	12.562	−892.978	−812.492	84.880
600	69.931	116.765	84.384	19.429	−892.097	−796.475	69.339
700	71.764	127.691	89.807	26.519	−891.149	−780.613	58.250
800	73.078	137.364	95.159	33.764	−890.166	−764.889	49.942
900	74.057	146.030	100.338	41.122	−889.204	−749.288	43.488
1000	74.852	153.875	105.306	48.569	−888.340	−733.789	38.329
1100	75.479	161.039	110.052	56.086	−887.647	−718.369	34.113
1200	76.023	167.630	114.579	63.662	−891.115	−702.884	30.596
1300	76.525	173.736	118.897	71.290	−890.050	−687.242	27.614
1400	76.944	179.423	123.020	78.964	−889.049	−671.679	25.061
1400.000	76.944	179.423	123.020	78.964	GLASS <––> LIQUID		
1400.000	100.416	179.423	123.020	78.964	TRANSITION		
1500	100.416	186.351	127.014	89.006	−885.798	−656.268	22.853
1600	100.416	192.832	130.927	99.047	−882.679	−641.068	20.929
1700	100.416	198.919	134.749	109.089	−879.701	−626.059	19.236
1800	100.416	204.659	138.475	119.131	−876.879	−611.221	17.737
1900	100.416	210.088	142.103	129.172	−874.225	−596.536	16.400
2000	100.416	215.239	145.632	139.214	−886.438	−581.532	15.188
2100	100.416	220.138	149.064	149.255	−884.906	−566.324	14.087
2130.000	100.416	221.563	150.075	152.268	––– CRYSTAL <––> LIQUID –––		
2200	100.416	224.809	152.402	159.297	−883.396	−551.189	13.087
2300	100.416	229.273	155.648	169.339	−881.909	−536.122	12.176
2400	100.416	233.547	158.805	179.380	−880.444	−521.120	11.342
2500	100.416	237.646	161.877	189.422	−879.001	−506.177	10.576
2600	100.416	241.584	164.868	199.463	−877.579	−491.293	9.870
2700	100.416	245.374	167.780	209.505	−876.179	−476.462	9.218
2800	100.416	249.026	170.617	219.547	−874.799	−461.682	8.613
2900	100.416	252.550	173.381	229.588	−873.438	−446.953	8.050
3000	100.416	255.954	176.077	239.630	−872.098	−432.269	7.526
3100	100.416	259.247	178.707	249.671	−870.775	−417.630	7.037
3200	100.416	262.435	181.274	259.713	−869.471	−403.034	6.579
3300	100.416	265.525	183.781	269.755	−868.184	−388.478	6.149
3400	100.416	268.522	186.229	279.796	−866.914	−373.960	5.745
3500	100.416	271.433	188.622	289.838	−865.660	−359.480	5.365
3600	100.416	274.262	190.962	299.879	−864.422	−345.035	5.006
3700	100.416	277.013	193.251	309.921	−1272.296	−322.836	4.558
3800	100.416	279.691	195.491	319.963	−1269.853	−297.207	4.085
3900	100.416	282.300	197.683	330.004	−1267.478	−271.642	3.638
4000	100.416	284.842	199.830	340.046	−1265.171	−246.138	3.214

PREVIOUS: September 1966   CURRENT: December 1973

Titanium Oxide (TiO_2) $O_2Ti_1(l)$

Titanium Oxide (TiO_2) CRYSTAL(rutile)-LIQUID

M_r = 79.8788 Titanium Oxide (TiO_2) $O_2Ti_1(cr,l)$

0 to 2130 K crystal, rutile
above 2130 K liquid

Refer to the individual tables for details.

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−8.636	−939.870	−939.870	INFINITE
100	18.502	10.142	89.638	−7.950	−942.649	−925.506	483.435
200	42.012	30.807	54.969	−4.833	−944.360	−907.579	237.035
298.15	55.103	50.292	50.292	0.000	−944.747	−889.406	155.820
500	67.203	82.201	57.077	12.562	−943.670	−852.157	89.024
600	69.931	94.712	62.331	19.429	−942.789	−833.936	72.601
700	71.764	105.638	67.754	26.519	−941.841	−815.868	60.881
800	73.078	115.311	73.106	33.764	−940.857	−797.939	52.100
900	74.057	123.977	78.285	41.122	−939.896	−780.132	45.278
1000	74.852	131.822	83.253	48.569	−939.032	−762.428	39.825
1100	75.479	138.986	87.999	56.086	−938.339	−744.803	35.368
1200	76.023	145.577	92.526	63.662	−941.807	−727.113	31.650
1300	76.525	151.683	96.844	71.290	−940.742	−709.265	28.499
1400	76.944	157.370	100.967	78.964	−939.741	−691.497	25.800
1500	77.320	162.691	104.906	86.677	−938.819	−673.798	23.464
1600	77.655	167.692	108.676	94.426	−937.992	−656.158	21.421
1700	77.990	172.410	112.287	102.209	−937.274	−638.566	19.621
1800	78.283	176.876	115.753	110.022	−936.679	−621.013	18.021
1900	78.576	181.117	119.082	117.865	−936.224	−603.489	16.591
2000	78.868	185.155	122.286	125.738	−950.606	−585.531	15.293
2100	79.161	189.010	125.372	133.640	−951.213	−567.263	14.110
2130.000	79.228	190.133	126.276	136.016	CRYSTAL <−−> LIQUID TRANSITION		
2130.000	100.416	221.563	126.276	202.960			
2200	100.416	224.809	129.360	209.989	−883.396	−551.188	13.087
2300	100.416	229.273	133.608	220.030	−881.909	−536.122	12.176
2400	100.416	233.547	137.683	230.072	−880.444	−521.120	11.342
2500	100.416	237.646	141.601	240.114	−879.001	−506.177	10.576
2600	100.416	241.584	145.371	250.155	−877.579	−491.293	9.870
2700	100.416	245.374	149.005	260.197	−876.179	−476.462	9.218
2800	100.416	249.026	152.512	270.238	−874.799	−461.682	8.613
2900	100.416	252.550	155.901	280.280	−873.438	−446.953	8.050
3000	100.416	255.954	159.180	290.322	−872.098	−432.269	7.526
3100	100.416	259.247	162.355	300.363	−870.775	−417.630	7.037
3200	100.416	262.435	165.433	310.405	−869.471	−403.034	6.579
3300	100.416	265.525	168.420	320.446	−868.184	−388.478	6.149
3400	100.416	268.522	171.320	330.488	−866.914	−373.960	5.745
3500	100.416	271.433	174.139	340.530	−865.660	−359.480	5.365
3600	100.416	274.262	176.881	350.571	−864.422	−345.035	5.006
3700	100.416	277.013	179.550	360.613	−1272.296	−322.836	4.558
3800	100.416	279.691	182.151	370.654	−1269.853	−297.207	4.085
3900	100.416	282.300	184.685	380.696	−1267.478	−271.642	3.638
4000	100.416	284.842	187.157	390.738	−1265.171	−246.138	3.214

PREVIOUS: CURRENT December 1973

Titanium Oxide (TiO_2) $O_2Ti_1(cr,l)$

Titanium Oxide (TiO_2) IDEAL GAS $M_r = 79.8788$ Titanium Oxide (TiO_2) $O_2Ti_1(g)$

$\Delta_f H°(0\ K) = -303.28 \pm 12.6\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 260.148 \pm 4.2\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_f H°(298.15\ K) = -305.43 \pm 12.6\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	1	18880	[3]

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
962 (1)	[270] (1)	935 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: TiO = [1.62 ± 0.08] Å
Bond Angle: O–Ti–O = 110° ± 15°
Product of the Moments of Inertia: $I_A I_B I_C = [3.115429 \times 10^{-115}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

$\Delta_f H° = -73.0 \pm 3\ kcal\ mol^{-1}$ is selected from the ten data sets analyzed below. These include four different reactions studied by Knudsen effusion or mass spectrometry. Our adopted value is consistent with all but two of the data sets, namely reactions C[2] and D[5]. We presume that the less negative $\Delta_f H° = -59.1$ from reaction C is due to bias in the mass– spectrometric values[2] for the partial pressure of O(g). The more negative $\Delta_f H° = -86.0$ from the sublimation reaction D corresponds to effusion pressures too large by a factor of ~25, allowance for the activity of TiO_2 in the oxygen–deficient condensed phase[5] increases the discrepancy. Gross mass transport from the cell by species other than TiO_2 may have occurred,[3] since mass–spectrometric pressures[3, 6] are fairly consistent with our $\Delta_f H°$. We give little weight to reactions D and E due to problems in interpretation of the vapor composition[5, 6] and the activity of oxygen–deficient TiO_2(cr, l).

Activity effects appear to be minor for TiO_2 in TiO_x(cr) in the range $1.833 < X < 1.889$. Univariant, two–phase systems involving the crystals Ti_6O_{11}, Ti_7O_{13}, Ti_8O_{15} and Ti_9O_{17} occur in this region. Our calculations based on emf data[9] yield $a(TiO_2) \geq \sim 0.7$ at 1900 K; these values change only slowly with X and T. Sublimation experiments in this region may involve hysteresis, but the degree should be less than that found in equilibrium data[10] near 1300 K.

Drowart *et al.*[11] provided the key improvement in $\Delta_f H°$ by reinterpretation of the congruent vaporization[4] of Ti_3O_5(cr). Gilles and co–workers[1, 12] confirmed the congruency of vaporization and gave supportive mass–spectrometric data. We use JANAF auxiliary data[7] with $D°(TiO) = 158.5 \pm 2\ kcal{\cdot}mol^{-1}$ to recalculate the vaporization[4] as described in.[1, 11] Resulting partial pressures of TiO_2, TiO and O(g) are analyzed in terms of reaction C. Third–law analysis yields our selected value of $\Delta_f H°$ and $D°(TiO_2) = 302.8 \pm 3\ kcal{\cdot}mol^{-1}$. $D°$ would decrease by ~1 $kcal{\cdot}mol^{-1}$ if $D°(TiO)$ were increased by 2 $kcal{\cdot}mol^{-1}$ in the recalculation. The conclusion[1] that the ionization cross–section ratio (TiO/TiO_2) = 2.2 is unchanged in our recalculation; even larger ratios may be expected at low ionizing potentials.[13]

Source	Method	Reaction[a]	T/K	Data Points	$\delta S°$ cal·K⁻¹·mol⁻¹	$\Delta_f H°$(298.15 K), kcal·mol⁻¹ 2nd law	3rd law	$\Delta_f H°$(298.15) kcal mol⁻¹	$D_0°$
[1] Hampson	Mass spec.	A	2145–2318	5	−3.2 ± 4.0	−19.7 ± 8.9	−12.6 ± 1.0	−74.4 ± 3	304.2
[2] Balducci	Mass spec.	A	2165–2500	6	4.6 ± 0.4	−4.2 ± 0.9	−14.8 ± 1.2	−72.2 ± 3	302.0
[3] Berkowitz	Mass spec.	A	2194	1	–	–	−10.8	−76.2 ± 4	306.0
[1] Hampson	Mass spec.	B	1893	7	–	–	2.5 ± 0.5	−72.8 ± 7	302.6
[2] Balducci	Mass spec.	C	2015–2240	12	4.4 ± 2.5	141.0 ± 5.3	131.6 ± 1.0	−59.1 ± 3	288.9
[4] Wahlbeck	Effusion	C	1837–2014	Eqn.	3.5	152.3	145.6 ± 0.7	−73.0 ± 3	302.8
[5] Groves	Effusion	D	1849–2010	14	−5.5 ± 4.0	129.2 ± 7.7	139.8 ± 1.3	−86.0	315.8
[3] Berkowitz	Mass spec.	D	1881	3	–	–	152.3 ± 3.2	−73.5	303.3
[6] Semenov	Mass spec.	D	1850–2050	Eqn.	−3.6	142.7	149.8 ± 1.0	−76.0	305.8
[6] Semenov	Mass spec.	E	2263–2538	6	−7.2 ± 2.9	122.8 ± 6.9	139.9 ± 1.8	−73.8	303.6

[a] Reactions are A) $TiO_2(g) + Ti(g) = 2\ TiO(g)$ B) $TiO(g) + WO_3(g) = TiO_2(g) + WO_2(g)$ C) $TiO_2(g) = TiO(g) + O(g)$ D) $TiO_2(rutile) = TiO_2(g)$ E) $TiO_2(l) = TiO_2(g)$

Heat Capacity and Entropy

The electronic levels, bond angle and stretching frequencies are from infrared and emission spectra of TiO_2 isolated in rare– gas matrices.[14] We assume the emission at 5295 Å to be a forbidden triplet–singlet transition due to its similarity with CeO_2.[15] Frequency ν_1 was observed both in infrared and emission spectra. The bond angle was derived[14] from $u_3$sing splittings observed for the five Ti isotopes. Earlier electric–deflection experiments[16] at 2500 K had shown that the populated electronic states were polar (i.e., nonlinear) We estimate the bond length to be the same as that of ground–state TiO.[7] Principal moments of inertia are: $I_A = 2.7500 \times 10^{-3.9}$ $I_B = 9.3573 \times 10^{-39}$, and $I_C = 12.1072 \times 10^{-39}\ g{\cdot}cm^2$.

Continued on page 1815

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−11.357	−303.276	−303.276	INFINITE
100	35.950	217.025	296.659	−7.963	−303.347	−306.893	160.304
200	40.232	243.358	264.059	−4.140	−304.352	−310.081	80.985
250	42.214	252.547	260.864	−2.079	−304.913	−311.449	65.074
298.15	44.149	260.148	260.148	0.	−305.432	−312.660	54.777
300	44.222	260.422	260.149	0.082	−305.451	−312.705	54.447
350	46.106	267.382	260.695	2.341	−305.956	−313.873	46.843
400	47.777	273.651	261.929	4.689	−306.429	−314.971	41.131
450	49.210	279.363	263.553	7.114	−306.878	−316.012	36.682
500	50.419	284.612	265.400	9.606	−307.311	−317.004	33.117
600	52.280	293.979	269.402	14.746	−308.156	−318.863	27.759
700	53.591	302.143	273.509	20.044	−309.001	−320.581	23.922
800	54.532	309.363	277.548	25.452	−309.854	−322.177	21.036
900	55.222	315.828	281.448	30.942	−310.761	−323.664	18.785
1000	55.740	321.674	285.183	36.491	−311.795	−325.043	16.979
1100	56.136	327.006	288.747	42.086	−313.024	−326.310	15.495
1200	56.446	331.905	292.142	47.716	−318.438	−327.337	14.249
1300	56.693	336.433	295.377	53.373	−319.344	−328.042	13.181
1400	56.891	340.642	298.462	59.052	−320.337	−328.674	12.263
1500	57.053	344.573	301.406	64.750	−321.431	−329.233	11.465
1600	57.188	348.259	304.220	70.462	−322.641	−329.714	10.764
1700	57.300	351.730	306.914	76.187	−323.980	−330.116	10.143
1800	57.396	355.008	309.496	81.922	−325.465	−330.435	9.589
1900	57.478	358.113	311.973	87.666	−327.108	−330.667	9.091
2000	57.550	361.063	314.355	93.417	−343.612	−330.354	8.628
2100	57.614	363.873	316.646	99.175	−346.363	−329.624	8.199
2200	57.673	366.554	318.854	104.940	−349.130	−328.761	7.806
2300	57.727	369.119	320.985	110.710	−351.915	−327.773	7.444
2400	57.781	371.577	323.042	116.485	−354.716	−326.664	7.110
2500	57.833	373.937	325.031	122.266	−357.534	−325.437	6.800
2600	57.888	376.206	326.956	128.052	−360.368	−324.098	6.511
2700	57.945	378.392	328.820	133.843	−363.217	−322.648	6.242
2800	58.006	380.500	330.629	139.641	−366.081	−321.093	5.990
2900	58.072	382.537	332.384	145.445	−368.959	−319.436	5.754
3000	58.144	384.507	334.088	151.256	−371.849	−317.679	5.531
3100	58.223	386.415	335.746	157.074	−374.750	−315.825	5.322
3200	58.310	388.265	337.358	162.900	−377.661	−313.879	5.124
3300	58.405	390.060	338.928	168.736	−380.580	−311.841	4.936
3400	58.509	391.806	340.458	174.582	−383.505	−309.713	4.758
3500	58.622	393.503	341.949	180.438	−386.437	−307.501	4.589
3600	58.743	395.156	343.404	186.306	−389.371	−305.204	4.428
3700	58.874	396.768	344.825	192.187	−801.407	−295.037	4.165
3800	59.013	398.339	346.213	198.081	−803.110	−281.328	3.867
3900	59.161	399.874	347.569	203.990	−804.869	−267.574	3.584
4000	59.318	401.374	348.895	209.914	−806.679	−253.775	3.314
4100	59.483	402.841	350.193	215.854	−808.539	−239.929	3.057
4200	59.655	404.276	351.464	221.811	−810.446	−226.038	2.811
4300	59.834	405.682	352.709	227.785	−812.397	−212.100	2.577
4400	60.019	407.060	353.928	233.778	−814.390	−198.117	2.352
4500	60.210	408.411	355.124	239.789	−816.421	−184.088	2.137
4600	60.406	409.736	356.297	245.820	−818.489	−170.014	1.931
4700	60.607	411.037	357.448	251.871	−820.591	−155.894	1.733
4800	60.812	412.315	358.578	257.941	−822.725	−141.729	1.542
4900	61.019	413.571	359.687	264.033	−824.889	−127.518	1.359
5000	61.229	414.806	360.777	270.145	−827.081	−113.264	1.183
5100	61.440	416.021	361.849	276.279	−829.299	−98.966	1.014
5200	61.653	417.216	362.902	282.433	−831.542	−84.625	0.850
5300	61.865	418.392	363.938	288.609	−833.807	−70.238	0.692
5400	62.077	419.551	364.957	294.806	−836.095	−55.810	0.540
5500	62.289	420.692	365.960	301.025	−838.403	−41.340	0.393
5600	62.498	421.816	366.947	307.264	−840.731	−26.826	0.250
5700	62.706	422.924	367.920	313.524	−843.079	−12.272	0.112
5800	62.911	424.016	368.877	319.805	−845.444	2.325	−0.021
5900	63.113	425.093	369.821	326.106	−847.828	16.961	−0.150
6000	63.311	426.156	370.751	332.428	−850.230	31.640	−0.275

PREVIOUS: December 1973 (1 atm) CURRENT December 1973 (1 bar)

Vanadium Oxide (VO_2) IDEAL GAS $M_r = 82.9403$ Vanadium Oxide (VO_2) $O_2V_1(g)$

$\Delta_fH°(0\ K) = -230.56 \pm 41.8\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = [265.269 \pm 5.9]\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -232.63 \pm 41.8\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[970](1)
[300](1)
[930](1)

Ground State Quantum Weight: [2] $\sigma = [2]$
Point Group: [C_{2v}]
Bond Distance: V–O = [1.589] Å
Bond Angle: O–V–O = [110]°
Product of the Moments of Inertia: $I_AI_BI_C = [2.858786 \times 10^{-115}]\ g^3\cdot cm^6$

Enthalpy of Formation

Four independent mass spectrometric studies lead to values for $\Delta_fH°(VO_2, g, 298.15\ K)$.[1–4] Shchukarev *et al.*[2] studied the composition of the vapor above V_2O_4 during evaporation from the surface of a platinum strip. A 2nd law sublimation heat, $\Delta_{sub}H° = 104 \pm 2\ kcal\cdot mol^{-1}$, was reported for the range 1500–1800 K. Assuming the reported value corresponds to 1700 K and using auxiliary data,[5] we calculate $\Delta_fH°(VO_2, g, 298.15\ K) = -62.3 \pm 2.0\ kcal\cdot mol^{-1}$. The sublimation was described by $0.5\ V_2O_4(cr) = VO_2(g)$ More recent related work[3] yields a $\Delta_fH°(298.15\ K)$ value approximately 6 $kcal\cdot mol^{-1}$ more positive. This latter work and other investigations are summarized in the following table.

Reference	Reaction	Data Points	T/K	$\Delta_rH°(298.15\ K)$, $kcal\cdot mol^{-1}$ 2nd law	3rd law	Drift $cal\cdot K^{-1}\ mol^{-1}$	$\Delta_fH°(298.15\ K)$, $kcal\cdot mol^{-1}$ 2nd law	3rd law
[3]	A	Equation	1673–1818	114.29	114.32	0.02	−56.26	−56.23
[3]	B	Equation	1818–2273	104.90	103.77	−0.58	−54.30	−55.43
[1]	C	2	1948	–	−16.23	–	–	−45.97
[4]	C	1	2270	–	−12.86	–	–	−49.34
[4]	D	1	2270	–	−40.14	–	–	−32.94 (−39.79)**

**Value is based on recent determination by Farber *et al.*[8] for $\Delta_fH°(AlO, g, 298.15\ K)$.

Reactions:
(A) $0.5\ V_2O_4(cr) = VO_2(g)$
(B) $0.5\ V_2O_4(l) = VO_2(g)$
(C) $V(g) + VO_2(g) = 2\ VO(g)$
(D) $2\ AlO(g) + V(g) = 2\ Al(g) + VO_2(g)$

We adopt $\Delta_fH°(298.15\ K) = -55.6\ kcal\cdot mol^{-1}$ for $VO_2(g)$. This value is an average of the 2nd and 3rd law results of Frantseva and Semenov.[3] These results are independent of the VO(g) data and show small third law drifts. The results of our analysis for reaction (C) for the data of Berkowitz *et al.*[1] and Farber *et al.*[4] show good agreement in $\Delta_rH°(298.15\ K)$ but lead to values for $\Delta_fH°(298.15\ K)$ which are 6–10 $kcal\cdot mol^{-1}$ less negative than our adopted value. Killingbeck[6] studied the evaporation of V_2O_3 from a molybdenum effusion chamber and reported $\Delta_rH°(298.15\ K) = 279.5 \pm 5\ kcal\cdot mol^{-1}$ for $V_2O_3(cr) = VO(g) + VO_2(g)$. Using auxiliary data[5] we calculate $\Delta_fH°(298.15\ K) = -42.3 \pm 5.0\ kcal\cdot mol^{-1}$ for $VO_2(g)$.

The adopted $\Delta_fH°(298.15\ K)$ value corresponds to a dissociation energy $D° = 295.5\ kcal\cdot mol^{-1}$ (12.8 eV) for the process $VO_2(g) = V(g) + 2\ O(g)$. This $D°$ value is 1.96 times the dissociation energy of VO(g).[5]

Heat Capacity and Entropy

The vibrational frequencies and geometry of $VO_2(g)$ are estimated based on existing and estimated data for related metal dioxides such as $TiO_2(g)$, $TaO_2(g)$ and $WO_2(g)$.[5] The V–O bond distance is assumed to be the same as in VO(g).[5]

The ground state quantum weight of 2 is adopted so as to be consistent with $TaO_2(g)$.[5] This introduces an uncertainty of ±1.38 $cal\cdot K^{-1}\cdot mol^{-1}$ in $S°(298.15\ K)$. The estimation of ν_2 at 300 cm^{-1} results in an uncertainty of 0.72 $cal\ K^{-1}\ mol^{-1}$ in $S°(298.15\ K)$ for ±100 cm^{-1}. The estimates for $VO_2(g)$ are such that the 3rd law drifts as indicated in the above table are small. Nevertheless, until more data are available for $VO_2(g)$, the uncertainty in the entropy must be considered as ±1.4 $cal\cdot K^{-1}\cdot mol^{-1}$ for a bent molecule. The free energy functions suggested by Brewer and Rosenblatt[7] are roughly 3–4 $cal\cdot K^{-1}\cdot mol^{-1}$ lower than those adopted here. The main reason for the difference is that Brewer and Rosenblatt[7] treated $VO_2(g)$ as a linear molecule.

The electronic levels of the V^{+4} ion as reported by Moore[9] consist of a ground state with quantum weight four and an excited state at 620 cm^{-1} with a quantum weight six. The next excited state is listed at ~148000 cm^{-1}. Inclusion of an estimated state for $VO_2(g)$ at 620 cm^{-1} with a quantum weight of six would raise $S°(298.15\ K)$ by 1.06 $cal\cdot K^{-1}\cdot mol^{-1}$. This is within the estimated uncertainty of $S°(298.15\ K)$.

Continued on page 1815

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

T/K	$C_p°$ ($J\cdot K^{-1}mol^{-1}$)	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ ($kJ\cdot mol^{-1}$)	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−11.254	−230.561	−230.561	INFINITE
100	35.385	222.647	301.443	−7.880	−230.580	−234.796	122.645
200	39.819	248.608	269.153	−4.109	−231.557	−238.670	62.334
250	41.903	257.716	265.981	−2.066	−232.116	−240.383	50.225
298.15	43.907	265.269	265.269	0.	−232.630	−241.928	42.385
300	43.982	265.541	265.270	0.081	−232.650	−241.986	42.134
350	45.916	272.468	265.812	2.330	−233.144	−243.503	36.341
400	47.622	278 714	267.041	4.669	−233.597	−244.951	31.987
450	49.082	284.409	268.659	7.088	−234.017	−246.345	28.595
500	50.311	289.646	270.499	9.573	−234.412	−247.693	25.876
600	52.201	298.996	274.489	14.705	−235.162	−250.278	21 789
700	53.531	307.149	278.585	19.995	−235.902	−252.739	18.860
800	54 485	314.363	282.615	25.398	−236.669	−255.092	16.656
900	55.184	320.822	286.507	30.884	−237.491	−257.347	14.936
1000	55 708	326.665	290.236	36.429	−238.380	−259.506	13.555
1100	56.110	331.994	293.793	42.021	−239.344	−261.572	12.421
1200	56.424	336.891	297.183	47.649	−240.399	−263.547	11.472
1300	56.674	341.417	300.414	53.304	−241.552	−265.430	10.665
1400	56.875	345.625	303.495	58.982	−242.816	−267.220	9.970
1500	57.039	349.554	306.436	64.678	−244.192	−268.916	9.364
1600	57.175	353.240	309.247	70.388	−245.681	−270.516	8.831
1700	57.288	356.710	311.938	76.112	−247.293	−272.020	8.358
1800	57.384	359.987	314.517	81.846	−249.035	−273.425	7.935
1900	57.466	363.092	316.993	87.588	−250.919	−274.729	7.553
2000	57.536	366.041	319.372	93.338	−252.953	−275.931	7.207
2100	57.597	368.850	321.662	99.095	−255.148	−277.026	6.891
2200	57.649	371.531	323.868	104.857	−280.396	−277.908	6.598
2300	57.695	374 094	325.997	110.625	−283.080	−277.735	6.308
2400	57.736	376.551	328.052	116.396	−285.781	−277.445	6.038
2500	57.772	378.908	330.040	122.172	−288.501	−277.042	5.788
2600	57.804	381.175	331.963	127.951	−291.239	−276.530	5.556
2700	57.832	383.357	333.826	133.732	−293.995	−275.912	5.338
2800	57.858	385.461	335.633	139.517	−296.768	−275.191	5.134
2900	57.881	387.491	337.387	145.304	−299.559	−274.372	4.942
3000	57.902	389.454	339.090	151.093	−302.368	−273.455	4.761
3100	57.921	391.353	340.745	156.884	−305.193	−272.444	4.591
3200	57.938	393.192	342.356	162.677	−308.034	−271.343	4.429
3300	57.953	394.975	343.923	168.472	−310.891	−270.153	4.276
3400	57.967	396 705	345.450	174.268	−313.763	−268.875	4.131
3500	57.981	398.386	346.939	180.065	−316.650	−267.513	3.992
3600	57.992	400.020	348.391	185.864	−319.551	−266.068	3.861
3700	58.004	401.609	349.808	191.664	−769.272	−263.342	3.718
3800	58.014	403.156	351.191	197.465	−770.514	−249.651	3.432
3900	58.023	404.663	352.543	203.266	−771.819	−235.927	3.160
4000	58.032	406.132	353.865	209.069	−773.188	−222.169	2.901
4100	58.040	407.565	355.157	214.873	−774.623	−208.376	2.655
4200	58.047	408.964	356.421	220.677	−776.124	−194.547	2.420
4300	58.055	410.330	357.659	226.482	−777.691	−180.681	2.195
4400	58.061	411.664	358.872	232.288	−779.325	−166.779	1.980
4500	58.067	412.969	360.059	238.094	−781.026	−152.839	1.774
4600	58.073	414.245	361.223	243.901	−782.795	−138.860	1.577
4700	58.078	415.494	362.365	249.709	−784.634	−124.841	1.387
4800	58.083	416.717	363.485	255.517	−786.541	−110.783	1.206
4900	58.088	417.915	364.583	261.326	−788.518	−96.684	1.031
5000	58.092	419.089	365.662	267.135	−790.566	−82.544	0.862
5100	58.097	420.239	366.720	272.944	−792.686	−68.362	0.700
5200	58.101	421.367	367.761	278.754	−794.878	−54.140	0.544
5300	58.104	422.474	368.782	284.564	−797.144	−39.872	0.393
5400	58.108	423.560	369.787	290.375	−799.485	−25.563	0.247
5500	58.111	424.626	370.774	296.186	−801.902	−11.210	0.106
5600	58.114	425.673	371.745	301.997	−804.396	3.190	−0.030
5700	58.117	426.702	372.700	307.809	−806.969	17.633	−0.162
5800	58.120	427.713	373.640	313.621	−809.622	32.124	−0.289
5900	58.123	428.706	374.565	319.433	−812.356	46.658	−0.413
6000	58.126	429.683	375.476	325.245	−815.175	61.243	−0.533

PREVIOUS: December 1973 (1 atm) CURRENT. December 1973 (1 bar)

Tungsten Oxide (WO_2) CRYSTAL $M_r = 215.8488$ Tungsten Oxide (WO_2) $O_2W_1(cr)$

$S°(298.15\ K) = 50.528 \pm 0.29\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -584.745 \pm 0.88\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -589.693 \pm 0.88\ kJ \cdot mol^{-1}$
$\Delta_{sub} H°(298.15\ K) = 666.260\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation, $-140.94 \pm 0.21\ kcal \cdot mol^{-1}$, was determined by combustion calorimetry by Mah.[1] Griffis[2] has measured the enthalpy of combustion to $WO_3(cr)$ which yields $\Delta_f H°(WO_2, cr, 298.15\ K) = -139.8 \pm 1.5\ kcal \cdot mol^{-1}$. When recalculated with $\Delta_f H°(WO_3, cr, 298.15\ K) = -201.46\ kcal \cdot mol^{-1}$. This result is less certain because of the incomplete characterization of the final products.

Recent equilibrium data yield essentially the same average of the enthalpy of formation by the 3rd law method. The results are presented as follows.

Source	Reaction	T/K	Data Points	$\Delta_r H°(298.15\ K)$, $kcal \cdot mol^{-1}$ 3rd law	2nd law	Drift $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal \cdot mol^{-1}$
3	A	1275–1497	10	2.672	0.036	1.9 ± 0.6	−140.62
3	B	973–1467	6	11.994	12.076	0.2 ± 0.76	−139.58
4	C	923–1223	7	−70.281	−67.943	−2.2 ± 0.2	−140.56
5	B	1075–1210	5	12.949	13.051	−0.1 ± 0.4	−141.49
6	B	873–1273	30	12.550	10.295	2.1 ± 0.1	−140.70

Reactions: A) $1/2\ WO_2(cr) + CO(g) = 1/2\ W(cr) + CO_2(g)$
B) $1/2\ WO_2(cr) + H_2(g) = 1/2\ W(cr) + H_2O(g)$
C) $1/2\ W(cr) + 1/2\ O_2(g) = 1/2\ WO_2(cr)$

Heat Capacity and Entropy

King *et al.*[7] have measured the low temperature heat capacities (53–297 K) and high temperature enthalpy changes (396–1800 K) by drop calorimetry. The low temperature and high temperature heat capacities were joined smoothly at 298.15 K. The entropy was obtained from the heat capacities based on $S°(51\ K) = 0.52\ cal \cdot K^{-1} \cdot mol^{-1}$. It is possible that at temperatures below 50 K the entropy due to the uncoupling of the d^2 electrons will appear contributing an additional $1.3\ cal \cdot K^{-1} \cdot mol^{-1}$.

Decomposition Data

Tungsten dioxide (cr) has no melting point since disproportionation occurs to yield W(cr) and $WO_3(l)$ before melting starts. $T_{dcm} = 1997\ K$ is calculated as the temperature at which $\Delta_f G° = 0$ for $3\ WO_2(cr) = 2\ WO_3(l) + W(cr)$.

Sublimation Data

The enthalpy of sublimation is calculated from the difference between the enthalpies of formation of $WO_2(g)$ and $WO_2(cr)$.

References

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[3] G. R. St. Pierre, W. T. Ebihara, M. J. Pool and R. Speiser, Trans. AIME **224**, 259 (1962).
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Enthalpy Reference Temperature = T_r = 298.15 K

Standard State Pressure = $p°$ = 0.1 MPa

		$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−8.708	−584.745	−584.745	INFINITE
100	19.106	9.991	90.199	−8.021	−587.614	−570.321	297.905
200	42.211	30.893	55.247	−4.871	−589.383	−552.210	144.222
298.15	55.739	50.528	50.528	0.000	−589.693	−533.856	93.529
300	55.898	50.873	50.529	0.103	−589.689	−533.509	92.892
400	63.429	68.063	52.822	6.096	−589.131	−514.850	67.233
500	68.157	82.763	57.377	12.693	−588.107	−496.391	51.858
600	71.302	95.484	62.692	19.675	−586.843	−478.164	41.628
700	73.623	106.657	68.191	26.926	−585.447	−460.160	34.338
800	75.474	116.613	73.633	34.384	−583.971	−442.362	28.883
900	76.978	125.592	78.915	42.009	−582.440	−424.752	24.652
1000	78.174	133.767	83.998	49.769	−580.876	−407.315	21.276
1100	79.122	141.264	88.868	57.635	−579.298	−390.035	18.521
1200	79.968	148.184	93.526	65.590	−577.716	−372.899	16.232
1300	80.983	154.622	97.981	73.634	−576.126	−355.895	14.300
1400	82.969	160.690	102.245	81.823	−574.466	−339.016	12.649
1500	85.103	166.491	106.336	90.232	−572.661	−322.261	11.222
1600	88.031	172.080	110.272	98.893	−570.676	−305.631	9.978
1700	91.044	177.508	114.068	107.848	−568.471	−289.132	8.884
1800	93.847	182.791	117.740	117.092	−566.047	−272.769	7.916
1900	96.169	187.929	121.299	126.597	−563.434	−256.546	7.053
2000	98.198	192.914	124.756	136.316	−560.678	−240.465	6.280
2100	99.998	197.750	128.117	146.227	−557.802	−224.525	5.585
2200	101.755	202.442	131.390	156.315	−554.822	−208.723	4.956
2300	103.512	207.004	134.579	166.579	−551.738	−193.061	4.385
2400	105.228	211.445	137.689	177.014	−548.553	−177.534	3.864
2500	106.943	215.776	140.726	187.623	−545.268	−162.142	3.388
2600	108.617	220.003	143.695	198.401	−541.881	−146.884	2.951
2700	110.290	224.133	146.598	209.346	−538.423	−131.757	2.549
2800	111.964	228.175	149.439	220.459	−534.926	−116.759	2.178
2900	113.470	232.130	152.223	231.733	−531.436	−101.886	1.835
3000	115.102	236.004	154.951	243.160	−527.988	−87.133	1.517

PREVIOUS: June 1962 CURRENT: September 1966

Tungsten Oxide (WO_2) $O_2W_1(cr)$

Tungsten Oxide (WO_2) IDEAL GAS $M_r = 215.8488$ Tungsten Oxide (WO_2) $O_2W_1(g)$

$\Delta_fH°(0\ K) = 78.98 \pm 29.3\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = [285.499]\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = 76.57 \pm 29.3\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights ϵ_i, cm^{-1}	g_i
0	[3]
[25,000]	[10]

Vibrational Frequencies and Degeneracies ν, cm^{-1}
992 (1)
[300] (1)
928 (1)

Ground State Quantum Weight: [3] $\sigma = [2]$
Point Group: [C_{2v}]
Bond,uccircl Distance: W–O = [1.81] Å
Bond Angle: O–W–O = [110]°
Product of the Moments of Inertia: $I_AI_BI_C = [9.435202 \times 10^{-115}]\ g^3\cdot cm^6$

Enthalpy of Formation

DeMaria *et al.*[1] have reported the partial pressures of WO(g), $WO_2(g)$, $WO_3(g)$, and O(g) in a mass spectrometric study of aluminum oxide vaporized from a tungsten cell from 2188 to 2475 K. The adopted value, $\Delta_fH°(WO_2, g, 298.15\ K) = 18.3 \pm 7\ kcal\cdot mol^{-1}$, was calculated from $\Delta_rH°(298.15\ K) = -100.9\ kcal\cdot mol^{-1}$ for $W(cr) + 2\,O(g) \rightarrow WO_2(g)$, which was obtained from 3rd law treatment of their partial pressure data, using all JANAF functions. The 3rd law drift is $15.0 \pm 5.2\ cal\cdot K^{-1}\cdot mol^{-1}$. Partial pressures of $WO_2(g)$, $WO_3(g)$ and O(g) at 2242 K have also been reported by Chupka *et al.*[2] in a mass spectrometric study of beryllium oxide in a tungsten cell. Similar calculation gives $\Delta_rH°(298.15\ K) = -105.9\ kcal\cdot mol^{-1}$ which yields $\Delta_fH°(WO_2, g, 298.15\ K) = 13.2\ kcal\cdot mol^{-1}$.

Heat Capacity and Entropy

The $WO_2(g)$ was assumed to have a C_{2v} symmetry with a bond angle O–W–O = 110°. The bond distance W–O was estimated to be the same as that in WO(g). The symmetric and asymmetric stretching frequencies were obtained from the infrared spectrum of WO_2 in a neon matrix by Weltner and McLeod.[3] The bending vibrational frequency ($300\ cm^{-1}$) was estimated by comparison with other dioxides. The electronic levels and quantum weights were estimated from W^{+4} ion by analogy with Mo^{+4} ion. The principal moments of inertia are: $I_A = 4.8780 \times 10^{-39}$, $I_B = 11.6809 \times 10^{-39}$ and $I_C = 16.5589 \times 10^{-39}\ g\cdot cm^2$.

References

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

T/K	$J\cdot K^{-1}mol^{-1}$ $C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$kJ\cdot mol^{-1}$ $H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−11.246	78.977	78.977	INFINITE
100	35.385	242.910	321.628	−7.872	78.795	72.796	−38.025
200	39.783	268.864	289.376	−4.102	77.646	67.224	−17.557
250	41.834	277.961	286.210	−2.062	77.071	64.686	−13.515
298.15	43.812	285.499	285.499	0.	76.567	62.348	−10.923
300	43.887	285.771	285.500	0.081	76.549	62.259	−10.840
350	45.806	292.682	286.042	2.324	76.091	59.915	−8.942
400	47.508	298.913	287.267	4.658	75.691	57.632	−7.526
450	48.970	304.595	288.882	7.071	75.335	55.396	−6.430
500	50.204	309.820	290.718	9.551	75.011	53.199	−5.558
600	52.109	319.152	294.698	14.673	74.415	48.893	−4.256
700	53.454	327.292	298.785	19.954	73.842	44.684	−3.334
800	54.420	334.496	302.807	25.351	73.256	40.559	−2.648
900	55.129	340.949	306.693	30.830	72.641	36.508	−2.119
1000	55.662	346.786	310.415	36.371	71.986	32.528	−1.699
1100	56.071	352.111	313.967	41.958	71.285	28.616	−1.359
1200	56.390	357.004	317.353	47.582	70.536	24.769	−1.078
1300	56.644	361.528	320.579	53.234	69.735	20.988	−0.843
1400	56.849	365.734	323.656	58.909	68.880	17.270	−0.644
1500	57.016	369.662	326.593	64.602	67.970	13.614	−0.474
1600	57.154	373.346	329.401	70.311	67.001	10.022	−0.327
1700	57.270	376.814	332.089	76.033	65.974	6.492	−0.199
1800	57.368	380.091	334.666	81.765	64.886	3.024	−0.088
1900	57.451	383.195	337.139	87.506	63.735	−0.382	0.010
2000	57.523	386.143	339.516	93.254	62.520	−3.725	0.097
2100	57.585	388.952	341.804	99.010	61.240	−7.006	0.174
2200	57.639	391.632	344.008	104.771	59.894	−10.224	0.243
2300	57.686	394.195	346.135	110.537	58.481	−13.381	0.304
2400	57.728	396.651	348.189	116.308	57.001	−16.474	0.359
2500	57.766	399.008	350.175	122.083	55.452	−19.504	0.408
2600	57.801	401.275	352.097	127.861	53.839	−22.470	0.451
2700	57.833	403.457	353.959	133.643	52.134	−25.373	0.491
2800	57.863	405.560	355.765	139.428	50.303	−28.210	0.526
2900	57.892	407.591	357.517	145.216	48.306	−30.980	0.558
3000	57.920	409.555	359.219	151.006	46.118	−33.677	0.586
3100	57.949	411.454	360.874	156.800	43.696	−36.297	0.612
3200	57.978	413.294	362.483	162.596	41.008	−38.836	0.634
3300	58.009	415.079	364.050	168.395	38.031	−41.287	0.654
3400	58.042	416.811	365.577	174.198	34.731	−43.641	0.670
3500	58.077	418.494	367.065	180.004	31.042	−45.894	0.685
3600	58.115	420.131	368.516	185.813	26.871	−48.034	0.697
3700	58.156	421.724	369.933	191.627	−12.647	−49.861	0.704
3800	58.202	423.275	371.316	197.445	−14.494	−50.841	0.699
3900	58.252	424.788	372.668	203.267	−16.350	−51.773	0.693
4000	58.307	426.263	373.989	209.095	−18.214	−52.658	0.688
4100	58.367	427.704	375.282	214.929	−20.086	−53.496	0.682
4200	58.432	429.111	376.547	220.769	−21.963	−54.288	0.675
4300	58.502	430.487	377.785	226.615	−23.847	−55.035	0.669
4400	58.579	431.832	378.998	232.470	−25.735	−55.739	0.662
4500	58.661	433.150	380.187	238.331	−27.628	−56.400	0.655
4600	58.749	434.440	381.353	244.202	−29.524	−57.019	0.647
4700	58.844	435.704	382.496	250.082	−31.423	−57.596	0.640
4800	58.944	436.944	383.617	255.971	−33.325	−58.132	0.633
4900	59.050	438.161	384.718	261.871	−35.230	−58.629	0.625
5000	59.162	439.355	385.799	267.781	−37.136	−59.087	0.617
5100	59.280	440.528	386.860	273.703	−39.045	−59.507	0.609
5200	59.404	441.680	387.904	279.637	−40.956	−59.890	0.602
5300	59.532	442.813	388.929	285.584	−42.868	−60.235	0.594
5400	59.666	443.927	389.937	291.544	−44.783	−60.546	0.586
5500	59.805	445.023	390.929	297.517	−46.700	−60.820	0.578
5600	59.949	446.102	391.904	303.505	−48.620	−61.059	0.570
5700	60.097	447.164	392.865	309.507	−50.543	−61.264	0.561
5800	60.249	448.211	393.810	315.525	−52.470	−61.435	0.553
5900	60.405	449.242	394.741	321.557	−54.401	−61.575	0.545
6000	60.565	450.258	395.657	327.606	−56.337	−61.679	0.537

PREVIOUS. September 1966 (1 atm) CURRENT: September 1966 (1 bar)

Tungsten Oxide ($WO_{2.72}$) CRYSTAL $M_r = 227.3684$

Tungsten Oxide ($WO_{2.72}$) $O_{2.72}W_1(cr)$

$S°(298.15 K) = [68.425]\ J·K^{-1}·mol^{-1}$

$\Delta_fH°(0 K) = Unknown$

$\Delta_fH°(298.15 K) = -781.153 \pm 2.1\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation, $-186.7 \pm 0.5\ kcal·mol^{-1}$, is derived from recent equilibrium data which are in excellent agreement, the results are summarized below. In addition, Griffis[1] measured the enthalpy of combustion to $WO_3(cr)$ which yields $\Delta_fH°(WO_{2.72}$, cr, 298.15 K) = $-185.4 \pm 1\ kcal·mol^{-1}$ when recalculated with $\Delta_fH°(WO_3$, cr, 298.15 K) = $-201.46\ kcal·mol^{-1}$. This result is less certain because of the incomplete characterization of the final products. The emf data reported by Geras,uccirclimov *et al.*[2] give the value of $-186.89\ kcal·mol^{-1}$ for the enthalpy of formation at 298.15 K. Ackermann and Rauh[3] have investigated the tungsten oxygen system by mass effusion, mass spectroscopy and X-ray diffraction. In the temperature range from 1300 to 1600 K, they have derived indirectly from their measurements the enthalpy of formation $-182.2\ kcal·mol^{-1}$ (corresponding to $-187.2\ kcal·mol^{-1}$ at 298.15 K, using the JANAF functions).

Source	Reaction*	T/K	Data Points	$\Delta_rH°(298.15 K)$, kcal·mol⁻¹ 2nd law	3rd law	Drift cal·K⁻¹·mol⁻¹	$\Delta_fH°(298.15 K$ kcal·mol⁻¹
[4]	A	830–1048	5	2.951	4.095	1.2 ± 0.2	−186.65
[5]	B	1173–1423	–	−45.739	–	–	−186.68
[6]	A	904–1066	4	2.676	4.279	1.6 ± 0.3	−186.83
[7]	A	873–1173	24	4.314	4.314	−0.01 ± 0.06	−186.87

A) $100/72\ WO_{2.72}(cr) + H_2(g) = 100/72\ WO_2(cr) + H_2O(g)$

B) $WO_2(cr) + 0.72\ O_2(g) = WO_{2.72}(cr)$

Heat Capacity and Entropy

The monoclinic unit cell of $WO_{2.72}$ corresponds to $W_{18}O_{49}$ as shown by the X-ray diffraction studies of Magneli *et al.*[8] The tabulated heat capacities of $WO_{2.72}(cr)$ were estimated from those of $WO_2(cr)$ and $WO_3(cr)$ because all three have similar monoclinic structures as identified by Magneli *et al.*

The entropy, $S°(298.15 K) = 16.35\ cal·K^{-1}·mol^{-1}$, was calculated from $\Delta_rS°(298.15 K) = 7.96 \pm 0.09\ cal·K^{-1}·mol^{-1}$ for reaction A, using all JANAF values. The value of $\Delta_r S°(298.15 K)$ was derived from the 2nd law analysis of Griffis' data.[7]

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[8] A. Magneli, G. Anderson, B. Blomberg and L. Kihlborg, Anal. Chem. 24, 1998 (1952).

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	68.283	68.425	68.425	0.000	−781.153	−708.632	124.149
300	68.408	68.848	68.426	0.126	−781.145	−708.183	123.306
400	76.902	89.731	71.216	7.406	−780.370	−683.959	89.316
500	82.927	107.581	76.748	15.417	−779.034	−660.002	68.950
600	86.985	123.079	83.207	23.923	−777.382	−636.347	55.399
700	89.810	136.719	89.897	32.775	−775.557	−612.984	45.741
800	91.839	148.850	96.522	41.862	−773.653	−589.889	38.516
900	93.471	159.765	102.953	51.131	−771.705	−567.035	32.910
1000	95.019	169.696	109.138	60.558	−769.720	−544.400	28.437
1100	96.441	178.819	115.064	70.131	−767.698	−521.965	24.786
1200	97.822	187.269	120.733	79.843	−765.637	−499.717	21.752
1300	99.286	195.155	126.158	89.697	−763.526	−477.642	19.192
1400	100.751	202.568	131.353	99.701	−761.353	−455.732	17.004
1500	102.006	209.562	136.336	109.838	−759.130	−433.979	15.113
1600	103.261	216.185	141.122	120.102	−756.864	−412.376	13.463
1700	104.516	222.483	145.724	130.491	−754.552	−390.916	12.011
1800	105.772	228.493	150.157	141.005	−752.196	−369.594	10.725
1900	107.027	234.245	154.432	151.645	−749.794	−348.404	9.578
2000	108.282	239.767	158.562	162.410	−747.347	−327.341	8.549
2100	109.537	245.080	162.556	173.301	−744.854	−306.402	7.621
2200	110.792	250.205	166.424	184.318	−742.316	−285.581	6.781
2300	112.048	255.158	170.175	195.460	−739.732	−264.879	6.016
2400	113.303	259.953	173.816	206.727	−737.103	−244.290	5.317
2500	114.558	264.603	177.355	218.120	−734.428	−223.811	4.676
2600	115.813	269.121	180.798	229.639	−731.704	−203.440	4.087
2700	117.068	273.515	184.151	241.283	−728.957	−183.173	3.544
2800	118.324	277.795	187.420	253.053	−726.221	−163.009	3.041
2900	119.579	281.970	190.608	264.948	−723.535	−142.943	2.575
3000	120.834	286.045	193.722	276.968	−720.925	−122.967	2.141

PREVIOUS: CURRENT: September 1966

Tungsten Oxide ($WO_{2.90}$) CRYSTAL $M_r = 230.2483$ Tungsten Oxide ($WO_{2.90}$) $O_{2.90}W_1(cr)$

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K) = [73.371]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -820.064 \pm 0.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation, $-196.0 \pm 3\ kcal \cdot mol^{-1}$, is a weighted average of those derived from equilibrium data, in addition the following results have been reported.

Griffis[1] has measured the enthalpy of combustion to $WO_3(cr)$ which yields $-195.6\ kcal \cdot mol^{-1}$ when recalculated with $\Delta_f H°(WO_3, cr, 298.15\ K) = -201.46\ kcal \cdot mol^{-1}$. This result is less certain because of the incomplete characterization of the final products. Ackermann and Rauh[2] have investigated the tungsten oxygen system by mass effusion, mass spectroscopy, and x-ray diffraction. In the temperature range from 1300 to 1600 K, they have derived indirectly two values of $\Delta_f H°(WO_{2.90}, cr) = -190.9$ and $-188.0\ kcal \cdot mol^{-1}$ (corresponding to -196.1 and $-193.3\ kcal \cdot mol^{-1}$, respectively, at 298.15 K, using all JANAF functions).

Source	Reaction	T/K	Data Points	$\Delta_r H°$(298 15 K), kcal mol¯1 2nd law	3rd law	Drift cal $k^{-1} \cdot mol^{-1}$	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
[3]	A	773–898	5	2.168	0.270	−2.3 ± 0.07	−195.4
[4]	A	897–993	4	2.178	0.240	−2.1 ± 0.01	−195.4
[5]	A	873–1073	18	1.504	0.284	−1.3 ± 0.02	−195.4
[3]	B	844–934	5	2.657	0.754	−2.1 ± 0.09	−197.9
[4]	B	915–1021	5	1.585	0.834	−0.76 ± 0.1	−197.9
[5]	B	873–1073	18	3.388	0.589	−2.88 ± 0.02	−197.7
[3]	C	737–798	5	6.762	5.013	−2.3 ± 0.9	−198.0
[6]	D	1023–1273	–	−7.97	–	–	−193.5
[6]	E	1173–1322	–	−13.67	–	–	−200.4

Reactions:
- A) $WO_3(cr) + 0.1\ H_2(g) = WO_{2.90}(cr) + 0.1\ H_2O(g)$
- B) $WO_{2.90}(cr) + 0.18\ H_2(g) = WO_{2.72}(cr) + 0.18\ H_2O(g)$
- C) $WO_{2.90}(cr) + 0.9\ H_2(g) = WO_2(cr) + 0.9\ H_2O(g)$
- D) $WO_{2.90}(cr) + 0.05\ O_2(g) = WO_3(cr)$
- E) $WO_{2.72}(cr) + 0.09\ O_2(g) = WO_{2.90}(cr)$

Heat Capacity and Entropy

The monoclinic unit cell of $WO_{2.90}$ corresponds to $WO_{20}O_{58}$ as shown by the X-ray diffraction studies of Magneli *et al.*[7] The tabulated heat capacities and the entropy, $S°(298.15\ K) = 17.536\ cal \cdot K^{-1} \cdot mol^{-1}$, were estimated from those of $WO_2(cr)$ and $WO_3(cr)$ because all three have the similar monoclinic structure as identified by Magneli *et al.*[7]

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

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0							
100							
200							
298.15	71.379	73.371	73.371	0.000	−820.064	−743.513	130.260
300	71.546	73.813	73.372	0.132	−820.056	−743.038	129.374
400	80.333	95 634	76.287	7.739	−819.221	−717.472	93.692
500	86.609	114.277	82.067	16.105	−817.804	−692.189	72.313
600	90.918	130.473	88.815	24.995	−816.053	−667.227	58.087
700	93.931	144.726	95.805	34.245	−814.124	−642.573	47.949
800	95.981	157.409	102.727	43.746	−812.106	−618.203	40.365
900	97.655	168.813	109.447	53.430	−810.049	−594.088	34.480
1000	99.244	179.189	115.910	63.279	−807.953	−570.205	29.784
1100	100.562	188.692	122.101	73.251	−805.849	−546.531	25.953
1200	101.880	197.496	128.021	83.370	−803.700	−523.051	22.768
1300	103.303	205.707	133.685	93.629	−801.506	−499.753	20.080
1400	104.558	213.411	139.107	104.025	−799.266	−476.625	17.783
1500	105.688	220.663	144.305	114.537	−796.996	−453.658	15.798
1600	106.818	227.520	149.293	125.162	−794.699	−430.844	14.066
1700	108.073	234.033	154.088	135.906	−792.364	−408.174	12.542
1800	109.328	240.246	158.703	146.777	−789.987	−385.643	11.191
1900	110.583	246.191	163.153	157.772	−787.566	−363.245	9.986
2000	111.838	251.895	167.448	168.893	−785.101	−340.976	8.905
2100	113.094	257.382	171.601	180.140	−782.593	−318.832	7.931
2200	114.349	262.672	175.621	191.512	−780.042	−296.806	7.047
2300	115.604	267.782	179.517	203.009	−777.448	−274.900	6.243
2400	116.859	272.729	183.299	214.633	−774.810	−253.107	5.509
2500	118.114	277.525	186.972	226.381	−772.128	−231.424	4.835
2600	119.370	282.182	190.545	238.255	−769.399	−209.849	4.216
2700	120.625	286.710	194.023	250.255	−766.648	−188.380	3.644
2800	121.880	291.120	197.413	262.380	−763.911	−167.013	3.116
2900	123.135	295.419	200.718	274.631	−761.226	−145.743	2.625
3000	124.390	299.614	203.945	287.007	−758.618	−124.564	2.169

PREVIOUS: CURRENT: September 1966

Tungsten Oxide ($WO_{2.90}$) $O_{2.90}W_1(cr)$

Tungsten Oxide ($WO_{2.96}$) CRYSTAL $M_r = 231.2082$

$\Delta_fH°(0\ K)$ = Unknown

$S°(298.15\ K) = [74.894]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_fH°(298.15\ K) = -834.959 \pm 12.6\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The adopted value, $\Delta_fH°(WO_{2.96}$, cr, 298.15 K) = −199.56 $kcal\cdot mol^{-1}$, was obtained by 3rd law treatment of $\Delta_fG° = 191{,}600 + 54.0\ T\ (cal\cdot K^{-1}\cdot mol^{-1})$ in the temperature range from 1300–1550 K, using all JANAF functions. The equation for $\Delta_fG°$ was reported by Ackermann and Rauh[-1], based on studies by mass spectroscopy and X–ray diffraction. In this study, $\Delta_fG°$ was obtained by comparison of the Gibbs free energies of sublimation (to gaseous W_2O_6, W_3O_8, W_3O_9 and W_4O_{12}) over the two systems W–WO_2(cr) and $WO_{2.96}$(cr) and $WO_{2.96}$(cr); thus $WO_{2.96}$(cr) was related to WO_2(cr) through the gaseous species.

Battles[2] has reported partial pressures of W_3O_9(g) and W_4O_{12}(g) in equilibrium with WO_3–$WO_{2.90}$(cr). In light of Ackermann and Rauh's observation, the condensed phase was presumed to have the composition of $WO_{2.96}$(cr). The pressure data are in reasonable agreement with the studies of Ackermann and Rauh as summarized below. Values of $\Delta_fH°(WO_{2.96}$, cr, 298.15 K) derived from the data of Battles are based on the same author's data for W_3O_9(g), and W_4O_{12}(g) in order to relate $WO_{2.96}$ to WO_2 directly.

Source	Reaction	T/K	$\Delta_rH°$(298.15 K), kcal·mol⁻¹ 2nd law	kcal·mol⁻¹ 3rd law	Drift cal·K⁻¹·mol⁻¹	$\Delta_fH°$(298.15 K) kcal·mol⁻¹
1	A	1300–1550	56.32	60.82	3.2 ± 0.6	−199.57
1	B	1300–1550	38.35	41.37	2.09 ± 0.09	−199.58
2	B	1274–1418	43.28	40.82	1.85 ± 0.05	−199.72
1	C	1300–1550	33.58	35.81	1.55 ± 0.09	−199.60
2	C	1333–1418	38.74	35.37	−2.46 ± 0.1	−199.95

Reactions:
A) $WO_{2.96}(cr) = 0.44\ W_2O_6(g) + 0.04\ W_3O_8(g)$
B) $WO_{2.96}(cr) = 0.29333\ W_3O_9(g) + 0.04\ W_3O_8(g)$
C) $WO_{2.96}(cr) = 0.22\ W_4O_{12}(g) + 0.04\ W_3O_8(g)$

Heat Capacity and Entropy

The tabulated heat capacities and the entropy at 298.15 K were estiamted from those of WO_2(cr) and WO_3(cr).

Ackermann and Rauh[1] have found that the composition $WO_{2.96}$ probably represents the azeotropic composition of the WO_{3-x} solid solution and is the only single phase which evaporates congruently below 1550 K.

References

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[2] J. E. Battles, Ph.D. Thesis, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide," Ohio State University (1964).

Tungsten Oxide ($WO_{2.96}$) $O_{2.96}W_1(cr)$

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	72.383	74.894	74.894	0.000	−834.959	−757.027	132.628
300	72.634	75.342	74.895	0.134	−834.950	−756.544	131.726
400	81.504	97.478	77.852	7.850	−834.095	−730.517	95.396
500	87.864	116.394	83.716	16.339	−832.648	−704.781	73.628
600	92.257	132.825	90.562	25.358	−830.863	−679.371	59.145
700	95.312	147.287	97.653	34.744	−828.895	−654.276	48.823
800	97.404	160.156	104.677	44.384	−826.838	−629.471	41.100
900	99.370	171.735	111.495	54.216	−824.734	−604.925	35.109
1000	100 709	182.264	118.053	64.211	−822.598	−580.616	30.328
1100	102.215	191.936	124.336	74.359	−820.421	−556.523	26.427
1200	103.512	200.886	130.347	84.647	−818.211	−532.630	23.185
1300	104.851	209.224	136.097	95.065	−815.965	−508.922	20.449
1400	106.106	217.041	141.603	105.613	−813.681	−485.389	18.110
1500	107.194	224.399	146.880	116.278	−811.368	−462.020	16.089
1600	108.282	231.351	151.944	127.052	−809.032	−438.806	14.326
1700	109.537	237.954	156.811	137.943	−806.662	−415.740	12.774
1800	110.792	244.250	161.495	148.959	−804.249	−392.814	11.399
1900	112.048	250.274	166.010	160.101	−801.794	−370.023	10.173
2000	113.303	256.053	170.369	171.369	−799.296	−347.363	9.072
2100	114.558	261.612	174.582	182.762	−796.755	−324.828	8.080
2200	115.813	266.970	178.660	194.280	−794 172	−302.415	7.180
2300	117.068	272.145	182.613	205.924	−791.546	−280.122	6.362
2400	118.324	277.154	186.449	217.694	−788.877	−257.944	5.614
2500	119.579	282.010	190.174	229.589	−786.165	−235.877	4.928
2600	120.834	286.724	193.798	241.610	−783.406	−213.920	4.298
2700	122.089	291.308	197.325	253.756	−780.627	−192.069	3.716
2800	123.344	295.771	200.761	266.028	−777.862	−170.321	3.177
2900	124.600	300.121	204.113	278.425	−775.148	−148.672	2.678
3000	125.855	304.367	207.384	290.948	−772.513	−127.114	2.213

PREVIOUS: CURRENT: September 1966

Tungsten Oxide ($WO_{2.96}$) $O_{2.96}W_1(cr)$

Zirconium Oxide (ZrO_2) CRYSTAL M_r = 123.2188 Zirconium Oxide (ZrO_2) $O_2Zr_1(cr)$

$\Delta_fH°(0\ K) = -1092.032 \pm 1.7\ kJ{\cdot}mol^{-1}$
$S°(298.15\ K) = [50.359 \pm 0.33]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = -1097.463 \pm 1.7\ kJ{\cdot}mol^{-1}$
$T_{trs} = 1478 \pm 5\ K$ $\Delta_{trs}H° = 5.941 \pm 0.4\ kJ{\cdot}mol^{-1}$
$T_{fus} = 2950\ K$ $\Delta_{fus}H° = [87.027]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(ZrO_2$, cr, 298.15 K) = $-262.3 \pm 0.4\ kcal{\cdot}mol^{-1}$ is an average of the values $261.5 \pm 0.2\ kcal{\cdot}mol^{-1}$ and $-263.1 \pm 0.5\ kcal{\cdot}mol^{-1}$ measured (by combustion calorimetry) by Humphrey[1] and Huber *et al.*,[2] respectively. measured calorimetrically by Neumann *et al.*,[3] Roth *et al.*[4] and by Sieverts *et al.*[5] and was found to be −258.2, −258.8 and $-256.1\ kcal{\cdot}mol^{-1}$, 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 Kelley.[6] The heat capacities in the temperature range 298–1478 K were calculated by using the Coughlin and King[7] equation, $C_p° = 16.64 + 1.80 \times 10^{-3}T - 3.36 \times 10^5\ T^2$, obtained from their measured enthalpy data (296.8–1841 K). The values from the two sources join smoothly at 298.15 K. Above the transition 1478 K, the heat capacity was taken as constant at $17.80\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. The entropy was calculated at 54.30 K using the Debye and Einstein function $D(345/T) + E(513/T) + E(861/T)$ given by Kelley.[6] The value, $S°(54.3\ K) = 0.5507\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, is thus calculated.

Transition Data

T_{trs} and $\Delta_{trs}H°$ were taken from Coughlin and King.[7]

Fusion Data

T_{fus} and $\Delta_{fus}H°$ were taken from U. S. Nat. Bur. Stand.[8]

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[8] U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).

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

		$J{\cdot}K^{-1}mol^{-1}$		$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.000	0.000	INFINITE	−8.749	−1092.032	−1092.032	INFINITE
100	18.927	9.488	90.390	−8.090	−1095.164	−1077.376	562.764
200	42.778	30.546	55.114	−4.914	−1097.091	−1058.694	276.502
298.15	56.191	50.359	50.359	0.000	−1097.463	−1039.724	182.155
300	56.262	50.707	50.360	0.104	−1097.460	−1039.366	180.970
400	63.848	68.064	52.675	6.155	−1096.940	−1020.063	133.207
500	67.764	82.769	57.264	12.753	−1096.026	−1000 945	104.568
600	70.237	95.356	62.589	19.660	−1094.969	−982.027	85.493
700	72.023	106.323	68.070	26 777	−1093.873	−963.289	71.882
800	73.450	116.036	73.471	34 053	−1092.785	−944.709	61.683
900	74.663	124.759	78.693	41.459	−1091.731	−926.264	53.759
1000	75.747	132.682	83.702	48.981	−1090.727	−907.933	47.426
1100	76.743	139.949	88.489	56.606	−1089.783	−889.699	42.248
1200	77.684	146.667	93.061	64.327	−1092.612	−871.328	37.928
1300	78.580	152.921	97.428	72.141	−1091.250	−852.942	34.272
1400	79.450	158.776	101.603	80.042	−1089.872	−834.662	31.142
1478.000	80.108	163.101	104.735	86.265		I <−−> II	
1478.000	74.475	167.121	104.735	92.207		TRANSITION	
1500	74.475	168.222	105.658	93.845	−1082.674	−816.569	28.435
1600	74.475	173.028	109.720	101.293	−1081.921	−798.854	26.080
1700	74.475	177.543	113.578	108.740	−1081.266	−781.183	24.003
1800	74.475	181.800	117.251	116.188	−1080.720	−763.547	22.158
1900	74.475	185.827	120.756	123.635	−1080.293	−745.939	20.507
2000	74.475	189.647	124.105	131.083	−1079.995	−728.349	19.023
2100	74.475	193.280	127.314	138.530	−1079.836	−710.772	17.679
2200	74.475	196.745	130.392	145.978	−1101.150	−692.452	16.441
2300	74.475	200.056	133.349	153.425	−1101.717	−673.863	15.304
2400	74.475	203.225	136.195	160.873	−1102.306	−655.248	14.261
2500	74.475	206.265	138.937	168.320	−1102.918	−636.608	13.301
2600	74.475	209.186	141.583	175.768	−1103.550	−617.943	12.415
2700	74.475	211.997	144.140	183.215	−1104.204	−599.253	11.593
2800	74.475	214.706	146.612	190.663	−1104.878	−580.539	10.830
2900	74.475	217.319	149.005	198.110	−1105.572	−561.801	10.119
2950.000	74.475	218.592	150.174	201.834	-----	II <−−> LIQUID	-----
3000	74.475	219.844	151.325	205.558	−1106.286	−543.038	9.455
3100	74.475	222.286	153.575	213.005	−1107.018	−524.250	8.834
3200	74.475	224.650	155.759	220.453	−1107.768	−505.440	8.250
3300	74.475	226.942	157.881	227.900	−1108.536	−486.606	7.702
3400	74.475	229.165	159.945	235.348	−1109.320	−467.747	7.186
3500	74.475	231.324	161.954	242.795	−1110.120	−448.866	6.699

PREVIOUS: June 1961 CURRENT: December 1965

Zirconium Oxide (ZrO_2) LIQUID $M_r = 123.2188$

$S°(298.15\ K) = [74.657]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 2950\ K$

$\Delta_f H°(298.15\ K) = [-1023.155]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = [87.027]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(ZrO_2$, l, 298.15 K) is calculated from $\Delta_f H°(ZrO_2$, cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2950\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 2000 K. The heat capacity below 2000 K was obtained from the heat capacity of the crystal. Above 2000 K the heat capacity was assumed constant and estimated to be 21.0 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ or 7 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ per g-atom as suggested by Kubaschewski and Evans.[1] The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

$T_{vap}(1\ atm) = 4548\ K$ is calculated as the temperature at which the fugacity is 1 atm for the reaction $ZrO_2(l) \rightarrow ZrO_2(g)$. The difference between $\Delta_f H°(4548\ K)$ for $ZrO_2(g)$ and $ZrO_2(l)$ gives $\Delta_{vap}H°(4548\ K) = 149.2\ kcal{\cdot}mol^{-1}$.

Reference

[1] O. Kubaschewski and E. LL. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York (1958).

Zirconium Oxide (ZrO_2) $O_2Zr_1(l)$

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	56.191	74.657	74.657	0.000	−1023.155	−972.661	170.406
300	56.262	75.004	74.658	0.104	−1023.152	−972.347	169.301
400	63.848	92.361	76.972	6.155	−1022.632	−955 474	124.772
500	67.764	107.066	81.561	12.753	−1021.718	−938.785	98.074
600	70.237	119.653	86.886	19.660	−1020.661	−922.297	80.293
700	72.023	130.621	92.367	26.777	−1019.565	−905.989	67.606
800	73.450	140.333	97.768	34.053	−1018.477	−889.839	58.101
900	74.663	149.056	102.990	41.459	−1017.423	−873.823	50.715
1000	75.747	156.979	107.999	48.981	−1016.420	−857.922	44.813
1100	76.743	164.246	112.786	56.606	−1015.475	−842.118	39.989
1200	77.684	170.964	117.358	64.327	−1018.304	−826.176	35.963
1300	78.580	177.218	121.725	72.141	−1016.942	−810.221	32.555
1400	79.450	183.073	125.900	80.042	−1015.565	−794.371	29.638
1478.000	80.107	187.398	129.032	86.265	I <--> II		
1478.000	74.475	191.418	129.032	92.207	TRANSITION		
1500	74.475	192.519	129.955	93.845	−1008.367	−778.707	27.117
1600	74.475	197.325	134.017	101.293	−1007.613	−763.421	24.923
1700	74.475	201.840	137.875	108.740	−1006.958	−748.180	22.989
1800	74.475	206 097	141.548	116.188	−1006.412	−732.974	21.270
1900	74.475	210.124	145.053	123.635	−1005.985	−717.795	19.734
2000	74.475	213.944	148.403	131.083	−1005.687	−702.636	18.351
2000.000	74.475	213.944	148.403	131.083	GLASS <--> LIQUID		
2000.000	87.864	213.944	148.403	131.083	TRANSITION		
2100	87.864	218.231	151.626	139.869	−1004 189	−687.521	17.101
2200	87.864	222.318	154.748	148.655	−1024.164	−671.727	15.949
2300	87.864	226.224	157.771	157.442	−1023.393	−655.725	14.892
2400	87.864	229.963	160.702	166.228	−1022.643	−639.756	13.924
2500	87.864	233.550	163.544	175.015	−1021.916	−623.817	13.034
2600	87.864	236.996	166.304	183.801	−1021.209	−607.908	12.213
2700	87.864	240.312	168.984	192.587	−1020.524	−592.024	11.453
2800	87.864	243.508	171.588	201.374	−1019.860	−576.166	10.749
2900	87.864	246.591	174.122	210.160	−1019.215	−560.332	10.093
2950.000	87.864	248.093	175.363	214.553	----- II <--> LIQUID -----		
3000	87.864	249.570	176.587	218.947	−1018.589	−544.518	9.481
3100	87.864	252.451	178.988	227.733	−1017.983	−528.726	8.909
3200	87.864	255.240	181.328	236.519	−1017.394	−512.953	8.373
3300	87.864	257.944	183.609	245.306	−1016.823	−497.199	7.870
3400	87.864	260.567	185.834	254.092	−1016.268	−481.460	7.397
3500	87.864	263.114	188.006	262.879	−1015.729	−465.739	6.951
3600	87.864	265.589	190.127	271.665	−1015.206	−450.032	6.530
3700	87.864	267.997	192.199	280.451	−1014.698	−434.340	6.132
3800	87.864	270.340	194.224	289.238	−1014.204	−418.661	5.755
3900	87.864	272.622	196.206	298.024	−1013.724	−402.995	5.398
4000	87.864	274.847	198.144	306.811	−1013.257	−387.341	5.058
4100	87.864	277.016	200.041	315.597	−1012.803	−371.699	4.736
4200	87.864	279.133	201.899	324.383	−1012.362	−356.068	4.428
4300	87.864	281.201	203.720	333.170	−1011.933	−340.446	4.136
4400	87.864	283.221	205.504	341.956	−1011.517	−324.836	3.856
4500	87.864	285.195	207.253	350.743	−1011.112	−309.235	3.590
4600	87.864	287.127	208.968	359.529	−1010.720	−293.642	3.334
4700	87.864	289.016	210.651	368.315	−1010.340	−278.057	3.090
4800	87.864	290.866	212.303	377.102	−1570.909	−250.863	2.730
4900	87.864	292.678	213.925	385.888	−1570.207	−223.369	2.381
5000	87.864	294.453	215.518	394.675	−1569.534	−195.889	2.046

PREVIOUS: June 1961 CURRENT: December 1965

Zirconium Oxide (ZrO_2) CRYSTAL(I–II)-LIQUID M_r = 123.2188 Zirconium Oxide (ZrO_2) O_2Zr_1(cr,l)

0 to 1478 K crystal, I
1478 to 2950 K crystal, II
above 2950 K liquid

Refer to the individual tables for details.

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.000	0.000	INFINITE	−8.749	−1092.032	−1092.032	INFINITE
100	18.927	9.488	90.390	−8.090	−1095.164	−1077.376	562.764
200	42.778	30.546	55.114	−4.914	−1097.091	−1058.694	276.502
298.15	56.191	50.359	50.359	0.000	−1097.463	−1039.724	182.155
300	56.262	50.707	50.360	0.104	−1097.460	−1039.366	180.970
400	63.848	68.064	52.675	6.155	−1096.940	−1020.063	133.207
500	67.764	82.769	57.264	12.753	−1096.026	−1000.945	104.568
600	70.237	95.356	62.589	19.660	−1094.969	−982.027	85.493
700	72.023	106.323	68.070	26.777	−1093.873	−963.289	71.882
800	73.450	116.036	73.471	34.053	−1092.785	−944.709	61.683
900	74.663	124.759	78.693	41.459	−1091.731	−926.264	53.759
1000	75.747	132.682	83.702	48.981	−1090.727	−907.933	47.426
1100	76.743	139.949	88.489	56.606	−1089.783	−889.699	42.248
1200	77.684	146.667	93.061	64.327	−1092.612	−871.328	37.928
1300	78.580	152.921	97.428	72.141	−1091.250	−852.942	34.272
1400	79.450	158.776	101.603	80.042	−1089.872	−834.662	31.142
1478.000	80.107	163.101	104.735	86.265	I <– –> II		
1478.000	74.475	167.121	104.735	92.207	TRANSITION		
1500	74.475	168.222	105.658	93.845	−1082.675	−816.569	28.435
1600	74.475	173.028	109.720	101.293	−1081.921	−798.854	26.080
1700	74.475	177.543	113.578	108.740	−1081.266	−781.183	24.003
1800	74.475	181.800	117.251	116.188	−1080.720	−763.547	22.158
1900	74.475	185.827	120.756	123.635	−1080.293	−745.939	20.507
2000	74.475	189.647	124.105	131.083	−1079.995	−728.349	19.023
2100	74.475	193.280	127.314	138.530	−1079.836	−710.772	17.679
2200	74.475	196.745	130.392	145.978	−1101.150	−692.452	16.441
2300	74.475	200.056	133.349	153.425	−1101.717	−673.862	15.304
2400	74.475	203.225	136.195	160.873	−1102.306	−655.248	14.261
2500	74.475	206.265	138.937	168.320	−1102.918	−636.608	13.301
2600	74.475	209.186	141.583	175.768	−1103.550	−617.943	12.415
2700	74.475	211.997	144.140	183.215	−1104.204	−599.253	11.593
2800	74.475	214.706	146.612	190.663	−1104.878	−580.539	10.830
2900	74.475	217.319	149.005	198.110	−1105.572	−561.801	10.119
2950.000	74.475	218.592	150.174	201.834	II <– –> LIQUID		
2950.000	87.864	248.093	150.174	288.861	TRANSITION		
3000	87.864	249.570	151.818	293.254	−1018.589	−544.518	9.481
3100	87.864	252.451	155.018	302.041	−1017.983	−528.726	8.909
3200	87.864	255.240	158.107	310.827	−1017.394	−512.953	8.373
3300	87.864	257.944	161.091	319.614	−1016.823	−497.199	7.870
3400	87.864	260.567	163.979	328.400	−1016.268	−481.460	7.397
3500	87.864	263.114	166.775	337.186	−1015.729	−465.739	6.951
3600	87.864	265.589	169.486	345.973	−1015.206	−450.032	6.530
3700	87.864	267.997	172.116	354.759	−1014.698	−434.340	6.132
3800	87.864	270.340	174.670	363.546	−1014.204	−418.661	5.755
3900	87.864	272.622	177.152	372.332	−1013.724	−402.995	5.398
4000	87.864	274.847	179.567	381.118	−1013.257	−387.341	5.058
4100	87.864	277.016	181.917	389.905	−1012.803	−371.699	4.736
4200	87.864	279.133	184.207	398.691	−1012.362	−356.068	4.428
4300	87.864	281.201	186.439	407.478	−1011.933	−340.446	4.136
4400	87.864	283.221	188.615	416.264	−1011.517	−324.836	3.856
4500	87.864	285.195	190.740	425.050	−1011.112	−309.234	3.590
4600	87.864	287.127	192.814	433.837	−1010.720	−293.642	3.334
4700	87.864	289.016	194.841	442.623	−1010.340	−278.057	3.090
4800	87.864	290.866	196.822	451.410	−1570.909	−250.863	2.730
4900	87.864	292.678	198.760	460.196	−1570.207	−223.369	2.381
5000	87.864	294.453	200.656	468.982	−1569.534	−195.889	2.046

PREVIOUS: CURRENT December 1965

Zirconium Oxide (ZrO_2) O_2Zr_1(cr,l)

Zirconium Oxide (ZrO_2) IDEAL GAS $M_r = 123.2188$ Zirconium Oxide (ZrO_2) $O_2Zr_1(g)$

$S°(298.15\ K) = 273.746\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -284.01 \pm 46.0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -286.19 \pm 46.0\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
884 (1)
[137] (1)
818 (1)

Ground State Quantum Weight: 1
Point Group: C_{2v}
Bond Distance: O–Zr = 1.711 Å
Bond Angle: O–Zr–O = 109°
Product of the Moments of Inertia: $I_A I_B I_C = 5.682779 \times 10^{-115}\ g^3 \cdot cm^6$

$\sigma = 2$

Enthalpy of Formation

$\Delta_f H°(ZrO_2, g, 298.15\ K) = -68.4 \pm 11\ kcal \cdot mol^{-1}$ was calculated from the $\Delta_r H°(298.15\ K) = 193\ 867 \pm 11.25\ kcal \cdot mol^{-1}$ for the reaction $ZrO_2(cr) \rightarrow ZrO_2(g)$. The value of $\Delta_r H°(298.15\ K)$ was obtained by the 3rd law method using the determined vapor pressures (at the range 2331–2480 K) by Chupka *et al.*[1] They observed the variation of the ZrO_2^+ ion intensity over ZrO_2 reported equilibrium constants for the reaction $ZrO_2(cr) \rightarrow ZrO_2(g)$ in the range 2331–2480 K. The 3rd law drift is 80 ± 23 $cal \cdot K^{-1} \cdot mol^{-1}$.

Heat Capacity and Entropy

The vibrational frequencies $\nu_1 = 884$, $\nu_2 = [137]$, $\nu_3 = 818$ and angle O–Zr–O = 109° were obtained from Linevsky.[2] The bond distance r_e(O–Zr) = 1.711 Å was obtained from Uhler and Akerline.[3] The principal moments of inertia are: $I_A = 3.8834 \times 10^{-39}$, $I_B = 10.3101 \times 10^{-39}$, $I_C = 14.1935 \times 10^{-39}\ g \cdot cm^2$.

References

[1] W. A. Chupka, J. Berkowitz and M. G. Inghram, J. Chem. Phys. 26, 1207 (1957).
[2] M. J. Linevsky, Spectroscopic Studies of the Vaporization of Refractory Materials, AFML TR–64–420, Air Force Materials Lab. Research and Technology Division, Wright Patterson Air Force Base, Ohio (1965).
[3] U. Uhler and L. Akerlind, Arkiv Fysik 10, 431 (1955).

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.008	−284.013	−284.013	INFINITE
100	39.345	227.980	312.150	−8.417	−284.213	−288.275	150.579
200	42.320	256.161	277.836	−4.335	−285.235	−291.960	76.252
250	44.193	265.801	274.494	−2.173	−285.747	−293.581	61.340
298.15	46.061	273.746	273.746	0.	−286.186	−295.049	51.691
300	46.131	274.031	273.747	0.085	−286.201	−295.105	51.382
350	47.910	281.279	274.315	2.437	−286.597	−296.556	44.259
400	49.444	287.779	275.599	4.872	−286.945	−297.955	38.909
450	50.727	293.679	277.285	7.377	−287.262	−299.312	34.743
500	51.787	299.081	279.198	9.941	−287.560	−300.635	31.407
600	53.383	308.673	283.332	15.205	−288.147	−303.195	26.395
700	54.482	316.990	287.559	20.601	−288.772	−305.654	22.808
800	55.258	324.318	291.705	26.090	−289.469	−308.019	20.112
900	55.822	330.861	295.699	31.646	−290.267	−310.291	18.009
1000	56.242	336.765	299.515	37.250	−291.180	−312.468	16.322
1100	56.561	342.141	303.149	42.891	−292.220	−314.548	14.937
1200	56.810	347.074	306.607	48.560	−297.101	−316.305	13.768
1300	57.007	351.629	309.897	54.251	−297.862	−317.875	12.772
1400	57.165	355.860	313.031	59.960	−298.677	−319.384	11.916
1500	57.294	359.808	316.019	65.683	−299.559	−320.833	11.172
1600	57.401	363.509	318.873	71.418	−300.518	−322.221	10.519
1700	57.490	366.992	321.602	77.163	−301.566	−323.545	9.941
1800	57.565	370.280	324.216	82.916	−302.714	−324.806	9.426
1900	57.629	373.394	326.723	88.676	−303.975	−325.999	8.962
2000	57.684	376.352	329.131	94.441	−305.358	−327.123	8.544
2100	57.731	379.167	331.447	100.212	−306.876	−328.175	8.163
2200	57.772	381.854	333.678	105.987	−329.863	−328.404	7.797
2300	57.808	384.423	335.829	111.766	−332.098	−328.289	7.456
2400	57.840	386.884	337.905	117.549	−334.353	−328.075	7.140
2500	57.868	389.246	339.912	123.334	−336.626	−327.767	6.848
2600	57.893	391.516	341.853	129.122	−338.918	−327.367	6.577
2700	57.915	393.701	343.733	134.912	−341.229	−326.879	6.324
2800	57.935	395.808	345.556	140.705	−343.559	−326.305	6.087
2900	57.952	397.841	347.324	146.499	−345.906	−325.648	5.866
3000	57.969	399.806	349.041	152.295	−348.271	−324.908	5.657
3100	57.983	401.707	350.709	158.093	−350.653	−324.090	5.461
3200	57.997	403.548	352.332	163.892	−353.052	−323.196	5.276
3300	58.009	405.333	353.911	169.692	−355.466	−322.226	5.100
3400	58.020	407.065	355.449	175.494	−357.897	−321.181	4.934
3500	58.030	408.747	356.948	181.296	−360.342	−320.066	4.777
3600	58.039	410.382	358.409	187.100	−362.802	−318.881	4.627
3700	58.048	411.972	359.836	192.904	−365.276	−317.627	4.484
3800	58.056	413.520	361.228	198.709	−367.763	−316.305	4.348
3900	58.063	415.028	362.588	204.515	−370.263	−314.918	4.218
4000	58.070	416 498	363.918	210.322	−372.776	−313.468	4.093
4100	58.076	417.932	365.218	216.129	−375.301	−311.954	3.974
4200	58.082	419.332	366.490	221.937	−377.839	−310.378	3.860
4300	58.087	420.699	367.735	227.745	−380.388	−308.741	3.750
4400	58.092	422.034	368.954	233.554	−382.949	−307.046	3.645
4500	58.097	423.340	370.148	239.364	−385.521	−305.292	3.544
4600	58.102	424.617	371.318	245.174	−388.106	−303.481	3.446
4700	58.106	425.866	372.465	250.984	−390.702	−301.613	3.352
4800	58.110	427.090	373.591	256.795	−954.246	−288.073	3.135
4900	58.113	428.288	374.695	262.606	−956.519	−274.170	2.923
5000	58.117	429.462	375.778	268.418	−958.821	−260.221	2.719
5100	58.120	430.613	376.842	274.230	−961.152	−246.226	2.522
5200	58.123	431.741	377.887	280.042	−963.511	−232.186	2.332
5300	58.126	432.849	378.914	285.854	−965.897	−218.098	2.149
5400	58.129	433.935	379.923	291.667	−968.310	−203.967	1.973
5500	58.131	435.002	380.914	297.480	−970.749	−189.790	1.802
5600	58.134	436.049	381.890	303.293	−973.213	−175.568	1.638
5700	58.136	437.078	382.849	309.107	−975.703	−161.303	1.478
5800	58.138	438.089	383.793	314.920	−978.218	−146.992	1.324
5900	58.140	439.083	384.721	320.734	−980.757	−132.641	1.174
6000	58.142	440.060	385.636	326.548	−983.321	−118.243	1.029

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

Zirconium Oxide (ZrO_2) $O_2Zr_1(g)$

Ozone (O_3) IDEAL GAS $M_r = 47.9982$ Ozone (O_3) $O_3(g)$

$S°(298.15\ K) = 238.932\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 145.348 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 142.674 \pm 1.7\ kJ \cdot mol^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}
1110 (1)
705 (1)
1043 (1)

Ground State Quantum Weight: 1			$\sigma = 2$
Point Group: C_{2v}			
Rotational Constants:	$A_{000} = 3.55381\ cm^{-1}$	$B_{000} = 0.44530\ cm^{-1}$	$C_{000} = 0.39477\ cm^{-1}$
Anharmonicity Constants:	$X_{11} = -3.8\ cm^{-1}$	$X_{33} = -4.0\ cm^{-1}$	$X_{23} = -3.5\ cm^{-1}$
	$X_{22} = -3.5\ cm^{-1}$	$X_{12} = -2.0\ cm^{-1}$	$X_{31} = -9.0\ cm^{-1}$

Enthalpy of Formation

Gunther *et al.*[1] measured ΔE for the reaction $O_3(g) \rightarrow 3/2\ O_2(g)$ in a calorimeter calibrated by 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, $\Delta_f H°(298.15\ K)$ is calculated to be 33.89 ± 0.36 $cal \cdot mol^{-1}$. Kailan and Jahn[2] measured $\Delta_r H°$ 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 current joule–calorie conversion factor is used, $\Delta_f H°(298.15\ K)$ is found to be 34.3 ± 0.6 $kcal \cdot mol^{-1}$. Variability in the O_3 content of the feed gas is allowed for in the uncertainty. The value adopted here is 34.1 ± 0.4 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Gordon[3] has calculated the thermodynamic functions from 298.15 to 6000 K by the method of Pennington and Kobe[4] which takes vibration–rotation interaction and anharmonicity into account. Gordon's data are from Pierce.[5] The functions below 298.15 K have been calculated for a rigidly rotating harmonic oscillator.

References

[1] P. Gunther, E. Wassmuth and L. A. Schryver, Z. Phys. Chem. 158, 297 (1932).
[2] A. Kailan and S. Jahn, Z. Anorg. Chem. 68, 243 (1910).
[3] J. S. Gordon, Thiokol Chemical Corp., personal communication, (April 1961).
[4] R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954).
[5] L. Pierce, J. Chem. Phys. 24, 139 (1956).

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−10.351	145.348	145.348	INFINITE
100	33.292	200.791	271.040	−7.025	144.318	150.235	−78.474
200	35.058	224.221	242.401	−3.636	143.340	156.541	−40.884
298.15	39.238	238.932	238.932	0.000	142.674	163.184	−28.589
300	39.330	239.175	238.933	0.073	142.665	163.311	−28.435
400	43.744	251.116	240.531	4.234	142.370	170.247	−22.232
500	47.262	261.272	243.688	8.792	142.340	177.224	−18.514
600	49.857	270.129	247.373	13.654	142.462	184.191	−16.035
700	51.752	277.963	251.194	18.738	142.665	191.130	−14.262
800	53.154	284.969	254.986	23.986	142.907	198.037	−12.931
900	54.208	291.292	258.674	29.356	143.169	204.913	−11.893
1000	55.024	297.048	262.228	34.819	143.439	211.759	−11.061
1100	55.660	302.323	265.637	40.355	143.711	218.578	−10.379
1200	56.174	307.189	268.899	45.947	143.980	225.372	−9.810
1300	56.593	311.702	272.020	51.586	144.245	232.144	−9.328
1400	56.948	315.909	275.007	57.264	144.502	238.896	−8.913
1500	57.245	319.849	277.866	62.974	144.750	245.629	−8.554
1600	57.501	323.551	280.607	68.711	144.987	252.347	−8.238
1700	57.722	327.044	283.237	74.473	145.211	259.050	−7.960
1800	57.919	330.349	285.763	80.255	145.419	265.740	−7.712
1900	58.095	333.485	288.193	86.056	145.611	272.419	−7.489
2000	58.250	336.469	290.533	91.873	145.784	279.089	−7.289
2100	58.396	339.315	292.789	97.705	145.938	285.750	−7.108
2200	58.526	342.035	294.966	103.552	146.072	292.406	−6.943
2300	58.647	344.639	297.069	109.410	146.185	299.054	−6.792
2400	58.764	347.137	299.104	115.281	146.276	305.698	−6.653
2500	58.869	349.538	301.073	121.163	146.346	312.339	−6.526
2600	58.969	351.849	302.982	127.055	146.393	318.978	−6.408
2700	59.066	354.077	304.833	132.956	146.419	325.616	−6.299
2800	59.158	356.226	306.631	138.868	146.424	332.253	−6.198
2900	59.245	358.304	308.377	144.788	146.408	338.889	−6.104
3000	59.329	360.314	310.075	150.716	146.371	345.527	−6.016
3100	59.409	362.260	311.727	156.653	146.314	352.167	−5.934
3200	59.488	364.148	313.336	162.598	146.238	358.808	−5.857
3300	59.563	365.980	314.904	168.551	146.144	365.451	−5.785
3400	59.639	367.759	316.432	174.511	146.033	372.100	−5.717
3500	59.714	369.489	317.923	180.479	145.905	378.750	−5.653
3600	59.781	371.172	319.379	186.453	145.761	385.405	−5.592
3700	59.852	372.811	320.801	192.435	145.601	392.063	−5.535
3800	59.919	374.408	322.191	198.424	145.427	398.728	−5.481
3900	59.986	375.965	323.550	204.419	145.239	405.396	−5.430
4000	60.053	377.485	324.879	210.421	145.038	412.069	−5.381
4100	60.120	378.968	326.181	216.429	144.823	418.747	−5.335
4200	60.183	380.418	327.455	222.445	144.597	425.431	−5.291
4300	60.245	381.835	328.703	228.466	144.358	432.121	−5.249
4400	60.308	383.220	329.926	234.494	144.106	438.815	−5.209
4500	60.371	384.576	331.126	240.528	143.844	445.516	−5.171
4600	60.434	385.904	332.302	246.568	143.568	452.222	−5.135
4700	60.492	387.204	333.457	252.614	143.281	458.935	−5.100
4800	60.555	388.479	334.590	258.667	142.981	465.655	−5.067
4900	60.614	389.728	335.702	264.725	142.667	472.381	−5.036
5000	60.672	390.953	336.795	270.789	142.340	479.113	−5.005
5100	60.731	392.155	337.869	276.859	141.999	485.853	−4.976
5200	60.789	393.335	338.924	282.935	141.643	492.597	−4.948
5300	60.848	394.493	339.962	289.017	141.270	499.351	−4.921
5400	60.906	395.631	340.982	295.105	140.880	506.110	−4.896
5500	60.965	396.749	341.986	301.199	140.472	512.876	−4.871
5600	61.024	397.848	342.974	307.298	140.045	519.653	−4.847
5700	61.078	398.929	343.946	313.403	139.596	526.434	−4.824
5800	61.137	399.992	344.903	319.514	139.126	533.226	−4.802
5900	61.191	401.037	345.846	325.630	138.631	540.023	−4.781
6000	61.250	402.066	346.774	331.752	138.111	546.832	−4.761

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

Lead Silicate ($PbSiO_3$) CRYSTAL $M_r = 283.2837$ Lead Silicate ($PbSiO_3$) $O_3Pb_1Si_1(cr)$

$S°(298.15\ K) = 109.927 \pm 1.3\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$T_{fus} = 1037\ K$

$\Delta_fH°(0\ K) = -1138.091 \pm 4.2\ kJ{\cdot}mol^{-1}$

$\Delta_fH°(298.15\ K) = -1144.993 \pm 4.2\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The enthalpy of the reaction $PbO(red) + SiO_2(cr) \rightarrow PbSiO_3(cr)$ was reported by Kelley.[1] This value for the enthalpy of reaction of the oxides has been converted to the enthalpy of formation using JANAF auxiliary data.[4] The above $\Delta_fH°(298.15\ K) = 3.75 \pm 0.12\ kcal{\cdot}mol^{-1}$.

Heat Capacity and Entropy

In the low temperature region (53.25–298.15 K) the $C_p°$ values are those determined by King.[2] 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 $D(140/T) + E(213/T) + 2E(596/T) + E(1440/T)$ given by King.[2] $S°(53.25\ K) = 3.662\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

Fusion Data

T_{fus} was taken from Geller *et al.*[3]

References

[1] K. K. Kelley, U. S. Bur. Mines RI 5901, (1962).
[2] E. G. King, J. Amer. Chem. Soc. **81**, 799–800 (1959).
[3] Geller, Creamer and Bunting, J. Res. Nat. Bur. Stand. **13**, 237 (1934).
[4] JANAF Thermochemical Tables: PbO(cr, red), 3-31-62; SiO_2(cr), 12-31-62.

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.000	0.000	INFINITE	−16.219	−1138.091	−1138.091	INFINITE
100	44.683	37.168	177.245	−14.008	−1142.269	−1115.924	582.899
200	72.562	77.500	117.638	−8.028	−1144.359	−1088.626	284.320
298.15	90.040	109.927	109.927	0.000	−1144.993	−1061.094	185.899
300	90.333	110.485	109.929	0.167	−1144.995	−1060.574	184.662
400	102.843	138.266	113.631	9.854	−1144.615	−1032.467	134.826
500	111.964	162.238	121.011	20.614	−1143.535	−1004.544	104.944
600	118.742	183.282	129.672	32.166	−1141.987	−976.885	85.045
700	123.428	201.958	138.690	44.288	−1145.017	−948.711	70.794
800	126.566	218.655	147.661	56.795	−1143.041	−920.801	60.122
900	128.784	233.697	156.399	69.568	−1140.924	−893.146	51.837
1000	130.332	247.349	164.822	82.527	−1138.724	−865.733	45.221
1100	131.545	259.829	172.900	95.622	−1136.473	−838.542	39.819
1200	132.591	271.321	180.629	108.831	−1134.180	−811.559	35.326
1300	133.428	281.967	188.020	122.132	−1131.864	−784.767	31.532
1400	134.223	291.884	195.089	135.514	−1129.547	−758.154	28.287
1500	135.018	301.173	201.854	148.978	−1127.234	−731.708	25.480
1600	135.645	309.907	208.338	162.512	−1124.940	−705.414	23.029
1700	136.189	318.147	214.557	176.103	−1172.856	−678.816	20.857
1800	136.775	325.949	220.530	189.753	−1170.401	−649.826	18.857
1900	137.152	333.354	226.275	203.450	−1167.953	−620.972	17.072
2000	137.444	340.397	231.807	217.180	−1165.526	−592.246	15.468

PREVIOUS: CURRENT: June 1965

Lead Silicate ($PbSiO_3$) $O_3Pb_1Si_1(cr)$

Sulfur Trioxide (SO_3) IDEAL GAS $M_r = 80.0582$ Sulfur Trioxide (SO_3) $O_3S_1(g)$

$S°(298.15\ K) = 256.769\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -390.025 \pm 0.71\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -395.765 \pm 0.71\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1068 (1)
495 (1)
1391 (2)
529 (2)

Ground State Quantum Weight: 1 $\sigma = 6$
Point Group: D_{3h}
Bond Distance: S–O = 1.43 Å
Bond Angle: O–S–O = 120°
Product of the Moments of Inertia: $I_AI_BI_C = 1.0824273 \times 10^{-114}\ g^3{\cdot}cm^6$

Enthalpy of Formation

The enthalpy of formation is 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 2nd and 3rd law treatment of the data is given below.

Source	T/K	Data Points	$\Delta_fH°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-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
*	801–1170 K	23*	−23.40 ± 0.2	−23.638	−0.9 ± 0.2

*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 reference 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 are taken from the electron diffraction data of Palmer.[4] The vibrational frequencies are taken from the infrared studies of Lovejoy *et al.*[5] which are in excellent accord with those of Bent and Ladner[6] using different techniques. These values differ from the assignment used by Stockmayer *et al.*[7] in their analysis of the thermodynamic properties of SO_3.

The principal moments of inertia are: $I_A = I_B = 8.1493 \times 10^{-39}$ and $I_C = 16.2987 \times 10^{-39}\ g{\cdot}cm^2$.

References

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[3] A. F. Kapustinsky and L. M. Shamovsky, Acta Physicochem. USSR 4, 791 (1936).
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[6] R. Bent and W. R. Ladner, Spectrochim. Acta 19, 931 (1963).
[7] W. H. Stockmayer, G. M. Kavanagh and H. S. Mickley, J. Chem. Phys. **12**, 408 (1944).

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

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_fH°$ (kJ·mol^{-1})	$\Delta_fG°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−11.697	−390.025	−390.025	INFINITE
100	34.076	212.371	295.976	−8.361	−391.735	−385.724	201.481
200	42.336	238.259	261.145	−4.577	−393.960	−378.839	98.943
250	46.784	248.192	257.582	−2.348	−394.937	−374.943	78.340
298.15	50.661	256.769	256.769	0.	−395.765	−371.016	65.000
300	50.802	257.083	256.770	0.094	−395.794	−370.862	64.573
350	54.423	265.191	257.402	2.726	−396.543	−366.646	54.719
400	57.672	272.674	258.849	5.530	−399.412	−362.242	47.304
450	60.559	279.637	260.777	8.487	−400.656	−357.529	41.501
500	63.100	286.152	262.992	11.580	−401.878	−352.668	36.843
600	67.255	298.041	267.862	18.107	−403.675	−342.647	29.830
700	70.390	308.655	272.945	24.997	−405.014	−332.365	24.801
800	72.761	318.217	278.017	32.160	−406.068	−321.912	21.019
900	74.570	326.896	282.973	39.531	−460.062	−310.258	18.007
1000	75.968	334.828	287.768	47.060	−459.581	−293.639	15.338
1100	77.065	342.122	292.382	54.714	−459.063	−277.069	13.157
1200	77.937	348.866	296.811	62.466	−458.521	−260.548	11.341
1300	78.639	355.133	301.060	70.296	−457.968	−244.073	9.807
1400	79.212	360.983	305.133	78.189	−457.413	−227.640	8.493
1500	79.685	366.465	309.041	86.135	−456.863	−211.247	7.356
1600	80.079	371.620	312.793	94.124	−456.323	−194.890	6.363
1700	80.410	376.485	316.398	102.149	−455.798	−178.567	5.487
1800	80.692	381.090	319.865	110.204	−455.293	−162.274	4.709
1900	80.932	385.459	323.203	118.286	−454.810	−146.009	4.014
2000	81.140	389.616	326.421	126.390	−454.351	−129.768	3.389
2100	81.319	393.579	329.525	134.513	−453.919	−113.549	2.824
2200	81.476	397.366	332.523	142.653	−453.514	−97.350	2.311
2300	81.614	400.990	335.422	150.807	−453.137	−81.170	1.843
2400	81.735	404.466	338.227	158.975	−452.790	−65.006	1.415
2500	81.843	407.805	340.944	167.154	−452.472	−48.855	1.021
2600	81.939	411.017	343.578	175.343	−452.183	−32.716	0.657
2700	82.025	414.111	346.133	183.541	−451.922	−16.587	0.321
2800	82.102	417.096	348.614	191.748	−451.690	−0.467	0.009
2900	82.171	419.978	351.026	199.961	−451.487	15.643	−0.282
3000	82.234	422.765	353.571	208.182	−451.311	31.748	−0.553
3100	82.290	425.462	355.653	216.408	−451.161	47.849	−0.806
3200	82.342	428.076	357.876	224.640	−451.038	63.943	−1.044
3300	82.389	430.610	360.042	232.876	−450.940	80.034	−1.267
3400	82.432	433.070	362.153	241.117	−450.866	96.124	−1.477
3500	82.472	435.460	364.214	249.363	−450.817	112.210	−1.675
3600	82.508	437.784	366.225	257.612	−450.792	128.297	−1.862
3700	82.542	440.045	368.190	265.864	−450.789	144.382	−2.038
3800	82.573	442.247	370.110	274.120	−450.809	160.469	−2.206
3900	82.601	444.392	371.987	282.379	−450.850	176.556	−2.365
4000	82.628	446.484	373.824	290.640	−450.914	192.643	−2.516
4100	82.653	448.524	375.621	298.904	−450.999	208.733	−2.659
4200	82.676	450.516	377.381	307.171	−451.105	224.825	−2.796
4300	82.697	452.462	379.104	315.439	−451.234	240.921	−2.927
4400	82.717	454.364	380.793	323.710	−451.383	257.019	−3.051
4500	82.735	456.223	382.449	331.983	−451.555	273.120	−3.170
4600	82.753	458.041	384.072	340.257	−451.749	289.225	−3.284
4700	82.769	459.821	385.665	348.533	−451.965	305.336	−3.393
4800	82.785	461.564	387.228	356.811	−452.205	321.452	−3.498
4900	82.799	463.271	388.763	365.090	−452.469	337.573	−3.599
5000	82.813	464.944	390.270	373.371	−452.757	353.700	−3.695
5100	82.825	466.584	391.750	381.653	−453.071	369.832	−3.788
5200	82.837	468.192	393.205	389.936	−453.412	385.969	−3.877
5300	82.849	469.770	394.634	398.220	−453.780	402.116	−3.963
5400	82.860	471.319	396.040	406.505	−454.178	418.268	−4.046
5500	82.870	472.840	397.423	414.792	−454.605	434.427	−4.126
5600	82.879	474.333	398.783	423.079	−455.065	450.597	−4.203
5700	82.889	475.800	400.121	431.368	−455.557	466.773	−4.277
5800	82.897	477.242	401.439	439.657	−456.084	482.960	−4.350
5900	82.906	478.659	402.735	447.947	−456.647	499.153	−4.419
6000	82.913	480.052	404.012	456.238	−457.248	515.359	−4.487

PREVIOUS September 1965 (1 atm) CURRENT. September 1965 (1 bar)

Titanium Oxide (Ti_2O_3) CRYSTAL M_r = 143.7582 Titanium Oxide (Ti_2O_3) $O_3Ti_2(cr)$

$S°(298.15\ K) = 77.253 \pm 0.21\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs} = 470 \pm 20\ K$
$T_{fus} = 2115 \pm 10\ K$

$\Delta_fH°(0\ K) = -1512.287 \pm 8.4\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -1520.884 \pm 8.4\ kJ{\cdot}mol^{-1}$
$\Delta_{trs}H° = 1.138\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = [105]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

Humphrey[1] measured $\Delta_rH°(298.15\ K) = -88.11 \pm 0.1\ kcal{\cdot}mol^{-1}$ for the reaction $Ti_2O_3(cr) + 0.5\ O_2(g) = 2\ TiO_2$(rutile) using bomb calorimetry. When combined with $\Delta_fH°(298.15\ K) = -225.8\ kcal{\cdot}mol^{-1}$ for rutile, this yields $-363.5 \pm 2\ kcal{\cdot}mol^{-1}$ as the adopted $\Delta_fH°(298.15\ K)$ for Ti_2O_3. The less negative value of $-362.8 \pm 0.8\ kcal{\cdot}mol^{-1}$ was obtained by Ariya *et al.*[2] from their heats of combustion of various compositions in the Ti–O system. Ariya *et al.*[2] used an estimated correction for the formation of TiO_{2-x}, while Humphrey[1] obtained values of 0.1 to 1.3 $kcal{\cdot}mol^{-1}$ by grinding the product and reburning it with while oil. Most of the assigned uncertainty arises from this problem [see TiO_2(rutile) for further details].

Heat Capacity and Entropy

$C_p°$ is based on data of Sjostrand and Keesom, (0.4–20 K)[3] and Paukov and Berezovskii, (12–305 K).[4] The two sets of data disagree in the region of overlap. Paukov[4] appears to have a positive bias at the lowest temperatures (12–18 K), so we adopt a curve which shifts gradually from Sjostrand at 10 K to Paukov at 30 K. Deviations of Paukov[4] from the adopted $C_p°$ are +36% (12 K) and +3% (20 K). Earlier data of Shomate, (53–296 K)[5] deviate by +0.6% to +4.1% with extreme deviations of 3.0% at 53 K and 2.9 to 4.1% in a "hump" observed by Shomate near 240 K. No hump was found by Paukov. $S°$ is derived from $C_p°$ based on an extrapolation which is negligible.

$C_p°$ between 298 K and 470 K is a smooth extrapolation of the low temperature curve using the approximate shape found by Barros *et al.*,[6] (150–700 K) via differential scanning calorimetry (Perkin–Elmer DSC–1B). The DSC data[6] have a positive bias of ~10%, over twice as large as we might expect for this apparatus so the results do not help establish $C_p°$ between 298 K and T_{trs}. Data measured by a conduction type calorimeter, (323–523 K)[7] have a large negative bias near 400 K. Drop-calorimetric data, (375–472 K)[8] deviate from the adopted enthalpies by +5 to +2%.

$C_p°$ above the λ-transition is derived from enthalpy data, (487–1750 K)[8] by fitting only the region above 549 K. Maximum deviations from the adopted cruve are ±0.4% in the fitted region and +0.9% at 526 K. Enthalpy data (493–1082 K) reported graphically by Erofeeva *et al.*[9] deviate by about −6 to −2%.

Slyusar *et al.*[15] recently reported new enthalpy data for Ti_2O_3, Ti_3O_5, Ti_4O_7 and TiO_2. The new data for Ti_3O_5 and $TiO_2$are in reasonable agreement with existing JANAF Tables,[16] but those for Ti_2O_3 cross the adopted values near 1100 K and deviate by −4.5 ± 1% (672–878 K) and +3.4 ± 1.1% (1158–2027 K). The transition vanishes for Ti_2O_3 samples doped with 4% V_2O_3[6] and may be affected by other impurities or non stoichiometry. We feel that Slyusar *et al.*[15] have not characterized their sample adequately. We tentatively reject their data pending new measurements on a well characterized sample.

Transition Data

We arbitrarily choose $T_{trs} = 470 \pm 20$ K and derive $\Delta_{trs}H°$ as the difference between the adopted enthalpy curves at that temperature. Reported values of $\Delta_{trs}H°$ include 0.380 ± 0.025[6], 0.036[7] and 0.215 $kcal{\cdot}mol^{-1}$;[8] each derives from different data and difference base lines.

Convenience dictates that we treat the electrical transition as first order although recent $C_p°$ data[6] suggest a gradual λ-type anomaly peaking near 470 K and extending from about 380 to 560 K. There is no change in the corundum type symmetry, but the lattice parameters shift rapidly in this temperature range.[10, 11] Honig[11] summarized evidence on the nature of the change from semiconductor to semimetal and noted that the transition can be explained without invoking antiferromagnetic ordering. Recent studies[6, 12, 14] are consistent with this interpretation.

Fusion Data

Refer to the liquid table for details.

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[16] JANAF Thermochemical Tables, 2nd ed., NSRDS-NBS-37, 1971: Ti_3O_5(cr, α, β), 3–31–67; TiO_2(cr, rutile), 3–31–67.

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.000	0.000	INFINITE	−14.088	−1512.287	−1512.287	INFINITE
100	26.175	11.058	143.900	−13.284	−1516.961	−1490.419	778.515
200	70.793	43.832	85.316	−8.297	−1520.175	−1462.405	381.941
298.15	95.814	77.253	77.253	0.000	−1520.884	−1433.829	251.201
300	96.190	77.847	77.255	0.178	−1520.881	−1433.288	249.558
400	117.529	108.277	81.264	10.805	−1519.938	−1404.187	183.368
470.010	141.716	128.963	86.822	19.807	ALPHA <--> BETA TRANSITION		
470.010	127.653	131.384	86.822	20.945			
500	130.248	139.362	89.735	24.813	−1515.999	−1375.626	143.711
600	136.440	163.704	100.081	38.174	−1513.028	−1347.825	117.339
700	140.331	185.051	110.727	52.027	−1509.833	−1320.542	98.540
800	142.967	203.971	121.223	66.199	−1506.516	−1293.726	84.472
900	144.892	220.928	131.375	80.597	−1503.208	−1267.327	73.554
1000	146.356	236.272	141.110	95.162	−1500.078	−1241.288	64.838
1100	147.528	250.277	150.407	109.858	−1497.276	−1215.547	57.722
1200	148.532	263.158	159.273	124.662	−1502.785	−1189.806	51.791
1300	149.369	275.081	167.729	139.558	−1499.224	−1163.870	46.765
1400	150.080	286.177	175.798	154.531	−1495.789	−1138.203	42.467
1500	150.750	296.554	183.506	169.573	−1492.509	−1112.777	38.750
1600	151.377	306.304	190.879	184.680	−1489.413	−1087.564	35.505
1700	151.921	315.497	197.942	199.845	−1486.531	−1062.538	32.648
1800	152.465	324.197	204.716	215.065	−1483.892	−1037.675	30.113
1900	152.925	332.452	211.224	230.334	−1481.528	−1012.950	27.848
2000	153.427	340.309	217.483	245.652	−1508.838	−987.436	25.789
2100	153.888	347.806	223.512	261.018	−1508.597	−961.372	23.913
2115.000	153.953	348.902	224.398	263.327	---- BETA <--> LIQUID ----		
2200	154.306	354.975	229.326	276.427	−1508.348	−935.318	22.207
2300	154.766	361.844	234.939	291.881	−1508.087	−909.278	20.650
2400	155.185	368.440	240.365	307.379	−1507.817	−883.249	19.223
2500	155.603	374.783	245.616	322.919	−1507.537	−857.231	17.911
2600	155.980	380.894	250.702	338.497	−1507.250	−831.224	16.700
2700	156.398	386.788	255.634	354.117	−1506.954	−805.229	15.578
2800	156.774	392.483	260.420	369.775	−1506.649	−779.244	14.537
2900	157.151	397.991	265.070	385.471	−1506.337	−753.272	13.568
3000	157.569	403.325	269.590	401.207	−1506.015	−727.309	12.664

PREVIOUS: June 1967 CURRENT: June 1973

Titanium Oxide (Ti_2O_3) LIQUID $M_r = 143.7582$ Titanium Oxide (Ti_2O_3) $O_3Ti_2(l)$

$S°(298.15\ K) = [127.126]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2115 \pm 10\ K$

$\Delta_fH°(298.15\ K) = [-1418.459]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [105]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(Ti_2O_3, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2115\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is estimated as 7.5 $cal·K^{-1}$ g atom.[1] Below the assumed glass transition at 1400 K, $C_p°$ is taken from the crystal, the high temperature curve is extrapolated down to 298.15 K. $S°(298.15\ K)$ is calculated in a manner analogous to that used for $\Delta_fH°(298.15\ K)$.

Fusion Data

T_{fus} is the value quoted by Wahlbeck and Gilles[1] based on work of K. D. Carlson. The adopted value is converted to IPTS–68. $\Delta_{fus}H°$ is estimated such that $\Delta_{fus}S°$ is 12 $cal·K^{-1}·mol^{-1}$ as observed[2] for Al_2O_3(α, *corundum*). Other reported melting points were summarized earlier.[3] Slyusar *et al.*[4] recently obtained $T_{fus} = 2043$ K in an enthalpy study, but we tentatively reject this work (see Ti_2O_3, crystal).

References

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

	$J·K^{-1}mol^{-1}$				$kJ·mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	94.851	127.126	127.126	0.000	−1418.459	−1346.273	235.861
300	95.521	127.714	127.127	0.176	−1418.458	−1345.825	234.329
400	119.118	158.902	131.219	11.073	−1417.245	−1321.744	172.602
500	130.248	186.808	139.609	23.600	−1414.787	−1298.137	135.615
600	136.440	211.151	149.550	36.961	−1411.816	−1275.081	111.006
700	140.331	232.498	159.907	50.814	−1408.621	−1252.543	93.466
800	142.967	251.418	170.186	64.986	−1405.305	−1230.471	80.342
900	144.892	268.374	180.170	79.384	−1401.996	−1208.817	70.158
1000	146.356	283.719	189.770	93.949	−1398.867	−1187.523	62.030
1100	147.528	297.724	198.956	108.644	−1396.065	−1166.527	55.394
1200	148.532	310.605	207.731	123.449	−1401.573	−1145.531	49.864
1300	149.369	322.528	216.109	138.345	−1398.013	−1124.339	45.177
1400	150.080	333.624	224.111	153.318	−1394.577	−1103.417	41.169
1400.000	150.080	333.624	224.111	153.318	______ GLASS <−−> LIQUID ______		
1400.000	156.900	333.624	224.111	153.318	TRANSITION		
1500	156.900	344.449	231.777	169.008	−1390.649	−1082.759	37.705
1600	156.900	354.575	239.139	184.698	−1386.969	−1062.354	34.682
1700	156.900	364.087	246.212	200.388	−1383.562	−1042.171	32.022
1800	156.900	373.055	253.012	216.078	−1380.453	−1022.181	29.663
1900	156.900	381.538	259.555	231.768	−1377.668	−1002.355	27.557
2000	156.900	389.586	265.857	247.458	−1404.606	−981.758	25 641
2100	156.900	397.241	271.933	263.148	−1404.042	−960.630	23.894
2115.000	156.900	398.358	272.825	265.502	−−−− BETA <−−> LIQUID −−−−		
2200	156.900	404.540	277.796	278.838	−1403.512	−939.527	22.307
2300	156.900	411.515	283.459	294.528	−1403.015	−918.449	20.859
2400	156.900	418.192	288.935	310.218	−1402.552	−897.391	19.531
2500	156.900	424.597	294.234	325.908	−1402.122	−876.351	18.310
2600	156.900	430.751	299.367	341.598	−1401.724	−855.329	17.184
2700	156.900	436.673	304.344	357.288	−1401.357	−834.320	16.141
2800	156.900	442.379	309.172	372.978	−1401.021	−813.324	15.173
2900	156.900	447.885	313.861	388.668	−1400.715	−792.342	14.272
3000	156.900	453.204	318.418	404.358	−1400.438	−771.368	13.431
3100	156.900	458.348	322.849	420.048	−1400.189	−750.402	12.644
3200	156.900	463.330	327.162	435.738	−1399.967	−729.446	11.907
3300	156.900	468.158	331.361	451.428	−1399.771	−708.496	11.215
3400	156.900	472.842	335.454	467.118	−1399.600	−687.550	10.563
3500	156.900	477.390	339.445	482.808	−1399.454	−666.610	9.949

PREVIOUS: June 1967 — CURRENT: June 1973

Titanium Oxide (Ti_2O_3) CRYSTAL(α–β)–LIQUID

0 to 470 K crystal, α
470 to 2115 K crystal, β
above 2115 K liquid

Refer to the individual tables for details.

M_r = 143.7582 Titanium Oxide (Ti_2O_3) $O_3Ti_2(cr,l)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
0	0.000	0.000	INFINITE	−14.088	−1512.287	−1512.287	INFINITE
100	26.175	11.058	143.900	−13.284	−1516.961	−1490.419	778.515
200	70.793	43.832	85.316	−8.297	−1520.175	−1462.405	381.941
298.15	95.814	77.253	77.253	0.000	−1520.884	−1433.829	251.201
300	96.190	77.847	77.255	0.178	−1520.881	−1433.288	249.558
400	117.529	108.277	81.264	10.805	−1519.938	−1404.187	183.368
470.010	141.716	128.963	86.822	19.807	ALPHA <--> BETA		
470.010	127.653	131.384	86.822	20.945	TRANSITION		
500	130.248	139.362	89.735	24.813	−1515.999	−1375.626	143.711
600	136.440	163.704	100.081	38.174	−1513.028	−1347.825	117.339
700	140.331	185.051	110.727	52.027	−1509.833	−1320.542	98.540
800	142.967	203.971	121.223	66.199	−1506.516	−1293.726	84.472
900	144.892	220.928	131.375	80.597	−1503.208	−1267.327	73.554
1000	146.356	236.272	141.110	95.162	−1500.078	−1241.288	64.838
1100	147.528	250.277	150.407	109.858	−1497.276	−1215.547	57.722
1200	148.532	263.158	159.273	124.662	−1502.785	−1189.806	51.791
1300	149.369	275.081	167.729	139.558	−1499.224	−1163.870	46.765
1400	150.080	286.177	175.798	154.531	−1495.789	−1138.203	42.467
1500	150.750	296.554	183.506	169.573	−1492.509	−1112.777	38.750
1600	151.377	306.304	190.879	184.680	−1489.413	−1087.564	35.505
1700	151.921	315.497	197.942	199.845	−1486.531	−1062.538	32.648
1800	152.465	324.197	204.716	215.065	−1483.892	−1037.675	30.113
1900	152.925	332.452	211.224	230.334	−1481.528	−1012.950	27.848
2000	153.427	340.309	217.483	245.652	−1508.838	−987.436	25.789
2100	153.888	347.806	223.512	261.018	−1508.597	−961.372	23.913
2115.000	153.953	348.902	224.398	263.327	BETA <--> LIQUID		
2115.000	156.900	398.358	224.398	367.927	TRANSITION		
2200	156.900	404.540	231.239	381.263	−1403.512	−939.527	22.307
2300	156.900	411.515	238.927	396.953	−1403.015	−918.449	20.859
2400	156.900	418.192	246.258	412.643	−1402.552	−897.391	19.531
2500	156.900	424.597	253.264	428.333	−1402.122	−876.351	18.310
2600	156.900	430.751	259.973	444.023	−1401.724	−855.329	17.184
2700	156.900	436.673	266.408	459.713	−1401.357	−834.320	16.141
2800	156.900	442.379	272.592	475.403	−1401.021	−813.324	15.173
2900	156.900	447.885	278.542	491.093	−1400.715	−792.342	14.272
3000	156.900	453.204	284.276	506.783	−1400.438	−771.368	13.431
3100	156.900	458.348	289.809	522.473	−1400.189	−750.402	12.644
3200	156.900	463.330	295.154	538.163	−1399.967	−729.446	11.907
3300	156.900	468.158	300.324	553.853	−1399.771	−708.496	11.215
3400	156.900	472.842	305.329	569.543	−1399.600	−687.550	10.563
3500	156.900	477.390	310.180	585.233	−1399.454	−666.610	9.949

PREVIOUS: CURRENT: June 1973

Vanadium Oxide (V_2O_3) CRYSTAL M_r = 149.8812 Vanadium Oxide (V_2O_3) $O_3V_2(cr)$

$\Delta_fH°(0\ K) = -1213.971 \pm 6.3\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = 98.067 \pm 1.3\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -1218.799 \pm 6.3\ kJ\cdot mol^{-1}$

$T_{trs} = 168.8 \pm 0.2\ K$ $\Delta_{trs}H° = 1.623\ kJ\cdot mol^{-1}$

$T_{fus} = 2340 \pm 20\ K$ $\Delta_{fus}H° = [117.152]\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpies of formation for the vanadium oxides, and in particular V_2O_3(cr), are based on the combustion studies by Mah and Kelley.[1] The adopted value is $\Delta_fH°(V_2O_3$, cr, 298.15 K$) = -291.3\ kcal\cdot mol^{-1}$ as reported by Mah and Kelley.[1] For more details refer to the V_2O_5(cr) table.[2] We assign an uncertainty limit of $\pm$ 1.5 $kcal\cdot mol^{-1}$.

Charlu and Kleppa[3] reported a enthalpy of formation value of $-$ 291.0 $\pm$ 0.9 $kcal\cdot mol^{-1}$ for V_2O_3 based on oxidation studies to V_2O_5(cr) in a high temperature microcalorimeter. An advantage of this technique is that complete oxidation to V_2O_5(cr) was achieved whereas in the study by Mah and Kelley[1] a mixture of the two oxides V_2O_4 and V_2O_5 was obtained. Other combustion studies have been reported by Siemonsen and Ulich[4] and Vol'f and Ariya.[5] Additional enthalpy of formation values may be obtained from the sodium peroxide fusion studies by Mixter[6] and Ruff and Friedrich[7] and the following equilibrium studies involving vanadium and its oxides. H_2O/H_2 by Kobayashi,[8] Muller,[9] and Karasev, Polyakov and Samarin;[10] and CO/CO_2 by Spencer and Justice.[11] As an example, the study by Spencer and Justice[11] leads to $\Delta_fH°(298.15\ K) = -287.9\ kcal\cdot mol^{-1}$ for V_2O_3(cr). The analysis, based on data in the range 1024–1169 K, indicates a third law drift of $-0.96 \pm 0.43\ cal\cdot K^{-1}\cdot mol^{-1}$.

Heat Capacity and Entropy

Anderson[12] measured the heat capacity of V_2O_3(cr) in the range 57–287 K. The data indicated an anomaly in the region 165–182 K. These heat capacity data are joined smoothly at 298 K with the high temperature heat capacity values as derived from the enthalpy measurements of Cook.[13] The adopted $C_p°$ values are based on these two studies.[12,13] Using the combination of Debye and Einstein functions as suggested by Anderson,[12] we calculate $S°(50\ K) = 0.783\ cal\cdot K^{-1}\cdot mol^{-1}$ and $H°(50;0) = 0.0284\ kcal\cdot mol^{-1}$. There is considerable scatter in the data of Cook;[13] the deviations from the adopted values range from -0.8 to 0.6% except for the data point at 369.1 K which is -1.4% low (~25 $cal\cdot K^{-1}\cdot mol^{-1}$).

Khlyustov *et al.*[14] measured the heat capacity of V_2O_3 in the region 120–190 K. For $T < T_{trs}$, this latter study lies above the Anderson data by ~7% while for $T > T_{trs}$, it is 10% higher. Three other studies examined the heat capacity in the range 343–573 K.[15,16,17] These latter three studies indicated irregularities in the $C_p°$ values in the region of investigation. We do not adopt these works, pending further independent verification.

Phase Data

A review of the literature of the V–O system by Stringer[18] stated that V_2O_3 has a homogeneity range of roughly $VO_{1.44}$ to $VO_{1.65}$. On cooling V_2O_3(cr) through T_{trs}, the crystal undergoes a structural distortion from hexagonal corundum to monoclinic. Numerous references as to the homogeneity range and crystal structure are contained, for example, in the reviews by Stringer[18] and Adler[19] as well as in the x–ray study by Minomura and Nagasaki.[20]

Transition Data

The heat capacity data of Anderson[12] indicated an anomaly at 168.8 K. The anomaly appeared similar to a λ-type transition and a smooth curve is easily drawn joining the heat capacity data on either side of the transition. Anderson[12] made five measurements to determine the energy necessary to heat V_2O_3(cr) through the transition. The mean enthalpy of the five measurements from 161.3 to 180.0 K was reported as 692.2 $\pm$ 2.4 $cal\cdot K^{-1}\cdot mol^{-1}$. Subtracting the calculated base heat in this same region, we calculate $\Delta_{trs}H° = 0.388\ kcal\cdot mol^{-1}$. We adopt $T_{trs} = 168.8$ K and $\Delta_{trs}H° = 0.388\ kcal\cdot mol^{-1}$, and consider it to be first order.

Khlyustov *et al.*[14] reported heat capacity data in the region 123–184 K and reported a transition which resembled a type with a maximum at 165.66 K with $\Delta_{trs}H° = 0.356\ kcal\cdot mol^{-1}$. Although both heat capacity studies[12,14] appeared to indicate a second order transition, Minomura and Nagasaki[20] determined through x–ray measurements that V_2O_3(cr) undergoes a discontinuous volume contraction (~3%) at T_{trs}, indicative of a first order transition. Austin[21] and Feinlieb and Paul[22] studied the pressure dependence of T_{trs} and reported $(dT_{trs}/dP)_{trs}$ values. Using the Clausius Clapeyron equation for a first order transition with $\Delta_{trs}V$ from Minomura and Nagasaki,[20] we calculate $\Delta_{trs}H° = 0.863$ and 1.020 $kcal\cdot mol^{-1}$, respectively. The calorimetric value for $\Delta_{trs}H°$ is more reliable than these latter two determinations. For further information on this transition, the review by Adler[19] is suggested. There are indications of possible transitional behavior above room temperature.[15,16,17,19] We adopt only regular behavior above 298.15 K.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The experimental evidence indicated that, although V_2O_3(cr) sublimes congruently, the vapors do not contain V_2O_3(g).[23]

Continued on page 1815

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

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.000	0.000	INFINITE	−17.476	−1213.971	−1213.971	INFINITE
100	28.627	14.163	179.288	−16.512	−1218.342	−1192.325	622.807
168.800	63.053	38.652	116.725	−13.179		I <−−> II	
168.800	63.136	48.269	116.725	−11.555		TRANSITION	
200	80.107	60.767	107.019	−9.250	−1219.118	−1165.403	304.372
298.15	104.963	98.067	98.067	0.000	−1218 799	−1139.036	199.554
300	105.260	98.717	98.069	0.194	−1218.779	−1138.542	198.238
400	117.540	130.898	102.373	11.410	−1217.149	−1112.018	145.215
500	123.750	157.887	110.854	23.516	−1214.951	−1085.983	113.452
600	127.326	180.791	120.651	36.084	−1212.566	−1060.412	92.317
700	130.071	200.631	130.691	48.958	−1210.125	−1035.245	77.251
800	132.639	218.168	140.550	62.094	−1207.662	−1010.430	65.974
900	135.246	233.940	150.065	75.488	−1205.180	−985.925	57.222
1000	137.957	248.329	159.182	89.147	−1202.658	−961.698	50.234
1100	140.786	261.609	167.897	103.083	−1200.079	−937.726	44.529
1200	143.718	273.984	176.228	117.307	−1197.445	−913.992	39.785
1300	146.741	285.607	184.199	131.830	−1194.750	−890.480	35.780
1400	149.841	296.594	191.839	146.658	−1191.997	−867.177	32.355
1500	153.005	307.040	199.173	161.800	−1189.178	−844.074	29.393
1600	156.221	317.017	206.229	177.261	−1186.283	−821.161	26.808
1700	159.481	326.585	213.029	193.045	−1183.324	−798.431	24.533
1800	162.782	335.794	219.595	209.158	−1180.305	−775.877	22.515
1900	166.112	344.684	225.946	225.603	−1177.243	−753.492	20.715
2000	169.468	353.290	232.099	242.382	−1174.151	−731.269	19.099
2100	172.847	361.640	238.070	259.497	−1171.047	−709.202	17.640
2200	176.246	369.759	243.872	276.952	−1213.709	−687.072	16.313
2300	179.655	377.669	249.518	294.747	−1210.901	−663.196	15.062
2340.000	181.021	380.778	251.736	301.960	−−−−− II <−−> LIQUID −−−−−		
2400	183.086	385.388	255.019	312.884	−1207.784	−639.449	13.917
2500	186.526	392.931	260.386	331.364	−1204.357	−615.837	12.867
2600	189.978	400.314	265.626	350.189	−1200.617	−592.369	11.901
2700	193.437	407.549	270.749	369.360	−1196.563	−569.051	11.009
2800	196.907	414.646	275.762	388.877	−1192.193	−545.888	10.184

PREVIOUS: CURRENT: December 1973

Vanadium Oxide (V_2O_3) LIQUID M_r = 149.8812

$S°$(298.15 K) = [152.250] J·K^{-1}·mol^{-1}
T_{fus} = 2340 ± 20 K

$\delta_f H°$(298.15 K) = [−1093.054] kJ·mol^{-1}
$\Delta_{fus}H°$ = [117.152] kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H°$(V_2O_3, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°$(2340 K)–$H°$(298.15 K), between the crystal and the liquid.

Heat Capacity and Entropy

$C_p°$ for the liquid phase is estimated to be a constant 7.5 cal·K^{-1} g atom.[1] Below the assumed glass transition temperature at 1600 K, $C_p°$ is taken from the crystal. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} = 2340 ± 20 K is the value extracted from the V–O phase diagram proposed by Stringer.[1] This value is adopted and corrected to IPTS–68. $\Delta_{fus}H°$ is estimated such that $\Delta_{fus}S°$ is 12 cal·K^{-1}·mol^{-1} as observed[2] for Al_2O_3(α, corundum).

Vaporization Data

There is no evidence as to the existence of V_2O_3(g) and thus we do not report any heat of vaporization. See VO(g) and VO_2(g) tables for more information.[2]

References

[1] J. Stringer, J. Less Common Metals 8, 1 (1965).

[2] JANAF Thermochemical Tables: Al_2O_3(cr, α), 6–30–72; VO(g) and VO_2(g), 12–31–73.

Vanadium Oxide (V_2O_3) O_3V_2(l)

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0							
100							
200							
298.15	104.964	152.250	152.250	0.000	−1093.054	−1029.446	180.355
300	105.260	152.900	152.252	0.194	−1093.033	−1029.051	179.174
400	117.540	185.081	156.556	11.410	−1091.403	−1007.946	131.624
500	123.750	212.069	165.037	23.516	−1089.206	−987.329	103.146
600	127.326	234.974	174.833	36.084	−1086.821	−967.176	84.200
700	130.071	254.813	184.873	48.958	−1084.380	−947.427	70 698
800	132.639	272.350	194.733	62.094	−1081.917	−928.031	60.594
900	135.246	288.123	204.247	75.488	−1079.435	−908.944	52.754
1000	137.957	302.511	213.365	89.147	−1076.912	−890.135	46.496
1100	140.786	315.792	222.080	103.083	−1074.334	−871.582	41.388
1200	143.718	328.167	230.411	117.307	−1071.700	−853.265	37.142
1300	146.741	339.789	238.382	131.830	−1069.004	−835.172	33.558
1400	149.841	350.777	246.021	146.658	−1066.252	−817.287	30.493
1500	152.464	361.210	253.356	161.782	−1063.451	−799.602	27.845
1600	157.846	371.198	260.410	177.261	−1060.537	−782.105	25.533
1600.000	157.846	371.198	260.410	177.261	GLASS <−−> LIQUID TRANSITION		
1600.000	156.900	371.198	260.410	177.261			
1700	156.900	380.710	267.210	192.951	−1057.674	−764.793	23.499
1800	156.900	389.678	273.767	208.641	−1055.077	−747.641	21.696
1900	156.900	398.162	280.093	224.331	−1052.770	−730.625	20.086
2000	156.900	406.209	286.199	240.021	−1050.767	−713.723	18.641
2100	156.900	413.865	292.098	255.711	−1049.088	−696.914	17.335
2200	156.900	421.164	297.800	271.401	−1093.514	−679.966	16.144
2300	156.900	428.138	303.316	287.091	−1092.811	−661.185	15.016
2340.000	156.900	430.843	305.473	293.367	−−−−−− II <−−> LIQUID −−−−−		
2400	156.900	434.816	308.657	302.781	−1092.141	−642.434	13.982
2500	156.900	441.221	313.832	318.471	−1091.505	−623.709	13.032
2600	156.900	447.374	318.851	334.161	−1090.900	−605.009	12.155
2700	156.900	453.296	323.722	349.851	−1090.326	−586.332	11.343
2800	156.900	459.002	328.452	365.541	−1089 784	−567.675	10.590
2900	156.900	464.508	333.049	381.231	−1089.271	−549.038	9.889
3000	156.900	469.827	337.520	396.921	−1088.787	−530.417	9.235
3100	156.900	474.972	341.871	412.611	−1088.332	−511.812	8.624
3200	156.900	479.953	346.109	428.301	−1087.903	−493.223	8.051
3300	156.900	484.781	350.238	443.991	−1087.500	−474.646	7.513
3400	156.900	489.465	354.265	459.681	−1087.123	−456.079	7.007
3500	156.900	494.013	358.193	475.371	−1086.769	−437.525	6.530
3600	156.900	498.433	362.027	491.061	−1086.439	−418.979	6.079
3700	156.900	502.732	365.772	506.751	−1979.745	−398.042	5.619
3800	156.900	506.916	369.432	522.441	−1976.085	−355.342	4.885
3900	156.900	510.992	373.010	538.131	−1972.548	−312.736	4.189
4000	156.900	514.964	376.509	553.821	−1969.135	−270.222	3.529

PREVIOUS: CURRENT: December 1973

Vanadium Oxide (V_2O_3) O_3V_2(l)

Vanadium Oxide (V_2O_3) CRYSTAL(I–II)-LIQUID

0 to 168.8 K crystal, I
168.8 to 2340 K crystal, II
above 2340 K liquid

Refer to the individual tables for details.

M_r = 149.8812 Vanadium Oxide (V_2O_3) O_3V_2(cr,l)

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	S°	−[G°−H°(T_r)]/T	H°−H°(T_r)	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.000	0.000	INFINITE	−17.476	−1213.971	−1213.971	INFINITE
100	28.627	14.163	179.288	−16.512	−1218.342	−1192.325	622.807
168.800	63.053	38.652	116.725	−13.179	I <– –> II		
168.800	63.136	48.269	116.725	−11.555	TRANSITION		
200	80.107	60.767	107.019	−9.250	−1219.118	−1165.403	304.372
298.15	104.963	98.067	98.067	0.000	−1218.799	−1139.036	199.554
300	105.260	98.717	98.069	0.194	−1218.779	−1138.542	198.238
400	117.540	130.898	102.373	11.410	−1217.149	−1112.018	145.215
500	123.750	157.887	110.854	23.516	−1214.951	−1085.983	113.452
600	127.326	180.791	120.651	36.084	−1212.566	−1060.412	92.317
700	130.071	200.631	130.691	48.958	−1210.125	−1035.245	77.251
800	132.639	218.168	140.550	62.094	−1207.662	−1010.430	65.974
900	135.246	233.940	150.065	75.488	−1205.180	−985.925	57.222
1000	137.957	248.329	159.182	89.147	−1202.658	−961.698	50.234
1100	140.786	261.609	167.897	103.083	−1200.079	−937.726	44.529
1200	143.718	273.984	176.228	117.307	−1197.445	−913.992	39.785
1300	146.741	285.607	184.199	131.830	−1194.750	−890.480	35.780
1400	149.841	296.594	191.839	146.658	−1191.997	−867.177	32.355
1500	153.005	307.040	199.173	161.800	−1189.178	−844.074	29.393
1600	156.221	317.017	206.229	177.261	−1186.283	−821.161	26.808
1700	159.481	326.585	213.029	193.045	−1183.324	−798.431	24.533
1800	162.782	335.794	219.595	209.158	−1180.305	−775.877	22.515
1900	166.112	344.684	225.946	225.603	−1177.243	−753.492	20.715
2000	169.468	353.290	232.099	242.382	−1174.151	−731.269	19.099
2100	172.847	361.640	238.070	259.497	−1171.047	−709.202	17.640
2200	176.246	369.759	243.872	276.952	−1213.709	−687.072	16.313
2300	179.655	377.669	249.518	294.747	−1210.901	−663.196	15.062
2340.000	181.021	380.778	251.736	301.960	II <– –> LIQUID		
2340.000	156.900	430.843	251.736	419.112	TRANSITION		
2400	156.900	434.816	256.263	428.526	−1092.141	−642.434	13.982
2500	156.900	441.221	263.534	444.216	−1091.505	−623.709	13.032
2600	156.900	447.374	270.487	459.906	−1090.900	−605.009	12.155
2700	156.900	453.296	277.149	475.596	−1090.326	−586.332	11.343
2800	156.900	459.002	283.543	491.286	−1089.784	−567.675	10.590
2900	156.900	464.508	289.688	506.976	−1089.271	−549.038	9.889
3000	156.900	469.827	295.605	522.666	−1088.787	−530.418	9.235
3100	156.900	474.972	301.308	538.356	−1088.332	−511.812	8.624
3200	156.900	479.953	306.814	554.046	−1087.903	−493.223	8.051
3300	156.900	484.781	312.134	569.736	−1087.500	−474 646	7.513
3400	156.900	489.465	317.281	585.426	−1087.123	−456.079	7.007
3500	156.900	494.013	322.266	601.116	−1086.769	−437.525	6.530
3600	156.900	498.433	327.098	616.806	−1086.439	−418.979	6.079
3700	156.900	502.732	331.787	632.496	−1979 745	−398.042	5.619
3800	156.900	506.916	336.341	648.186	−1976.085	−355.342	4.885
3900	156.900	510.992	340.767	663.876	−1972.548	−312.736	4.189
4000	156.900	514.964	345.073	679.566	−1969.135	−270.222	3.529

PREVIOUS: CURRENT December 1973

Tungsten Oxide (WO_3) CRYSTAL $M_r = 231.8482$

$S°(298.15\ K) = 75.912 \pm 1.3\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs} = 1050\ K$
$T_{fus} = 1745\ K$

$\Delta_f H°(298.15\ K) = -842.909 \pm 0.8\ kJ{\cdot}mol^{-1}$
$\Delta_{trs} H° = 1.485\ kJ{\cdot}mol^{-1}$
$\Delta_{fus} H° = 73.429\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The selected enthalpy of formation, $\Delta_f H°(WO_3, cr, 298\ 15\ K) = -201.46 \pm 0.2\ kcal{\cdot}mol^{-1}$, was determined by Mah[1] using bomb calorimetry. Huff *et al.*[2] have reviewed the literature enthalpy of formation data and also measured calorimetrically the enthalpy of formation, $-201.84 \pm 0.1\ kcal{\cdot}mol^{-1}$, which is in good agreement with the value selected. Other combustion values were reported as $\Delta_f H°(298.15\ K) = -199 \pm 1\ kcal{\cdot}mol^{-1}$ by Griffis,[3] and $\Delta_f H°(298.15\ K) = -205.3\ kcal{\cdot}mol^{-1}$ by Vasil'eva *et al.*[4] Griffis[5] also derived the enthalpy of formation, $-202.8 \pm 1\ kcal{\cdot}mol^{-1}$, from equilibrium data.

Heat Capacity and Entropy

The low temperature (55–296.7 K) heat capacities and high temperature (399.6–1835.8 K) enthalpy data have been measured by King *et al.*,[6] and these data have been used to derive the tabulated heat capacities. Low temperature and high temperature values were joined smoothly at 298.15 K. The entropy was calculated from the heat capacities based on $S°(51\ K) = 1.31\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

King *et al.*[6] were apparently unaware of the transition near 593 K which was reported by Perri *et al.*,[7] and they did not take sufficient points in that region for the precise enthalpy curve. We have adopted only one curve through the region because of the insufficiency of the data and also because the heat effects appear to be small or gradual.

Transition and Fusion Data

The enthalpy of transition, the transition point, the enthalpy of melting and the melting point were derived from the high temperature enthalpy data of King *et al.*[6]

The melting point, 1746 ± 1 K, has also been quoted by Schneider.[8]

In the high temperature x-ray diffractometric studies, Perri *et al.*[7] indicate that WO_3 undergoes a phase transition from monoclinic to orthorhombic at approximately 593 K and from orthorhombic to tetragonal at 993 K.

Sublimation Data

The values of $\Delta_{sub} H°(298.15\ K)$ are calculated as the enthalpy of sublimation of one mole of crystal to one mole of monomer, 1/2 mole of dimer, 1/3 mole of trimer and 1/4 mole of tetramer, respectively.

References

[1] A. D. Mah, J. Amer. Chem. Soc. **81**, 1582 (1959).
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[8] S. J. Schneider, U.S. Nat. Bur. Stand. Monograph 68, (1963).

Tungsten Oxide (WO_3) $O_3W_1(cr)$

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
0	0.000	0.000	INFINITE	−12.349	−837.259	−837.259	INFINITE
100	30.449	18.862	130.106	−11.124	−841.044	−815.973	426.221
200	58.196	49.480	82.212	−6.546	−842.841	−790.036	206.336
298.15	73.139	75.912	75.912	0.000	−842.909	−764.057	133.860
300	73.304	76.365	75.914	0.135	−842.900	−763.568	132.949
400	82.209	98.738	78.904	7.934	−842.022	−737.237	96.273
500	88.641	117.815	84.825	16.495	−840.563	−711.200	74.299
600	93.113	134.397	91.736	25.597	−838.758	−685.493	59.677
700	96.141	148.993	98.894	35.069	−836.769	−660.104	49.258
800	98.239	161.975	105.983	44.794	−834.694	−635.007	41 462
900	99.923	173.645	112.864	54.703	−832.582	−610.173	35.414
1000	101.671	184.261	119.480	64.781	−830.431	−585.575	30.587
1050.000	102.508	189.242	122.684	69.886		I <--> II	
1050.000	98.144	190.655	122.684	71.369		TRANSITION	
1100	98.963	195.239	125.879	76.296	−826.958	−561.262	26.652
1200	100.601	203.920	132.025	86.275	−825.128	−537.188	23.383
1300	102.238	212.037	137.871	96.417	−823.230	−513.269	20.623
1400	103.875	219.674	143.444	106.722	−821.261	−489.499	18.263
1500	105.512	226.896	148.769	117.192	−819.216	−465.873	16.223
1600	107.149	233.758	153.868	127.825	−817.094	−442.386	14.442
1700	108.787	240.303	158.761	138.621	−814.892	−419.034	12.875
1745.000	109.537	243.155	160.901	143.534	-----	II <--> LIQUID	-----
1800	110.458	246.569	163.467	149.583	−812.608	−395.814	11.486
1900	112.131	252.586	168.000	160.713	−810.240	−372.723	10.247
2000	113.805	258.380	172.375	172.010	−807.788	−349.758	9.135
2100	115.478	263.973	176.604	183.474	−805.252	−326.919	8.132
2200	117.152	269.383	180.699	195.105	−802.632	−304.201	7.223
2300	118.826	274.628	184.670	206.904	−799.928	−281.606	6.395
2400	120.499	279.720	188.524	218.870	−797.139	−259.130	5.640
2500	122.173	284.673	192.272	231.004	−794.266	−236.772	4.947
2600	123.846	289.498	195.919	243.305	−791.305	−214.530	4.310
2700	125.520	294.203	199.472	255.773	−788.282	−192.404	3.722
2800	127.194	298.798	202.938	268.409	−785.231	−170.389	3.179
2900	128.867	303.291	206.321	281.212	−782.191	−148.486	2.675
3000	130.541	307.688	209.627	294.182	−779.188	−126.684	2.206

PREVIOUS: March 1963 CURRENT September 1966

Tungsten Oxide (WO_3) $O_3W_1(cr)$

Tungsten Oxide (WO_3) LIQUID $M_r = 231.8482$ Tungsten Oxide (WO_3) $O_3W_1(l)$

$S°(298.15\ K) = [103.508]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 1745\ K$

$\Delta_f H°(298.15\ K) = [-788.915]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 73.429\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1745\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity between the melting point and 1836 K was determined from the enthalpy measurement by King *et al.*[1] The heat capacity was assumed constant above and below the measured range. At 1000 K, a glass transition was assumed below which the heat capacity was assumed to be that of the crystal. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion and Vaporization Data

The heat and temperature of melting were obtained from King *et al.*[1]

T_{vap}(to equilibrium vapor) = 2110 K is the temperature at which the total pressure reaches one atm based on the calculated partial pressures of $WO_3(g)$, $W_2O_6(g)$, $W_3O_8(g)$, $W_3O_9(g)$, and $W_4O_{12}(g)$. $\Delta_{vap}H°$(to equilbrium vapor) = 18.3 kcal·mol^{-1} at the boiling point is calculated as the enthalpy of vaporization of one mole of the liquid to vapor containing 23.7 mole percent of $W_2O_6(g)$, 0.57 mole percent of $W_3O_8(g)$, 58.2 mole percent of $W_3O_9(g)$ and 17.53 mole percent of $W_4O_{12}(g)$.

Reference

[1] E. G. King, W. W. Weller and A. U. Christensen, U. S. Bur. Mines RI 5664, (1960).

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	73.140	103.508	103.508	0.000	−788.915	−718.291	125.842
300	73.304	103.961	103.509	0.135	−788.906	−717.853	124.989
400	82.209	126.334	106.499	7.934	−788.028	−694.281	90.664
500	88.641	145.410	112.421	16.495	−786.570	−671.004	70.099
600	93.113	161.993	119.332	25.597	−784.764	−648.056	56.418
700	96.141	176.589	126.490	35.069	−782.775	−625.427	46.670
800	98.239	189.571	133.579	44.794	−780.701	−603 090	39.378
900	99.923	201.241	140.459	54.703	−778.588	−581.015	33.721
1000	101.671	211.857	147.076	64.781	−776.437	−559.177	29.208
1000.000	101.671	211.857	147.076	64.781	GLASS <−−> LIQUID		
1000.000	131.796	211.857	147.076	64.781	TRANSITION		
1100	131.796	224.418	153.545	77.961	−771.300	−537.701	25.533
1200	131.796	235.886	159.936	91.140	−766.268	−516.687	22.491
1300	131.796	246.435	166.190	104.320	−761.333	−496.090	19.933
1400	131.796	256.203	172.275	117.499	−756.490	−475.869	17.755
1500	131.796	265.296	178.176	130.679	−751.735	−455.991	15.879
1600	131.796	273.802	183.890	143.859	−747.066	−436.427	14.248
1700	131.796	281.792	189.416	157.038	−742.481	−417.153	12.818
1745.000	131.796	285.235	191.843	162.969	−−−−− II <−−> LIQUID −−−−−		
1800	131.796	289.325	194.759	170.218	−737.980	−398.147	11.554
1900	131.796	296.451	199.926	183.397	−733.562	−379.388	10.430
2000	131.796	303.211	204.922	196.577	−729.227	−360.860	9.425
2100	131.796	309.641	209.757	209.757	−724.975	−342.546	8.520
2200	131.796	315.772	214.438	222.936	−720.807	−324.433	7.703
2300	131.796	321.631	218.972	236.116	−716.722	−306.508	6.961
2400	131.796	327.240	223.367	249.295	−712.720	−288.759	6.285
2500	131.796	332.620	227.630	262.475	−708.802	−271.175	5.666
2600	131.796	337.790	231.769	275.655	−704.962	−253.746	5.098
2700	131.796	342.764	235.788	288.834	−701.227	−236.462	4.575
2800	131.796	347.557	239.695	302.014	−697.633	−219.314	4.091
2900	131.796	352.182	243.494	315.193	−694.216	−202.294	3.644
3000	131.796	356.650	247.192	328.373	−691.004	−185.386	3.228

PREVIOUS: March 1963   CURRENT: September 1966

Tungsten Oxide (WO_3) $O_3W_1(l)$

Tungsten Oxide (WO_3) CRYSTAL(I–II)–LIQUID

0 to 1050 K crystal, I
1050 to 1745 K crystal, II
above 1745 K liquid

Refer to the individual tables for details.

$M_r = 231.8482$ Tungsten Oxide (WO_3) $O_3W_1(cr,l)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
0	0.000	0.000	INFINITE	−12.349	−837.259	−837.259	INFINITE
100	30.449	18.862	130.106	−11.124	−841.044	−815.973	426.221
200	58.196	49.480	82.212	−6.546	−842.841	−790.036	206.336
298.15	73.139	75.912	75.912	0.000	−842.909	−764.057	133.860
300	73.304	76.365	75.914	0.135	−842.900	−763.568	132.949
400	82.209	98.738	78.904	7.934	−842.022	−737.237	96.273
500	88.641	117.815	84.825	16.495	−840.563	−711.200	74.299
600	93.113	134.397	91.736	25.597	−838.758	−685.493	59.677
700	96.141	148.993	98.894	35.069	−836.769	−660.104	49.258
800	98.239	161.975	105.983	44.794	−834.694	−635.007	41.462
900	99.923	173.645	112.864	54.703	−832.582	−610.173	35.414
1000	101.671	184.261	119.480	64.781	−830.431	−585.575	30.587
1050.000	102.508	189.242	122.684	69.886		I <- -> II	
1050.000	98.144	190.655	122.684	71.369		TRANSITION	
1100	98.963	195.239	125.879	76.296	−826.958	−561.262	26.652
1200	100.601	203.920	132.025	86.275	−825.128	−537.188	23.383
1300	102.238	212.037	137.871	96.417	−823.230	−513.269	20.623
1400	103.875	219.674	143.444	106.722	−821.261	−489.499	18.263
1500	105.512	226.896	148.769	117.192	−819.216	−465.873	16.223
1600	107.149	233.758	153.868	127.825	−817.094	−442.386	14.442
1700	108.787	240.303	158.761	138.621	−814.892	−419.034	12.875
1745.000	109.537	243.155	160.901	143.534		II <- -> LIQUID	
1745.000	131.796	285.235	160.901	216.963		TRANSITION	
1800	131.796	289.325	164.763	224.212	−737.980	−398.147	11.554
1900	131.796	296.451	171.508	237.391	−733.562	−379.388	10.430
2000	131.796	303.211	177.926	250.571	−729.227	−360.860	9.425
2100	131.796	309.641	184.046	263.750	−724.975	−342.546	8.520
2200	131.796	315.772	189.895	276.930	−720.807	−324.433	7.703
2300	131.796	321.631	195.496	290.110	−716.722	−306.508	6.961
2400	131.796	327.240	200.870	303.289	−712.720	−288.759	6.285
2500	131.796	332.620	206.033	316.469	−708.802	−271.175	5.666
2600	131.796	337.790	211.002	329.648	−704.962	−253.746	5.098
2700	131.796	342.764	215.790	342.828	−701.227	−236.462	4.575
2800	131.796	347.557	220.411	356.008	−697.633	−219.314	4.091
2900	131.796	352.182	224.876	369.187	−694.216	−202.294	3.644
3000	131.796	356.650	229.194	382.367	−691.004	−185.386	3.228

PREVIOUS: CURRENT: September 1966

Tungsten Oxide (WO_3) IDEAL GAS $M_r = 231.8482$ Tungsten Oxide (WO_3) $O_3W_1(g)$

$S°(298.15\ K) = [286.440]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -288.47 \pm 29.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -292.88 \pm 29.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	 ν, cm^{-1}
[564](1)	1040 (2)
[347](1)	[320](2)

Ground State Quantum Weight: 1 $\sigma = [6]$
Point Group: $[D_{3h}]$
Bond,uccircl Distance: W–O = [1.81] Å
Bond Angle: O–W–O = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [4.4509666 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The Gibbs energy of formation of gaseous tungsten trioxide, $\Delta_f G°(WO_3, g) = -75{,}700 + 15.54\,T\ cal \cdot K^{-1} \cdot mol^{-1}$, over the temperature range 1920–2020 K has been reported by Ackermann and Thorn,[1] using the reaction $3\ MgO(cr) + W(cr) \rightarrow 3\ Mg(g) + WO_3(g)$. 3rd law calculation gives $\Delta_f H°(WO_3, g, 298.15\ K) = -71.3\ kcal \cdot mol^{-1}$ using JANAF functions. The 2nd law value of $\Delta_f H°(298.15\ K)$ is $-74.8\ kcal \cdot mol^{-1}$.

DeMaria *et al.*[2] have reported the partial pressures of $WO(g)$, $WO_2(g)$, $WO_3(g)$ and $O(g)$ in a mass spectrometric study of aluminum oxide vaporized from a tungsten cell from 2188 to 2475 K. 3rd law treatment of their partial pressure data gives $\Delta_f H°(298.15\ K) = -245.2\ kcal \cdot mol^{-1}$ for $W(cr) + 3\ O(g) \rightarrow WO(g)$ which yields $\Delta_f H°(WO_3, g, 298.15\ K) = -66.5\ kcal \cdot mol^{-1}$. The 3rd law drift is $21 \pm 7\ cal \cdot K^{-1} \cdot mol^{-1}$. Partial pressures of $WO_2(g)$, $WO_3(g)$, and $O(g)$ at 2242 K have also been reported by Chupka *et al.*[3] in a mass spectrometric study of beryllium oxide in a tungsten cell. Similar calculation gives $\Delta_f H°(WO_3, g, 298.15\ K) = -73.0\ kcal \cdot mol^{-1}$.

The value, $-70 \pm 7\ kcal \cdot mol^{-1}$, is selected for the enthalpy of formation at 298.15 K.

Heat Capacity and Entropy

The $WO_3(g)$ was assumed to be a planar D_{3h} molecule with a bond angle O–W–O = 120°. The bond distance W–O was estimated to be the same as that in WO(g). Weltner and McLeod[4] have observed the vibrational frequency of 1040 cm^{-1} in the infrared spectrum by matrix isolation, and also estimated the frequencies 347 and 564 cm^{-1} based on the stretching force constant of WO(g). The estimation of 320 cm^{-1} was obtained from DeMaria *et al.*[2] These frequencies have been adopted in the tabulation. The principal moments of inertia are $I_A = I_B = 13.0559 \times 10^{-39}$, and $I_C = 26.1119 \times 10^{-39}\ g \cdot cm^2$.

References

[1] R. J. Ackermann and R. J. Thorn, J. Phys. Chem. 64, 350 (1960).
[2] G. DeMaria, R. P. Burns, J. Drowart and M. G. Inghram, J. Chem. Phys. 32, 1373 (1960).
[3] W. A. Chupka, J. Berkowitz and C. F. Giese, J. Chem. Phys. 30, 827 (1959).
[4] W. Weltner, Jr. and D. McLeod, Jr., J. Mol. Spectrosc. 17, 276 (1965).

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.592	−288.474	−288.474	INFINITE
100	38.449	232.689	334.270	−10.158	−290.049	−286.361	149.580
200	52.190	263.843	291.760	−5.583	−291.849	−281.917	73.629
250	57.112	276.037	287.423	−2.847	−292.456	−279.361	58.369
298.15	61.005	286.440	286.440	0.	−292.880	−276.798	48.494
300	61.141	286.817	286.441	0.113	−292.894	−276.698	48.177
350	64.479	296.501	287.198	3.256	−293.189	−273.973	40.888
400	67.241	305.297	288.919	6.551	−293.376	−271.214	35.417
450	69.521	313.353	291.193	9.972	−293.482	−268.437	31.159
500	71.402	320.778	293.785	13.497	−293.533	−265.651	27.752
600	74.248	334.064	299.417	20.788	−293.538	−260.073	22.641
700	76.231	345.667	305.213	28.318	−293.491	−254.499	18.991
800	77.646	355.944	310.925	36.015	−293.444	−248.932	16.254
900	78.681	365.152	316.447	43.834	−293.422	−243.370	14.125
1000	79.457	373.484	321.741	51.743	−293.440	−237.808	12.422
1100	80.052	381.086	326.796	59.720	−293.506	−232.241	11.028
1200	80.516	388.072	331.615	67.749	−293.625	−226.667	9.867
1300	80.885	394.532	336.209	75.820	−293.799	−221.081	8.883
1400	81.182	400.538	340.592	83.924	−294.031	−215.478	8.040
1500	81.425	406.147	344.778	92.054	−294.325	−209.858	7.308
1600	81.626	411.409	348.779	100.207	−294.683	−204.216	6.667
1700	81.794	416.363	352.611	108.379	−295.106	−198.549	6.101
1800	81.936	421.042	356.284	116.565	−295.598	−192.855	5.597
1900	82.057	425.475	359.810	124.765	−296.159	−187.132	5.145
2000	82.160	429.687	363.199	132.976	−296.793	−181.378	4.737
2100	82.250	433.698	366.461	141.197	−297.501	−175.590	4.368
2200	82.328	437.526	369.605	149.426	−298.283	−169.766	4.031
2300	82.396	441.187	372.638	157.662	−299.141	−163.906	3.722
2400	82.456	444.695	375.568	165.904	−300.077	−158.007	3.439
2500	82.509	448.062	378.401	174.153	−301.089	−152.067	3.177
2600	82.557	451.299	381.143	182.406	−302.175	−146.085	2.935
2700	82.599	454.416	383.799	190.664	−303.363	−140.058	2.710
2800	82.637	457.420	386.375	198.926	−304.686	−133.986	2.500
2900	82.671	460.321	388.876	207.191	−306.184	−127.865	2.303
3000	82.701	463.124	391.304	215.460	−307.882	−121.687	2.119
3100	82.729	465.836	393.665	223.731	−309.824	−115.449	1.945
3200	82.754	468.463	395.961	232.005	−312.041	−109.145	1.782
3300	82.778	471.010	398.197	240.282	−314.556	−102.767	1.627
3400	82.799	473.481	400.375	248.561	−317.404	−96.306	1.480
3500	82.818	475.882	402.499	256.842	−320.650	−89.758	1.340
3600	82.836	478.215	404.570	265.124	−324.387	−83.109	1.206
3700	82.852	480.485	406.591	273.409	−363.482	−76.159	1.075
3800	82.867	482.695	408.565	281.695	−364.915	−68.373	0.940
3900	82.881	484.847	410.493	289.982	−366.367	−60.549	0.811
4000	82.894	486.946	412.378	298.271	−367.838	−52.690	0.688
4100	82.906	488.993	414.222	306.561	−369.328	−44.793	0.571
4200	82.917	490.991	416.026	314.852	−370.835	−36.859	0.458
4300	82.927	492.942	417.792	323.144	−372.359	−28.889	0.351
4400	82.937	494.849	419.522	331.438	−373.901	−20.884	0.248
4500	82.946	496.713	421.217	339.732	−375.461	−12.844	0.149
4600	82.955	498.536	422.878	348.027	−377.037	−4.769	0.054
4700	82.963	500.320	424.507	356.323	−378.632	3.341	−0.037
4800	82.970	502.067	426.104	364.619	−380.244	11.485	−0.125
4900	82.977	503.778	427.672	372.917	−381.875	19.664	−0.210
5000	82.984	505.454	429.211	381.215	−383.524	27.876	−0.291
5100	82.990	507.097	430.722	389.513	−385.194	36.121	−0.370
5200	82.996	508.709	432.206	397.813	−386.883	44.396	−0.446
5300	83.001	510.290	433.665	406.113	−388.594	52.708	−0.519
5400	83.006	511.841	435.098	414.413	−390.328	61.050	−0.591
5500	83.011	513.365	436.507	422.714	−392.085	69.424	−0.659
5600	83.016	514.860	437.893	431.015	−393.867	77.833	−0.726
5700	83.021	516.330	439.257	439.317	−395.675	86.271	−0.791
5800	83.025	517.774	440.598	447.619	−397.510	94.743	−0.853
5900	83.029	519.193	441.918	455.922	−399.375	103.244	−0.914
6000	83.033	520.588	443.218	464.225	−401.270	111.780	−0.973

PREVIOUS: September 1966 (1 atm) CURRENT· September 1966 (1 bar)

Lead Silicate (Pb_2SiO_4) CRYSTAL $M_r = 506.4831$

$S°(298.15\ K) = 186.832 \pm 2.1\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1016\ K$

$\Delta_f H°(0\ K) = -1369.466 \pm 14.6\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1377.875 \pm 14.6\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of the reaction $2\ PbO(cr) + SiO_2(cr) \rightarrow Pb_2SiO_4(cr)$ was reported by Kubaschewski and Evans.[1] This value for the enthalpy of reaction of the oxides has been converted to the enthalpy of formation using JANAF auxiliary data.[4] The above $\Delta_f H°(298.15\ K) = -7.00 \pm 3.5\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

In the low temperature region (53.07–298.15 K) the $C_p°$ values are those determined by King.[2] 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 53.07 K using the Debye and Einstein functions $D(78.5/T) + 2E(164/T) + 3E(547/T) + E(1379/T)$ given by King.[2] $S°(53.07\ K) = 8.248\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

T_{fus} was taken from Geller *et al.*[3]

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Lead Silicate (Pb_2SiO_4) $O_4Pb_2Si_1(cr)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−25.932	−1369.466	−1369.466	INFINITE
100	73.789	72.007	291.667	−21.966	−1375.108	−1339.898	699.891
200	113.968	136.700	198.686	−12.397	−1377.589	−1303.493	340.437
298.15	136.984	186.832	186.832	0.000	−1377.875	−1267.007	221.974
300	137.235	187.680	186.835	0.254	−1377.866	−1266.320	220.486
400	152.005	229.255	192.403	14.741	−1376.901	−1229.256	160.524
500	163.762	264.478	203.383	30.547	−1375.118	−1192.537	124.583
600	173.343	295.224	216.181	47.426	−1372.712	−1156.238	100.659
700	180.121	322.489	229.458	65.122	−1379.617	−1118.781	83.484
800	184.180	346.822	242.636	83.349	−1376.607	−1081.721	70.629
900	186.774	368.668	255.447	101.899	−1373.401	−1045.052	60.653
1000	189.117	388.473	267.775	120.699	−1370.045	−1008.747	52.692
1100	190.790	406.580	279.582	139.698	−1366.569	−972.784	46.194
1200	192.046	423.232	290.868	158.836	−1363.015	−937.142	40.793
1300	193.719	438.670	301.651	178.125	−1359.374	−901.800	36.235
1400	195.309	453.086	311.959	197.578	−1355.656	−866.741	32.338
1500	196.648	466.607	321.823	217.177	−1351.892	−831.950	28.971
1600	197.903	479.339	331.273	236.906	−1348.109	−797.410	26.033
1700	199.033	491.371	340.340	256.753	−1394.502	−762.660	23.434
1800	200.121	502.778	349.050	276.710	−1390.499	−725.609	21.057
1900	201.292	513.629	357.429	296.780	−1386.467	−688.780	18.936
2000	202.506	523.985	365.500	316.970	−1382.402	−652.165	17.033

PREVIOUS: CURRENT: June 1965

Lead Silicate (Pb_2SiO_4) $O_4Pb_2Si_1(cr)$

Lead Oxide (Pb_3O_4) CRYSTAL $M_r = 685.5976$ Lead Oxide (Pb_3O_4) $O_4Pb_3(cr)$

$\Delta_fH°(0\ K) = -710.871 \pm 6.2\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 211.961 \pm 6.7\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -718.686 \pm 6.2\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Espada *et al.*[1] have measured the enthalpy of the reduction reaction $PbO_{1.3}(cr) + 1.3\ H_2(g) \rightarrow Pb(cr) + 1.3\ H_2O(l)$ as $-32.07\ kcal \cdot mol^{-1}$ as $-32.07\ kcal \cdot mol^{-1}$. They assumed that the sample consisted of 90.1% mol percent $PbO_{1.333}$ and 9.9 mol PbO and corrected the observed enthalpy of reaction to $-33.82 \pm 0.25\ kcal \cdot mol^{-1}$ for the reaction $PbO_{1.333}(cr) + 1.333\ H_2(g) \rightarrow Pb(cr) + 1.333\ H_2O(l)$. This leads to $\Delta_fH°(Pb_3O_4, cr) = -171.77 \pm 1.5\ kcal \cdot mol^{-1}$ which is adopted.

Andrews and Brown[2] used reversible cells to obtain $\Delta_rG°(298.15\ K) = -6940\ cal \cdot K^{-1} \cdot mol^{-1}$ for the reaction $Hg(l) + Pb_3O_4(cr) \rightarrow HgO(cr) + 3\ PbO(red, cr)$, with JANAF auxiliary data[3] this yields $\Delta_fG(Pb_3O_4, cr, 298.15\ K) = -142.76 \pm 0.6\ kcal \cdot mol^{-1}$ which is equivalent to $\Delta_fH°(Pb_3O_4, cr, 298.15\ K) = -170.73 \pm 1.1\ kcal \cdot mol^{-1}$. This value is in agreement with the adopted value within the combined uncertainties.

Reinders and Hamburger[4] and Otto[5] studied the decomposition pressure of the reaction $Pb_3O_4(cr) \rightarrow 3\ PbO(cr) + 0.5\ O_2(g)$ a 2nd and 3rd law analysis of their data is given below.

Source	Data Points	T/K	$\Delta_rH°(298.15\ K)$, 2nd law	$kcal \cdot mol^{-1}$ 3rd law	Drift $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_fH°(298.15\ K)$ $kcal \cdot mol^{-1}$
[4]	16	718–880	20.19 ± 0.14	19.08 ± 0.17	−1.4 ± 0.2	−175.44
[5]	19	757–911	20.84 ± 0.10	18.98 ± 0.22	−2.2 ± 0.1	−175.34

Although these two sets of data are in good agreement, they are outside the adopted enthalpy of formation uncertainty limits, and realistic adjustments of the entropy or heat capacity fail to eliminate this discrepancy.

In addition there have been cell measurements linking PbO_2 and Pb_3O_4, which serve to indicate the overall consistency of the lead oxygen system. The absolute uncertainty in the enthalpy of formation and the difficulty of preparing pure PbO_2 make it a poor choice on which to base the heat of formation of Pb_3O_4. Andrews and Brown[2] obtained $\Delta_rG°(298.15\ K) = -18.12\ kcal \cdot mol^{-1}$ for the reaction $2\ Hg(l) + 3\ PbO_2(cr) \rightarrow Pb_3O_4(cr) + 2\ HgO(cr)$. This yields $\Delta_fG°(Pb_3O_4, cr, 298.15\ K) = -144.62 \pm 2.1\ kcal \cdot mol^{-1}$ with JANAF auxiliary data,[3] which corresponds to $\Delta_fH°(Pb_3O_4, cr, 298.15\ K) = -172.59 \pm 2.6\ kcal \cdot mol^{-1}$. Millar[6] has recalculated the data of Glasstone for the reaction $3\ PbO_2(cr) + 2\ H_2(g) \rightarrow Pb_3O_4 + 2\ H_2O(l)$ as $\Delta_rG°(298.15\ K) = -104.36\ kcal \cdot mol^{-1}$ which with auxiliary data[3,7] yields $\Delta_fG°(Pb_3O_4, cr, 298.15\ K) = -145.45 \pm 2.1\ kcal \cdot mol^{-1}$ which corresponds to $\Delta_fH°(Pb_3O_4, cr, 298.15\ K) = -173.42 \pm 2.6\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The low temperature enthalpy capacity from 71.5 K to 292.6 K has been reported by Millar.[6] These values were used to calculate $S°(298.15\ K)$ based on $S°(70.8\ K) = 12.67\ cal \cdot K^{-1} \cdot mol^{-1}$.[7] Enthalpies in the range 365 to 781 K have been reported by Bousquet *et al.*[8] These data encompass the range where the dissociation pressure is significant (76 mm) and we have not used the data above 600 K. The mean heat capacities were plotted at the mean temperatures for the five points used and a smooth curve was drawn graphically through them and the low temperature data set. The four highest points of Millar[6] were not used since at least two were reported as bad points and they did not fit onto the smooth curve.

Decomposition Data

The decomposition pressure reaches 1 atm at 869.7 according to Reinders and Hamburger[4] and at 867.2 K according to Otto.[5] This table indicates a temperature of 690 K for the decomposition pressure to reach 1 atm. The significant difference is due to the fact that heat and entropy derived from the dissociation cannot be simultaneously satisfied by any realistic variation of the entropy and heat capacity of Pb_3O_4.

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

T/K	$C_p°$ ($J \cdot K^{-1} mol^{-1}$)	$S°$ ($J \cdot K^{-1} mol^{-1}$)	$-[G°-H°(T_r)]/T$ ($J \cdot K^{-1} mol^{-1}$)	$H°-H°(T_r)$ ($kJ \cdot mol^{-1}$)	$\Delta_fH°$ ($kJ \cdot mol^{-1}$)	$\Delta_fG°$ ($kJ \cdot mol^{-1}$)	log K_f
0	0.000	0.000	INFINITE	−30.188	−710.871	−710.871	INFINITE
100	87.195	79.860	331.486	−25.163	−716.955	−679.231	354.794
200	130.122	155.101	225.392	−14.058	−719.246	−640.309	167.232
298.15	154.934	211.961	211.961	0.000	−718.686	−601.606	105.399
300	155.344	212.921	211.964	0.287	−718.656	−600.879	104.622
400	173.050	260.195	218.289	16.762	−716.310	−561.936	73.381
500	184.096	300.077	230.766	34.656	−712.976	−523.715	54.712
600	190.790	334.272	245.237	53.421	−709.197	−486.213	42.329
700	194.974	363.996	260.126	72.709	−719.884	−446.962	33.353
800	199.158	390.305	274.785	92.416	−715.902	−408.241	26.655
900	203.342	414.004	288.958	112.541	−711.544	−370.041	21.477
1000	207.526	435.645	302.560	133.084	−706.789	−332.348	17.360
1100	211.710	455.620	315.578	154.046	−701.619	−295.150	14.016
1200	215.894	474.221	328.032	175.426	−696.018	−258.442	11.250
1300	220.078	491.667	339.955	197.225	−689.997	−222.219	8.929
1400	224.262	508.130	351.385	219.442	−683.595	−186.474	6.957
1500	228.446	523.745	362.360	242.078	−676.835	−151.199	5.265

PREVIOUS: March 1962 CURRENT: December 1971

Zinc Sulfate ($ZnSO_4$) CRYSTAL $M_r = 161.4376$ Zinc Sulfate ($ZnSO_4$) $O_4S_1Zn_1(cr)$

$\Delta_f H°(0\ K) = -969.934 \pm 0.10\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -980.144 \pm 0.10\ kJ \cdot mol^{-1}$
$\Delta_{trs1} H°(\alpha \to \alpha') = [5.021]\ kJ \cdot mol^{-1}$
$\Delta_{trs2} H°(\alpha' \to \beta) = 20.334 \pm 0.8\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 110.541 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs1}(\alpha \to \alpha', \text{proposed}) = [540]\ K$
$T_{trs2}(\alpha' \to \beta) = 1013 \pm 5\ K$

Enthalpy of Formation

Adami and King[1] determined calorimetrically the enthalpies of solution of crystalline ZnO and $ZnSO_4$ in hydrochloric acid solution. From these measurements they derived the enthalpy for the reaction $ZnC(cr) + H_2SO_4 \cdot 7.068\ H_2O(l) \rightarrow ZnSO_4(cr) + 8.068\ H_2O(l)$ as $\Delta_r H°(298.15\ K) = -9.250 \pm 0.080\ kcal \cdot mol^{-1}$. Combining this result with the enthalpies of formation of ZnO[2], $H_2SO_4 \cdot 7.068\ H_2O$,[3,4] and H_2O,[4] we derive $\Delta_f H°(ZnSO_4, cr, 298.15\ K)\ -234.26 \pm 0.25\ kcal \cdot mol^{-1}$ which is the value adopted for this tabulation.

The enthalpy of solution at infinite dilution, $\Delta_{sol} H°(ZnSO_4, cr, 298.15\ K) = -19.9 \pm 0.2\ kcal \cdot mol^{-1}$ was taken from the work of Larson *et al.*[5] When this result is combined with enthalpies of formation of the infinitely dilute ions from,[4] we obtain $\Delta_f H°(ZnSO_4, aq, |infinite|, 298.15\ K) = -254.06 \pm 0.14\ kcal \cdot mol^{-1}$ and $\Delta_f H°(ZnSO_4, cr, 298.15\ K) = -234.16 \pm 0.34\ kcal \cdot mol^{-1}$.

Ishikawa and Murooka[6] determined $\Delta_r H°(298.15\ K) = -56.330\ kcal \cdot mol^{-1}$ from cell measurements for the reaction $Zn(cr) + Hg_2SO_4(cr) = ZnSO_4(cr) + 2\ Hg(l)$ as reported by Kelley.[7] When this result is combined with JANAF auxiliary data for Zn(cr)[8] and with data from CODATA[9] for Hg(l) and $Hg_2SO_4(cr)$, we obtain $\Delta_f H°(ZnSO_4, cr, 298.15\ K) = -234.01 \pm 1.0\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Low temperature heat capacities of $ZnSO_4(cr, \alpha)$ have been measured by Weller[10] from 51.7–296.5 K. A small heat capacity maximum was observed at 124.37 K. Our adopted value of $S°(298.15\ K) = 26.42 \pm 0.3\ cal \cdot K^{-1} \cdot mol^{-1}$ obtained from $C_p°$ is based on $S°(51\ K) = 2.27\ cal \cdot K^{-1} \cdot mol^{-1}$ obtained by Weller[10] by extrapolation of the measured heat capacity with a combination of Debye and Einstein functions. We have smoothed the data of Weller[10] by fitting the data with orthogonal polynomials over selected overlapping temperature intervals.

High temperature enthalpy data have been measured by Hosmer and Krikorian,[11] 510–1168 K as well as by Voskresenskaya and Patsukova,[12] 523 806 K, Krestovnikov and Feigina,[13] 573–1073 K, and by Chizhikov and Khirik,[14] 373–973 K. The enthalpy data of Hosmer and Krikorian[11] is higher than the data of Voskresenskaya and Patsukova[12] or Krestovnikov and Feigina.[13] Wet chemical and x–ray analysis of their sample[11] indicate that the sample was pure zinc sulfate. The lower results of[12] and[13] may be due to decomposition to the oxy sulfate which can occur in vacuum dehydration.[11] We adopt the enthalpy results from Hosmer and Krikorian.[11] Problems remain in matching the low temperature heat capacity data to the high temperature enthalpy data (300–600 K region). There are at least three possibilities for the mismatch: 1) an unobserved transition occurs between 300–600 K, 2) the data of W.W. Weller[10] and P.K. Hosmer and O.H. Krikorian[11] are essentially correct but were measured on different materials, or 3) a bias exists in the data from one of the calorimeters. In the absence of other information, we arbitrarily adopt a transition at 540 K with $\Delta_{trs} H° = 1.20\ kcal \cdot mol^{-1}$. Below 540 K, we adopt heat capacities based on an extrapolation of the work of Weller.[10] Above 540 K, we adopt heat capacities based on the enthalpy data of Hosmer and Krikorian.[11]

Transition Data

$ZnSO_4(cr, \alpha)$ is the low–temperature form of zinc sulfate, also known as the mineral zinkosite and $ZnSO_4(cr, II)$. The crystals are orthorhombic, space group D_{2h}^{16}–Pnma.[15] The transition to the high–temperature (β–phase) cubic form (space group F43m),[16] occurs at 1013 ± 5 K.[15] The heat of transition is based on the drop calorimetry measurement of Hosmer and Krikorian[11] which is in good agreement with the DTA measurement of Ingraham and Marier,[17] 4.74 $kcal \cdot mol^{-1}$. Decomposition occurs through an oxy–sulfate intermediate which has the probable composition $ZnO \cdot 2\ ZnSO_4$.[11]

Hosmer and Krikorian[11] have also measured enthalpies of the high temperature $ZnSO_4(cr, \beta)$ phase of zinc sulfate. We adopt their results (1038–1168 K), which imply a constant heat capacity, and extrapolate this value to 2000 K.

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
0	0.000	0.000	INFINITE	−17.238	−969.934	−969 934	INFINITE
100	47.585	31.581	183.544	−15.196	−975.390	−940.983	491.519
200	78.053	75.224	118.947	−8.745	−978.636	−905.195	236.413
298.15	99.035	110.541	110.541	0.000	−980.144	−868.777	152.206
300	99.370	111.155	110.543	0.184	−980.158	−868.086	151.147
400	116.022	142.074	114.647	10.971	−982.499	−830.588	108 464
500	131.210	169.620	122.933	23.344	−982.857	−792.557	82.798
540.000	136.817	179.933	126.775	28.705		I <--> II	
540.000	136.817	189.231	126.775	33.726		TRANSITION	
600	137.444	203.678	133.755	41.954	−976.948	−755.128	65.740
700	138.574	224.950	145.301	55.755	−983.260	−718.162	53.590
800	139.704	243.528	156.442	69.668	−982.369	−680.351	44.422
900	140.875	260.050	167.053	83.698	−1034.546	−641.575	37.236
1000	142.005	274.954	177.110	97.844	−1032.317	−598.031	31.238
1013.000	142.130	276.789	178.377	99.691		ALPHA <--> BETA	
1013.000	145.185	296.862	178.377	120.025		TRANSITION	
1100	145.185	308.825	188.228	132.656	−1009.533	−556.465	26.424
1200	145.185	321.457	198.812	147.175	−1122.238	−513.448	22.350
1300	145.185	333.078	208.699	161.693	−1118.867	−462.853	18.598
1400	145.185	343.838	217.972	176.212	−1115.572	−412.515	15.391
1500	145.185	353.854	226.701	190.730	−1112.348	−362.410	12.620
1600	145.185	363.224	234.944	205.249	−1109 190	−312.517	10.203
1700	145.185	372.026	242.751	219.767	−1106.097	−262.820	8.075
1800	145.185	380.325	250.166	234.286	−1103.065	−213.304	6.190
1900	145.185	388.174	257.225	248.804	−1100.093	−163.954	4.507
2000	145.185	395.622	263.960	263.323	−1097.180	−114.759	2.997

PREVIOUS: CURRENT: March 1979

Zirconium Silicate ($ZrSiO_4$) CRYSTAL $M_r = 183.3031$ Zirconium Silicate ($ZrSiO_4$) $O_4Si_1Zr_1(cr)$

$\Delta_f H°(0\ K) = -2012.774 \pm 2.9\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 84.026 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -2023.951 \pm 2.9\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(ZrSiO_4$, cr, 298.15 K) was calculated from the $\Delta_r H°(298.15\ K)$ of its constituent oxides $ZrO_2(cr) + SiO(cr) = ZrSiO_4(cr)$ and the $\Delta_f H°(298.15\ K)$ values for $ZrO_2(cr)$ and $SiO_2(cr)$ in JANAF tables.[4] The $\Delta_r H°(298.15\ K) = -4.736\ kcal \cdot mol^{-1}$ was based on the Gibbs energy of formation of its constituent oxides at the decomposition temperature 1811 K.

Heat Capacity and Entropy

At low temperatures, $C_p°$ were used from Kelley.[1] From 298–940 K, $C_p°$ was calculated by using the Coughlin and King[2] equation $C_p° = 31.48 + 3.92 \times 10^{-3}T - 8.08 \times 10^5 T^{-2}$ which joined smoothly with the low temperature data. Above 940 K the data were estimated by extending the curve smoothly. The entropy was calculated at 52.7 K using the Debye and Einstein[3] functions $D(321/T) + 2E(407/T) + 2E(796/T) + E(1624/T)$ given by Kelley.[2] $S°(52.7\ K) = 0.65404\ cal \cdot K^{-1} \cdot mol^{-1}$.

Decomposition Data

T_{dcm} is the temperature at which $\Delta_f G° = 0$ for the reaction $ZrSiO_4(cr) \rightarrow ZrO_2(cr) + SiO_2(cr)$. $T_{dcm} = 1811$ K was taken from Curtis and Sowman.[3]

References

[1] K. K. Kelley, J. Amer. Chem. Soc. 63, 2750 (1941).
[2] J. P. Coughlin and E. G. King, J. Amer. Chem. Soc. 72, 2262 (1950).
[3] C. E. Curtis and H. G. Sowman, J. Amer. Chem. Soc. 36, 190 (1953).
[4] JANAF Thermochemical Tables: $ZrO_2(cr)$, 6–30–61; $SiO_2(cr)$, 12–31–62.

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−14.905	−2012.774	−2012.774	INFINITE
100	31.034	14.070	153.089	−13.902	−2018.733	−1983.690	1036.173
200	73.298	49.742	92.291	−8.510	−2022.535	−1946.946	508.490
298.15	98.659	84.026	84.026	0.000	−2023.951	−1909.475	334.532
300	99.119	84.638	84.028	0.183	−2023.961	−1908.764	332.345
400	114 642	115.379	88.114	10.906	−2023.861	−1870.349	244.243
500	125.938	142.241	96.311	22.965	−2022.823	−1832.076	191.396
600	133.679	165.925	105.980	35.967	−2021.207	−1794.071	156.188
700	138.825	186.935	116.073	49.603	−2019.294	−1756.364	131 061
800	142.674	205.738	126.127	63.689	−2017.241	−1718.942	112.235
900	145.268	222.698	135.931	78.091	−2015.160	−1681.779	97.608
1000	147.277	238.112	145.390	92.723	−2013.119	−1644.847	85.918
1100	148.741	252.222	154.470	107.528	−2011.159	−1608.115	76.363
1200	149.704	265.209	163.164	122.454	−2013.031	−1571.335	68.398
1300	150.164	277.211	171.481	137.449	−2010.811	−1534.618	61.662
1400	150.415	288.349	179.436	152.478	−2008.702	−1498.068	55.894
1500	150.624	298.735	187.047	167.532	−2006.718	−1461.664	50.900
1600	150.624	308.456	194.335	182.595	−2004.883	−1425.388	46.534
1700	150.624	317.588	201.319	197.657	−2053.390	−1388.775	42.672
1800	150.624	326.197	208.020	212.719	−2051.665	−1349.731	39.168
1900	150.624	334.341	214.456	227.782	−2050.081	−1310.778	36.036
2000	150.624	342.067	220.645	242.844	−2048.650	−1271.905	33.219
2100	150.624	349.416	226.603	257.907	−2047.382	−1233.100	30.672
2200	150.624	356.423	232.346	272.969	−2067.609	−1193.604	28.340
2300	150.624	363.118	237.887	288.031	−2067.111	−1153.889	26.206
2400	150.624	369.529	243.240	303.094	−2066.658	−1114.194	24.250
2500	150.624	375.678	248.415	318.156	−2066.249	−1074.516	22.451
2600	150.624	381.585	253.424	333.219	−2065.883	−1034.854	20.790
2700	150.624	387.270	258.277	348.281	−2065.559	−995.205	19.253
2800	150.624	392.748	262.982	363.343	−2065.275	−955.567	17.826
2900	150.624	398.033	267.549	378.406	−2065.032	−915.940	16.498
3000	150.624	403.140	271.984	393.468	−2064.827	−876.320	15.258

PREVIOUS: September 1961 CURRENT: June 1965

Vanadium Oxide (V_2O_4) CRYSTAL M_r = 165.8806

$S°(298.15\ K) = 103.525 \pm 2.1\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs} = 340 \pm 5\ K$
$T_{fus} = 1818 \pm 15\ K$

$\Delta_f H°(0\ K) = -1418.617 \pm 6.3\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -1427.162 \pm 6.3\ kJ{\cdot}mol^{-1}$
$\Delta_{trs}H° = 8.996 \pm 0.8\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 112.068 \pm 2.5\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°$ values for the vanadium oxides, and in particular V_2O_4(cr) are based on the combustion studies by Mah and Kelley.[1] The adopted value is −341.1 kcal·mol⁻¹ which was obtained by rounding the reported value of Mah and Kelley.[1] For more details refer to the V_2O_5(cr) table.[2] Charlu and Kleppa[3] reported a enthalpy of formation value at $\Delta_f H°(298.15\ K) = -342.4 \pm 0.78\ kcal{\cdot}mol^{-1}$ based on oxidation studies to V_2O_5(cr) in a high temperature microcalorimeter. The combustion by this technique yielded complete oxidation to V_2O_5(cr) as opposed to the method of Mah and Kelley,[1] whereby $\Delta_f H°$ for V_2O_4(cr) was determined simultaneously with that for V_2O_5(cr) due to incomplete combustion of V(cr). A combustion study by Siemonsen and Ulich[4] led to the reported value of −342 ± 2 kcal·mol⁻¹ for $\Delta_f H°(V_2O_4$, cr, 293 K). Additional thermodynamic data which relate V_2O_3(cr) with V_2O_4(cr) or V_2O_5(cr) is contained in the sodium oxide fusion studies by Mixter,[5] the H_2O–H_2 equilibrium study by Muller,[6] the CO–CO_2 equilibrium study by Spencer and Justice,[7] and the reduction of V_2O_5(cr) with SO_2 by Flood and Kleppa.[8] See V_2O_3(cr) table for some additional information.[2]

Heat Capacity and Entropy

Anderson[9] measured the heat capacity of V_2O_4 (reported purity of 99.5% or better) in the range 61.4–279.4 K. Using the combination of Debye and Einstein functions suggested by Anderson,[9] we calculate $S°(60\ K) = 1.48\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ and $H°(60;0) = 63.66\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. The data of Anderson[9] show considerable scatter from our adopted values, with a ± 2.0% deviation being typical for this data. Cook[10] measured the enthalpy of V_2O_4 in the range 315–1856 K. The enthalpy data for $T < T_{trs}$ appears too high to be fully consistent with $C_p°$ data of Anderson.[9] The adopted $C_p°$ values in the region 280–340 K join smoothly with a positive power polynomial fit of the data of Anderson[4] and lead to enthalpy values at 315.5, 322.8, and 323 0 K which are roughly 48, 34, and 39 kcal·mol⁻¹, respectively, less than the data of Cook.[10] This is a difference of 5–10%. The enthalpy data in the region T_{trs}–T_{fus} are fit to a Kelley type equation and then differentiated to yield our adopted $C_p°$ values. The data of Cook[10] also shows considerable scatter, with deviations ranging from −0.69% to +1.12%.

Three $C_p°$ studies concentrated on the region near T_{trs} but presented only graphical data.[11-13] Kawakubo and Nakagawa[11] reported $C_p°$ values between 30 °C and 90 °C which are roughly 18% higher than our adopted values below the transition and 25% higher above the transition. Ryder *et al.*[12] and Chandrashekhar *et al.*[13] measured $C_p°$ values in the range 40–375 K and 150–730 K. These latter two works agree well graphically in their region of overlap. The $C_p°$ values above T_{trs} are very similar to our adopted values; at 500 K the adopted values are less than 0.1 cal·K⁻¹·mol⁻¹ higher while at 700 K, roughly 0.75 cal·K⁻¹·mol⁻¹ lower. Below T_{trs}, the differences are more substantial; the adopted values lying approximately 1.5 cal·K⁻¹·mol⁻¹ higher.

Phase Data

Minomura and Nagasaki[14] referenced earlier x-ray data and provided additional data to show that V_2O_4 undergoes a structural distortion to lower symmetry on cooling through a transition temperature of 340 K; tetragonal rutile to a monoclinic structure with the unit cell doubling in size. Recent crystallographic investigations by Kawada *et al.*[15] verified the doubling of the size of the unit cell and also detected considerable distortion of the shape of the unit cell. The literature review on the V O system by Stringer[16] indicated that there are a series of oxides between V_2O_3 and V_2O_4. These oxides may be considered as members of a homologous series with $V_2O_4(VO_2)$ being the series limit.[16] Numerous references on phase data are contained in the reviews by Stringer,[16] Adler[17] and Neuberger.[18]

Transition Data

Minomura and Nagasaki[14] repored that the structural distortion occurs at 340 K. This value is consistent with the enthalpy data of Cook.[10] Kawakubo and Nakagawa[11] measured the temperature dependence of five physical properties through the transition point and concluded that the transition occurs at 338 K. We adopt $T_{trs} = 340 + 5$ K.

Using our adopted enthalpy values for $T < T_{trs}$ and $T > T_{trs}$, we calculate and adopt $\Delta_{trs}H° = 2.15 \pm 0.20\ kcal{\cdot}mol^{-1}$. Ryder *et al.*[12] reported a value of 2.040 ± 0.010 kcal·mol⁻¹ and Chandrashekhar *et al.*,[13] a value of 2.24 kcal·mol⁻¹. The values of $\Delta_{trs}H°$ = 1.60 and 1.50 kcal·mol⁻¹ reported by Klemm and Grimm[19] and Kawakubo and Nakagawa,[11] respectively, are considered too low. In our tabulation, the transition is treated as being first order. Controversy exists concerning the order of the transition, as discussed by Adler.[17] Additional references may be found in Stringer,[16] Adler[17] and Neuberger.[18]

Fusion Data

Refer to the liquid table for details.

References

[1] A. D. Mah and K. K. Kelley, U. S. Bur. Mines RI 5858, (1961).
[2] JANAF Thermochemical Tables: V_2O_5(cr), 6–30–73; V_2O_3(cr), 12–31–73.
[3] F. V. Charlu and O. J. Kleppa, High Temp. Soc. 5, 260 (1973).
[4] H. Siemonsen and H. Ulich, Z. Electrochem. 46, 141 (1940).
[5] W. G. Mixter, Amer. J. Sci. 34, 141 (1912).

Continued on page 1815

Vanadium Oxide (V_2O_4) O_4V_2(cr)

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−18.100	−1418.617	−1418.617	INFINITE
100	36.907	18.652	186.891	−16.824	−1424.127	−1389.894	726.006
200	90.274	62.333	113.357	−10.205	−1427.002	−1354.252	353.694
298.15	115.399	103.525	103.525	0.000	−1427.162	−1318.445	230.986
300	115.787	104.240	103.527	0.214	−1427.150	−1317 770	229.444
340 000	123.336	119.218	104.501	5.004	I <−−> II	TRANSITION	
340.000	127.621	145.675	104.501	13.999			
400	135.281	167.065	112.309	21.902	−1416.532	−1283.094	167.555
500	143.269	198.162	126.456	35.853	−1414.020	−1250.016	130.588
600	148.448	224.758	140.677	50.448	−1411.187	−1217.477	105.991
700	152.175	247.927	154.379	65.483	−1408.212	−1185.426	88.458
800	155.457	268.466	167.380	80.868	−1405.169	−1153.807	75.336
900	158.157	286.934	179.655	96.551	−1402.101	−1122.571	65.152
1000	160.682	303.729	191.236	112.494	−1399.025	−1091.677	57.023
1100	162.987	319.153	202.173	128.678	−1395.953	−1061.091	50.387
1200	165.209	333.430	212.523	145.089	−1392.908	−1030.784	44.869
1300	167.330	346.738	222.341	161.716	−1389.898	−1000.729	40.210
1400	169.406	359.215	231.677	178.553	−1386.944	−970.904	36.225
1500	171.429	370.972	240.575	195.595	−1384.045	−941.289	32.779
1600	173.427	382.100	249.076	212.838	−1381.201	−911.865	29.769
1700	175.302	392.669	257.214	230.273	−1378.439	−882.616	27.119
1800	177.343	402.746	265.022	247.904	−1375.760	−853.528	24.769
1818.000	177.728	404.513	266.394	251.100	−−−−− II <−−> LIQUID −−−−−		
1900	179.276	412.387	272.526	265.737	−1373.179	−824.586	22.669
2000	181.192	421.632	279.752	283.760	−1370.723	−795.777	20.784
2100	183.092	430.518	286.721	301.975	−1368.413	−767.087	19.080
2200	184.975	439.079	293.453	320.378	−1412.030	−738.293	17.529

PREVIOUS: September 1973 CURRENT: December 1973

Vanadium Oxide (V_2O_4) O_4V_2(cr)

Vanadium Oxide (V_2O_4) LIQUID $M_r = 165.8806$ Vanadium Oxide (V_2O_4) $O_4V_2(l)$

$S°(298.15 \text{ K}) = [173.473] \text{ J·K}^{-1}\text{·mol}^{-1}$
$T_{fus} = 1818 \pm 15 \text{ K}$

$\Delta_f H°(298.15 \text{ K}) = [-1332.151] \text{ kJ·mol}^{-1}$
$\Delta_{fus} H° = 112.068 \pm 2.5 \text{ kJ·mol}^{-1}$

Enthalpy of Formation

$\Delta_f H°(V_2O_4, l, 298.15 \text{ K})$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1818 \text{ K})–H°(298.15 \text{ K})$, between V_2O_4(cr) and V_2O_4(l).

Heat Capacity and Entropy

Cook[1] measured the enthalpy of V_2O_4(l) in the region 1829.7–1856.8 K and represented the data by the equation $H°(T)–H°(298.15 \text{ K}) = 51.00\,T–5910$ cal·K^{-1}·mol^{-1}. Thus $C_p°$ for the liquid is adopted as 51.00 cal·K^{-1}·mol^{-1}. Since the enthalpy measurements only cover a range of 39 K in the liquid region, the value of $C_p°$ should not be viewed as a precise value. A glass transition is assumed at 1200 K. Below 1200 K, the $C_p°$ values are those of the crystal with the exception that the values of $C_p°$ between 298 and 340 K are a smooth extrapolation of the crystal values above T_{tr}. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting point of V_2O_4(cr) is adopted as 1818 K, based on the enthalpy data of Cook.[1] The enthalpy of melting is calculated from the difference in $H°$–(1818 K) $H°(298.15 \text{ K})$ for V_2O_4(l) and V_2O_4(cr).

References – V_2O_4(l)

[1] O. A. Cook, J. Amer. Chem. Soc. 69, 331 (1947).

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0							
100							
200							
298.15	120.081	173.473	173.473	0.000	−1332.151	−1244.289	217.994
300	120.499	174.217	173.475	0.223	−1332.130	−1243.744	216.555
400	135.281	211.142	178.409	13.093	−1330.330	−1214.523	158.600
500	143.269	242.239	188.151	27.044	−1327.818	−1185.852	123.885
600	148.448	268.835	199.436	41.639	−1324.985	−1157.722	100.789
700	152.175	292.004	211.041	56.674	−1322.010	−1130.079	84.327
800	155.457	312.543	222.469	72.060	−1318.967	−1102.867	72.010
900	158.157	331.011	233.520	87.742	−1315.899	−1076.039	62.452
1000	160.682	347.807	244.122	103.685	−1312.823	−1049.552	54.823
1100	163.033	363.233	254.258	119.872	−1309.748	−1023.374	48.596
1200	165.209	377.513	263.942	136.286	−1306.700	−997.475	43.419
1200.000	165.209	377.513	263.942	136.286	GLASS <- -> LIQUID TRANSITION		
1200.000	213.384	377.513	263.942	136.286			
1300	213.384	394.593	273.344	157.624	−1298.979	−972.021	39.056
1400	213.384	410.407	282.576	178.963	−1291.523	−947.152	35.339
1500	213.384	425.129	291.595	200.301	−1284.329	−922.807	32.135
1600	213.384	438.900	300.375	221.639	−1277.389	−898.933	29.347
1700	213.384	451.836	308.908	242.978	−1270.723	−875.485	26.900
1800	213.384	464.033	317.191	264.316	−1264.336	−852.422	24.737
1818.000	213.384	466.156	318.655	268.157	II <- -> LIQUID		
1900	213.384	475.570	325.226	285.655	−1258.250	−829.705	22.810
2000	213.384	486.515	333.019	306.993	−1252.480	−807.301	21 085
2100	213.384	496.926	340.578	328.331	−1247.045	−785.177	19.530
2200	213.384	506.853	347.912	349.670	−1287.728	−763.093	18 118
2300	213.384	516.338	355.030	371.008	−1283.291	−739.346	16.791
2400	213.384	525.420	361.942	392.347	−1278.900	−715.792	15.579
2500	213.384	534.131	368.657	413.685	−1274.552	−692.418	14.467
2600	213.384	542.500	375.183	435.023	−1270.247	−669.218	13.445
2700	213.384	550.553	381.530	456.362	−1265.984	−646.182	12.501
2800	213.384	558.313	387.706	477.700	−1261.761	−623.303	11.628
2900	213.384	565.801	393.719	499.039	−1257.579	−600.576	10.818
3000	213.384	573.035	399.576	520.377	−1253.435	−577.991	10.064

PREVIOUS: CURRENT June 1973

Vanadium Oxide (V_2O_4) CRYSTAL(I–II)-LIQUID

0	to	340	K	crystal, I
340	to	1818	K	crystal, II
above		1818	K	liquid

Refer to the individual tables for details.

M_r = 165.8806 Vanadium Oxide (V_2O_4) $O_4V_2(cr,l)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−18.100	−1418.617	−1418.617	INFINITE
100	36.907	18.652	186.891	−16.824	−1424.127	−1389.894	726.006
200	90.274	62.333	113.357	−10.205	−1427.002	−1354.252	353.694
298.15	115.399	103.525	103.525	0.000	−1427.162	−1318.445	230.986
300	115.787	104.240	103.527	0.214	−1427.150	−1317.770	229.444
340.000	123.336	119.218	104.501	5.004		I <−−> II	
340.000	127.621	145.675	104.501	13.999		TRANSITION	
400	135.281	167.065	112.309	21.902	−1416.532	−1283.094	167.555
500	143.269	198.162	126.456	35.853	−1414.020	−1250.016	130.588
600	148.448	224.758	140.677	50.448	−1411.187	−1217.477	105.991
700	152.175	247.927	154.379	65.483	−1408.212	−1185.426	88.458
800	155.457	268.466	167.380	80.868	−1405.169	−1153.807	75.336
900	158.157	286.934	179.655	96.551	−1402.101	−1122.571	65.152
1000	160.682	303.729	191.236	112.494	−1399.025	−1091.677	57.023
1100	162.987	319.153	202.173	128.678	−1395.953	−1061.091	50.387
1200	165.209	333.430	212.523	145.089	−1392.908	−1030.784	44.869
1300	167.330	346.738	222.341	161.716	−1389.898	−1000.729	40.210
1400	169.406	359.215	231.677	178.553	−1386.944	−970.904	36.225
1500	171.429	370.972	240.575	195.595	−1384.045	−941.289	32.779
1600	173.427	382.100	249.076	212.838	−1381.201	−911.865	29.769
1700	175.302	392.669	257.214	230.273	−1378.439	−882.616	27.119
1800	177.343	402.746	265.022	247.904	−1375.760	−853.528	24.769
1818.000	177.728	404.513	266.394	251.100		II <−−> LIQUID	
1818.000	213.384	466.156	266.394	363.168		TRANSITION	
1900	213.384	475.570	275.220	380.666	−1258.250	−829.705	22.810
2000	213.384	486.515	285.513	402.004	−1252.480	−807.301	21.085
2100	213.384	496.926	295.335	423.342	−1247.045	−785.177	19.530
2200	213.384	506.853	304.725	444.681	−1287.728	−763.093	18.118
2300	213.384	516.338	313.721	466.019	−1283.291	−739.346	16.791
2400	213.384	525.420	322.354	487.358	−1278.900	−715.792	15.579
2500	213.384	534.131	330.652	508.696	−1274.552	−692.418	14.467
2600	213.384	542.500	338.640	530.034	−1270.247	−669.218	13.445
2700	213.384	550.553	346.341	551.373	−1265.984	−646.182	12.501
2800	213.384	558.313	353.773	572.711	−1261.761	−623.303	11.628
2900	213.384	565.801	360.956	594.050	−1257.579	−600.576	10.818
3000	213.384	573.035	367.906	615.388	−1253.435	−577.991	10.064

PREVIOUS. CURRENT. December 1973

$S°$(298.15 K) = 143.114 ± 1.3 J·K^{-1}·mol^{-1}
T_{fus} = 2058 ± 30 K

$\Delta_f H°$(0 K) = −2035.947 ± 4.2 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = −2045.976 ± 4.2 kJ·mol^{-1}
$\Delta_{fus}H°$ = [120.081 ± 16.7] kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H°$(Ta_2O_5, cr, 298.15 K) values show scatter due to uncertainties concerning the polymorphic state of the sample and/or the incomplete specification of sample purity.[1] The reported values for $\Delta_f H°$(Ta_2O_5, cr, 298.15 K) based on bomb calorimetry studies are as follows:

Source	Ta(cr) purity,%	% run*	$\Delta_f H°$(Ta2O5,cr,2 918.15K) kcal·mol^{-1}
2			309.5
3	99.96	>99.0	−498.3
4			−480.5
5	99.9	72.92–93.83	−486.0 ± 0.5
6			−499.9 ± 1.0
7	99.89	97.23–99.99	−489.0 ± 0.5**
8	99.80		−487.7 ± 0.9
9	99.16, 99.7	99.5–99.9	−489.3 ± 0.4
10			−480.0 ± 0.8

*Refers to extent of reaction 2 Ta(cr) + 5/2 O_2(g) = Ta_2O_5(cr)
**The reported value of −488.8 ± 0.5 was corrected by Huber *et al.*[8] in order to have the value based on the current atomic weight of Ta.

The value chosen for $\Delta_f H°$(Ta_2O_5, cr, 298.15 K) is −489.0 ± 0.5 based primarily on the work by Humphrey[7] and Kornilov *et al.*[9] Worrell,[17] using a high temperature galvanic cell, obtained $\Delta_f G$β values of Ta_2O_5 in the range 1050–1300 K which are approximately 0.6–1.1 kcal·mol^{-1} more negative than the values tabulated here. Ignatowicz and Davies[12] using a galvanic cell approach reported $\Delta_f G°$ values for Ta_2O_5 in the range 1073–1373 K. Barbi[11 13] determined $\Delta_f G°$ based on emf measurements in the range 1079–1776 K while Rezukhina and Kravchenko[16] worked in the range 1200–1350 K. A third law analysis of the reported smoothed results yields the following.

Source	$\Delta_f H°$(298.15 K), kcal·mol^{-1}	cal·K^{-1}·mol^{-1}
11	−484.8	0.85
12	−487.9	−0.65
13*	−484.7	+0.95
16	−487.9	+0.83

*Actual experimental data was analyzed.

These latter three works[12,13,16] did not specify purity of sample or the state of polymorphism.

Based on the recent critical review by Reisman and Holtzberg,[1] this discussion has been concerned with the low temperature β–phase of Ta_2O_5. Even though two $\Delta_f H°$(298.15 K) studies[9,10] apparently deal with the high temperature α phase, there does not appear to be any difference in the $\Delta_f H°$(298.15 K) values for the α phase or β–phase, within experimental error.[1]

Heat Capacity and Entropy

Kelley[14] measured the heat capacity of Ta_2O_5(cr) from 53.4 K to 294.2 K and fitted the data (29 data points) with a combination of Debye and Einstein functions. These functions were used to calculate $S°$(50 K) = 2.47 cal·K^{-1}·mol^{-1}. Orr[15] measured the enthalpy of Ta_2O_5(cr) from 395.6 K to 1802.6 K (15 data points). Nine data points at the high temperature end of the Kelley data were fitted by a four term polynomial, and integrated to yield enthalpy values in the vicinity of 298.15 K. These enthalpy values were combined with the Orr data, fitted to a six term polynomial, and extrapolated to 2800 K. The complete Kelley data was also fitted by a six term polynomial. The Nb_2O_5 heat capacity and enthalpy data presented in these tables are treated in the same manner so as to maintain consistency between the results for Nb_2O_5 and Ta_2O_5.

The Ta_2O_5(cr) sample used by Kelley[14] and Orr[15] was the same. Presumably both were using the low temperature β phase of Ta_2O_5, as discussed by Reisman and Holtzberg[1] and Orr.[15] The enthalpy data of Orr[15] did not conclusively indicate any phase transitions, i.e., the β → α transition, in the vicinity of 1633 K, as reported by Reisman and Holtzberg.[1]

Fusion Data

Refer to the liquid table for details.

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−23.041	−2035.947	−2035.947	INFINITE
100	58.082	37.108	243.530	−20.642	−2042.799	−1999.955	1044.669
200	108.311	94.161	154.766	−12.121	−2046.060	−1955.515	510.728
298.15	135.034	143.114	143.114	0.000	−2045.976	−1911.004	334.800
300	135.342	143.950	143.116	0.250	−2045.956	−1910.167	332.590
400	147.515	184.681	148.588	14 437	−2044.314	−1865.126	243.561
500	156.862	218.636	159.293	29.671	−2041.946	−1820.591	190.196
600	164.431	247.930	171.680	45.750	−2039.087	−1776.582	154.665
700	170.431	273.746	184.453	62.505	−2035.876	−1733.081	129.324
800	175.197	296.825	197.083	79.794	−2032.397	−1690.059	110.350
900	179.038	317.683	209.342	97.507	−2028.710	−1647.487	95.618
1000	182.753	336.753	221.144	115.610	−2024.820	−1605.335	83.854
1100	184.824	354.267	232.461	133.987	−2020.837	−1563.579	74.248
1200	187.071	370.448	243.294	152.584	−2016.807	−1522.187	66.259
1300	189.021	385.500	253.661	171.391	−2012.725	−1481.134	59.513
1400	190.740	399.572	263.586	190.380	−2008.590	−1440.398	53.742
1500	192.280	412.785	273.096	209.533	−2004.394	−1399.959	48.751
1600	193.673	425.239	282.220	228.831	−2000.138	−1359.802	44.393
1700	194.953	437.020	290.982	248.263	−1995.845	−1319.912	40.556
1800	196.138	448.197	299.409	267.819	−1991.558	−1280.276	37.153
1900	197.246	458.831	307.522	287.488	−1987.315	−1240.876	34.114
2000	198.288	468.975	315.343	307.265	−1983.130	−1201.698	31.385
2058.000	198.870	474.652	319.753	318.783	--- CRYSTAL <--> LIQUID ---		
2100	199.278	478.674	322.891	327.144	−1979.005	−1162.728	28.921
2200	200.225	487.967	330.185	347.120	−1974.946	−1123.952	26.686
2300	201.133	496.887	337.240	367.188	−1970.962	−1085.361	24.649
2400	202.012	505.466	344.072	387.345	−1967.065	−1046.941	22.786
2500	202.859	513.730	350.694	407.589	−1963.269	−1008.681	21.075
2600	203.685	521.702	357.119	427.916	−1959.594	−970.570	19.499
2700	204.491	529.404	363.358	448.325	−1956.062	−932.597	18.042
2800	205.275	536.855	369.422	468.814	−1952.699	−894.753	16.692

PREVIOUS: CURRENT: December 1972

Continued on page 1815

Tantalum Oxide (Ta_2O_5) LIQUID $M_r = 441.89128$

$S°(298.15\ K) = [183.050]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2058 \pm 30\ K$

$\Delta_f H°(298.15\ K) = [-1957.171]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [120.081 \pm 16.7]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Ta_2O_5, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2058\ K)–H°(298.15\ K)$, between $Ta_2O_5(cr)$ and $Ta_2O_5(l)$.

Heat Capacity and Entropy

The heat capacity for $Ta_2O_5(l)$ is estimated to be 58.00 $cal \cdot K^{-1} \cdot mol^{-1}$ by analogy with $Nb_2O_5(l)$. A glass transition temperature is assumed at 1400 K. The heat capacity values used below 1400 K are those of $Ta_2O_5(cr)$. The entropy at 298.15 K is calculated in a manner analogous to that used in calculating the enthalpy of formation.

Fusion Data

The melting point of β Ta_2O_5 is chosen as 2058 ± 30 K based on work by Reisman *et al.*[1] The melting point data and the Ta_2O_5 polymorphism are discussed by Reisman and Holtzberg[2] The heat of fusion, $\Delta_{fus}H°$, is estimated from the entropy of fusion for Nb_2O_5 as reported in these tables. Using the Nb_2O_5 entropy of fusion value of 24.92 $cal \cdot K^{-1} \cdot mol^{-1}$ and a melting temperature of 2058 K, the enthalpy of fusion for Ta_2O_5 is calculated to be 28.7 ± 4 $kcal \cdot mol^{-1}$.

References

[1] A. Reisman, F. Holtzberg, M. Berkenblit, and M. Berry, J. Amer. Chem. Soc. 8, 4514 (1956).
[2] A. Reisman and F. Holtzberg, High Temperature Oxides 2, 217 (1970).

Tantalum Oxide (Ta_2O_5) $O_5Ta_2(l)$

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	135.034	183.050	183.050	0.000	−1957.171	−1834.107	321.328
300	135.342	183.886	183.052	0.250	−1957.151	−1833.343	319.213
400	147.515	224.617	188.524	14.437	−1955.509	−1792.296	234.050
500	156.862	258.572	199.230	29.671	−1953.141	−1751.754	183.005
600	164 431	287.866	211.616	45.750	−1950.282	−1711.739	149.020
700	170.431	313.682	224.389	62.505	−1947.071	−1672.231	124.783
800	175.197	336.761	237.019	79.794	−1943.592	−1633.204	106.637
900	179.038	357.619	249.279	97.507	−1939.905	−1594.624	92.550
1000	182.753	376.690	261.080	115.610	−1936.016	−1556.467	81.301
1100	184.824	394.203	272.397	133.987	−1932.032	−1518.704	72.117
1200	187.071	410.384	283.230	152.584	−1928.002	−1481.306	64.480
1300	189.021	425.436	293.597	171.391	−1923.920	−1444.247	58.031
1400	190.740	439.508	303.522	190.381	−1919.785	−1407.503	52.515
1400.000	190.740	439.508	303.522	190.381	GLASS <−−> LIQUID		
1400.000	242.672	439.508	303.522	190.381	TRANSITION		
1500	242.672	456.251	313.152	214.648	−1910.474	−1371.238	47.751
1600	242.672	471.913	322.591	238.915	−1901.249	−1335.590	43.603
1700	242.672	486.624	331.811	263.182	−1892.121	−1300.516	39.960
1800	242.672	500.495	340.801	287.450	−1883.122	−1265.977	36.738
1900	242.672	513.616	349.554	311.717	−1874.282	−1231 933	33.868
2000	242.672	526.063	358.071	335.984	−1865.606	−1198.350	31.298
2058.000	242.672	533.001	362.904	350.059	−−− CRYSTAL <−−> LIQUID −−−		
2100	242.672	537.903	366.355	360.251	−1857.093	−1165.197	28.983
2200	242.672	549.192	374.411	384.518	−1848.743	−1132.445	26.888
2300	242.672	559.980	382.247	408.786	−1840.560	−1100.071	24.983
2400	242.672	570.308	389.869	433.053	−1832.552	−1068.049	23.245
2500	242.672	580.214	397.286	457.320	−1824.733	−1036.356	21.653
2600	242.672	589.732	404.506	481.587	−1817.118	−1004.971	20.190
2700	242.672	598.890	411.537	505.854	−1809.728	−973.875	18.841
2800	242.672	607.716	418.386	530.122	−1802.587	−943.049	17.593
2900	242.672	616.231	425.063	554.389	−1795.721	−912.475	16.435
3000	242.672	624.458	431.573	578.656	−1789.164	−882.130	15.359
3100	242.672	632.415	437.924	602.923	−1782.950	−851.997	14.356
3200	242.672	640.120	444.123	627.190	−1777.119	−822.063	13.419
3300	242.672	647.587	450.176	651.458	−1844 626	−791.361	12.526
3400	242.672	654.832	456.089	675.725	−1838.846	−759.529	11.669
3500	242.672	661.866	461.869	699.992	−1833.107	−727.869	10.863
3600	242.672	668.703	467.519	724.259	−1827.406	−696.371	10.104
3700	242.672	675.352	473.047	748.526	−1821.742	−665.033	9.389
3800	242.672	681.823	478.456	772.794	−1816.114	−633.844	8.713
3900	242.672	688.127	483.752	797.061	−1810.520	−602.804	8.074
4000	242.672	694.271	488.939	821.328	−1804.960	−571.909	7.468
4100	242.672	700.263	494.020	845.595	−1799.432	−541.151	6.894
4200	242.672	706.111	499.001	869.862	−1793.936	−510.528	6.349
4300	242.672	711.821	503.884	894.130	−1788.471	−480.034	5.831
4400	242.672	717.400	508.673	918.397	−1783.036	−449.670	5.338
4500	242.672	722.853	513.372	942.664	−1777.632	−419.428	4.869
4600	242.672	728.187	517.984	966.931	−1772.258	−389.306	4.421
4700	242.672	733.406	522.513	991.198	−1766.916	−359.298	3.993
4800	242.672	738.515	526.960	1015.466	−1761.604	−329.405	3.585
4900	242.672	743.519	531.328	1039.733	−1756.324	−299.621	3.194
5000	242.672	748.421	535.621	1064.000	−1751.077	−269.945	2.820

PREVIOUS: CURRENT: December 1972

Tantalum Oxide (Ta_2O_5) $O_5Ta_2(l)$

Tantalum Oxide (Ta_2O_5) CRYSTAL-LIQUID

0	to	2058	K crystal
above		2058	K liquid

Refer to the individual tables for details.

M_r = 441.8928 Tantalum Oxide (Ta_2O_5) $O_5Ta_2(cr,l)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.000	0.000	INFINITE	−23.041	−2035.947	−2035.947	INFINITE
100	58.082	37.108	243.530	−20.642	−2042.799	−1999.955	1044.669
200	108.311	94.161	154.766	−12.121	−2046.060	−1955.515	510.728
298 15	135.034	143.114	143.114	0.000	−2045.976	−1911.004	334.800
300	135.342	143.950	143.116	0.250	−2045.956	−1910.167	332.590
400	147.515	184.681	148.588	14 437	−2044.314	−1865 126	243.561
500	156.862	218.636	159.293	29.671	−2041.946	−1820.591	190.196
600	164.431	247.930	171.680	45.750	−2039.087	−1776.582	154.665
700	170.431	273.746	184.453	62.505	−2035.876	−1733.081	129.324
800	175.197	296.825	197.083	79.794	−2032.397	−1690.059	110.350
900	179.038	317.683	209.342	97.507	−2028.710	−1647.487	95.618
1000	182.753	336.753	221.144	115.610	−2024.820	−1605.335	83.854
1100	184.824	354.267	232.461	133.987	−2020.837	−1563.579	74.248
1200	187.071	370.448	243.294	152.584	−2016.807	−1522.187	66.259
1300	189.021	385.500	253.661	171.391	−2012.725	−1481.134	59.513
1400	190.740	399.572	263.586	190.380	−2008.590	−1440.398	53.742
1500	192.280	412.785	273.096	209.533	−2004.394	−1399.959	48.751
1600	193.673	425.239	282.220	228.831	−2000.138	−1359.802	44.393
1700	194.953	437.020	290.982	248.263	−1995.845	−1319.912	40.556
1800	196.138	448.197	299.409	267.819	−1991.558	−1280.276	37.153
1900	197.246	458.831	307.522	287.488	−1987.315	−1240.876	34.114
2000	198.288	468.975	315.343	307.265	−1983.130	−1201.698	31.385
2058.000	198.870	474 652	319.753	318.783	CRYSTAL <−−> LIQUID		
2058.000	242.672	533.001	319.753	438.864		TRANSITION	
2100	242.672	537.903	324.067	449.056	−1857.093	−1165.197	28.983
2200	242.672	549.192	334.045	473.323	−1848.743	−1132.445	26.888
2300	242.672	559.980	343.636	497.591	−1840.560	−1100.071	24.983
2400	242.672	570.308	352.867	521.858	−1832.552	−1068.049	23.245
2500	242.672	580.214	361 764	546.125	−1824.733	−1036.355	21.653
2600	242.672	589.732	370.350	570.392	−1817 118	−1004.971	20.190
2700	242.672	598.890	378.646	594.659	−1809.728	−973.875	18.841
2800	242.672	607.716	386.670	618.927	−1802.587	−943 049	17.593
2900	242.672	616.231	394.440	643.194	−1795.721	−912 475	16.435
3000	242.672	624.458	401.971	667 461	−1789.164	−882.130	15.359
3100	242.672	632.415	409.277	691.728	−1782.950	−851.997	14.356
3200	242.672	640.120	416.371	715.995	−1777.119	−822.063	13.419
3300	242.672	647.587	423.265	740.263	−1844.626	−791.361	12.526
3400	242.672	654.832	429.970	764.530	−1838.846	−759.529	11.669
3500	242.672	661.866	436.496	788.797	−1833 107	−727 869	10.863
3600	242.672	668.703	442.851	813.064	−1827.406	−696.371	10 104
3700	242.672	675.352	449.046	837.331	−1821.742	−665.033	9.389
3800	242.672	681.823	455.087	861.599	−1816.114	−633.844	8.713
3900	242.672	688.127	460 982	885.866	−1810.520	−602.804	8.074
4000	242.672	694.271	466.737	910.133	−1804.960	−571.909	7.468
4100	242.672	700.263	472.360	934.400	−1799.432	−541.151	6.894
4200	242.672	706.111	477.857	958.667	−1793.936	−510.528	6.349
4300	242.672	711.821	483.231	982.935	−1788.471	−480 034	5.831
4400	242.672	717.400	488.490	1007.202	−1783.036	−449.670	5.338
4500	242.672	722.853	493.638	1031.469	−1777.632	−419.428	4.869
4600	242.672	728.187	498.679	1055.736	−1772.258	−389.306	4 421
4700	242.672	733.406	503.618	1080.003	−1766.916	−359.298	3.993
4800	242.672	738.515	508.459	1104.271	−1761.604	−329.405	3.585
4900	242.672	743.519	513.205	1128.538	−1756.324	−299.621	3.194
5000	242.672	748.421	517.860	1152.805	−1751.077	−269.945	2.820

PREVIOUS.   CURRENT· December 1972

Titanium Oxide, Alpha (α–Ti_3O_5) CRYSTAL M_r = 223.6370

$\Delta_fH°(0\ K) = -2446.057\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 129.369 \pm 1.7\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -2459.146 \pm 4.2\ kJ \cdot mol^{-1}$

$T_{trs}(\alpha \rightarrow \beta) = 450 \pm 20\ K$ $\Delta_{trs}H° = [13.263 \pm 5.0]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(298.15\ K) = -587.75\ kcal \cdot mol^{-1}$ is calculated from that of TiO_2(rutile) using $\Delta_cH° = -89.65 \pm 0.05\ kcal \cdot mol^{-1}$ determined by Humphrey[1] from combustion calorimetry. Ariya *et al.*[2] reported $\Delta_fH° = -587.0 \pm 1.0\ kcal \cdot mol^{-1}$ derived from their own values of $\Delta_cH°$ for $Ti_3O_{5.03}$ and Ti(cr). Tests for incomplete combustion were made by grinding the product and igniting it to constant weight in air[1] or in moist oxygen.[2] Humphrey[1] reported that his rutile was bright yellow in color and did not gain weight. This implies an atomic ratio (0/Ti) ≥2.00, compared with the value of ~1.95 reported by Ariya *et al.*[2] New high–temperature calorimetry by Charlu *et al.*[9] gave $\Delta_cH°(1100) = -93.57 \pm 1.3\ kcal \cdot mol^{-1}$ after linear correction to (0/Ti) = 2.00 from 1.97 produced by combustion. Our reduction to 298 K and $Ti_3O_5(\alpha)$ yields $\Delta_cH° = -90.36 \pm 2.5\ kcal \cdot mol^{-1}$, including an assumed uncertainty allowance of 1% for the weight gains.

The calorimetric data are compared below with new high–temperature data for $\Delta_rG°$.[3,4] Emf data[4] for reaction B are consistent with the adopted $\Delta_fH°$, but integrated values of $\Delta_rG°$ for reaction A yield $\Delta_fH°$ more negative by 1.8 $kcal \cdot mol^{-1}$. Perhaps coincidentally, the $\Delta_cH°$ of Ariya *et al.*[2] yields $\Delta_fH°$ more negative by 1.9 $kcal \cdot mol^{-1}$ when combined with the JANAF $\Delta_fH°$[5] for TiO_2(rutile). Merritt *et al.*[3] obtained $\Delta_rG°$ for the combustion reaction A by integrating extensive data for equilibrium oxygen potentials of the many stable phases and solid solutions between TiO_2 and Ti_3O_5. They determined the oxide composition by mass during equilibration with ($H_2 + H_2O$) gas mixtures of known oxygen potential. Gross hysteresis was observed in three regions of composition. Oxygen potentials in these regions were deduced with a reasonable assumption, combined with Zador's emf data for oxygen–deficient rutile, and integrated to yield $\Delta_rG°(1304\ K) = -56.14 \pm 0.43\ kcal \cdot mol^{-1}$ for reaction A. We obtain $\Delta_rG° = -57.30\ kcal \cdot mol^{-1}$ at 1273 K and − 51.15 at 1473 K by similar integrations of oxygen potentials derived from emf data relative to Fe/FeO and Cr/Cr_2O_3 reported by Suzuki and Sambongi.[4]

Suzuki and Sambongi[4] also reported solid–state emf data which relate Ti_3O_5 to Ti_2O_3. We convert their (graphical) emf data[4] to oxygen potentials using the authors' self–consistent data for the reference couples. The results for reaction B yield $\Delta_rH°$ and $\Delta_rS°$ values consistent with our adopted tables. 3rd law values of $\Delta_rH°(298.15\ K)$ of −42.29, −42.15 and −42.13 $kcal \cdot mol^{-1}$agree with −42.52[1], −42.8 ± 1.3[2] and −42.0[9] which can be calculated from combustion calorimetry.

The discrepancy in reaction A may be due to undetected bias (2% too small in magnitude) in $\Delta_rG°$, but alternative possibilities include bias in $S°$ (see Ti_3O_5, β), $\Delta_cH°$ or enthalpy (see TiO_2, rutile).

Source	Method	Reaction[a]	T/K	δS cal·K⁻¹·mol⁻¹	$\Delta_rH°$(298.15 K) kcal·mol⁻¹	$\Delta_fH°$(298.15 K), kcal·mol⁻¹ Authors	 JANAF
1	$\Delta_cH°$	A	303→298	–	−89.65 ± 0.05	−586.9 ± 0.7	−587.75 ± 09
2	$\Delta_cH°$	A	293	–	−87.7	−587.0 ± 1.0	−589.7
9	$\Delta_cH°$	A	1100→298	–	−90.36 ± 2.5	−586.3	−587.0 ± 2.7
3	$\Delta_rG(O_2)$	A	1304	–	−87.81 ± 0.6	–	−589.6 ± 1.1
4	$\Delta_rG(O_2)$, emf	A	1273–1473	−3.5	−87.81 ± 1	–	−589.6 ± 1.4
4	emf, Cr/Cr_2O_3	B[b]	~940–1740	0.6	−42.29	–	−587.5[d]
	emf, Ta/Ta_2O_5	B[b]	~1100–1750	0.0	−42.15	–	−587.4[d]
	emf, "$TiO_{1.3}$"	B[b]	~1300–1700	0.0	−42.13	–	−587.4[d]

[a] Reactions: A) $Ti_3O_5(\alpha, \beta) + 1/2\ O_2 \rightarrow 3\ TiO_2$(rutile); B)$3/2\ Ti_2O_3(\alpha, \beta) + 1/4\ O_2 \rightarrow Ti_3O_5(\alpha, \beta)$.

[b] $\Delta_rG°$ from integration of Δ_rG(O)assuming negligible homogeneity range for TiO. Alternative $\Delta G°$, assuming a linear variation of $\Delta_f\bar{G}°(O_2)$ for 1.42 < X < 1.56, changes δS by ~0.2 and $\Delta_rH°$ and $\Delta_fH°$ by ~−0.3.

Heat Capacity and Entropy

$C_p°$ below 300 K is based on data of Shomate, (53–297 K)[6] and his Debye–Einstein extrapolation to absolute zero. The entropy is calculated by polynomial integration of $C_p°$ based on $S°(50\ K) = 0.87\ cal \cdot K^{-1} \cdot mol^{-1}$. Our assigned entropy uncertainty of $\pm 0.4\ cal \cdot K^{-1} \cdot mol^{-1}$ includes an additional contribution because the sample gave weak, fuzzy x–ray lines and was only 99.1% pure. Apparently there are new $C_p°$ data (12–300 K) which are unpublished and not yet available.[10] $C_p°$ is extrapolated smoothly from 300 K to 450 K and to higher temperatures where $Ti_3O_5(\beta)$ is the stable form. Our extrapolation probably represents the lower limit for the true $C_p°$ below T_{trs}, while the curve of Furukawa and Reilly[7] is an upper limit. The equations reported by Naylor[8] yield even higher enthalpies and fail to join properly with the low temperature data at 298 K. This is due to complications in the enthalpy data (see below) and to positive bias in the drop calorimeter in this temperature range.[5]

Naylor[8] measured enthalpy data (326–1340 K) which revealed a transition at ~450 K. When the samples were heated above this temperature, they did not return to the original state on cooling. Enthalpies were then systematically higher by up to 10%. The change in the enthalpy curve seemed to depend on both the temperature and time of heating above T_{trs}. Regrinding was the only method found for returning the sample to its original state. X–ray diffraction at room temperature revealed no difference between these two states, but failure to detect a difference may be due to the weak, fuzzy x–ray lines.[6,8] Possible explanations for the anomalous enthalpy data are noted in Transition Data.

Transition Data

Refer to the β–crystal table for details

Continued on page 1816

Titanium Oxide, Alpha (Ti_3O_5) $O_5Ti_3(cr)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.000	0.000	INFINITE	−23.108	−2446.057	−2446.057	INFINITE
100	46.116	21.062	237.166	−21.610	−2453.501	−2409.803	1258.752
200	114.445	75.659	142.352	−13.339	−2458.258	−2363.911	617.390
298.15	154.808	129.369	129.369	0.000	−2459.146	−2317.293	405.980
300	155.477	130.329	129.372	0.287	−2459.135	−2316.413	403.323
400	182.841	179.228	135.852	17.350	−2457.340	−2269.052	296.308
450	189.954	201.217	141.909	26.688	−2455.868	−2245.602	260.663
500	194.138	221.452	148.866	36.293	−2454.266	−2222.324	232.165
600	200.832	257.461	164.038	56.054	−2450.880	−2176.251	189.459
700	206.062	288.828	179.673	76.409	−2447.326	−2130.758	158.999
800	210.037	316.611	195.087	97.219	−2443.632	−2085.786	136.188
900	213.384	341.551	209.999	118.397	−2439.941	−2041.278	118.473
1000	215.894	364.163	224.302	139.861	−2436.495	−1997.170	104.321
1100	218.405	384.861	237.971	161.579	−2433.495	−1953.386	92.759
1200	220.497	403.954	251.017	183.524	−2442.906	−1909.496	83.118
1300	222.589	421.689	263.472	205.682	−2438.647	−1865.218	74.945
1400	224.262	438.246	275.371	228.025	−2434.515	−1821.264	67.952
1500	225.936	453.775	286.752	250.535	−2430.558	−1777.600	61.902

PREVIOUS: March 1967 CURRENT: December 1973

Titanium Oxide, Beta (β–Ti_3O_5) CRYSTAL M_r = 223.6370 Titanium Oxide, Beta (Ti_3O_5) $O_5Ti_3(cr)$

$S°(298.15\ K) = [157.617]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = [-2446.189]\ kJ{\cdot}mol^{-1}$

$T_{trs}(\alpha \rightarrow \beta) = 450 \pm 20\ K$ $\Delta_{trs}H°[13.263 \pm 5.0]\ kJ{\cdot}mol^{-1}$

$T_{fus} = 2050 \pm 20\ K$ $\Delta_{fus}H° = [171.544]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_fH°$ is calculated from that of $Ti_3O_5(\alpha)$ by adding $\Delta_{trs}H°$ to the difference in $H°(450\ K)$–$H°(298.15\ K)$ between the α– and β– phases. Experimental data for $\Delta_fG°$ of the β–phase are analyzed on the table for the α–phase.

Heat Capacity and Entropy

$C_p°$ of the β–phase is derived from fitting of enthalpy data of Naylor, (504–1340 K)[1] and Slyusar *et al.*, (580–1994 K).[2] Naylor's data below 482 K are omitted due to thermal hysteresis in the transition; even the points near 500 K show unusual scatter. The new data of Slyusar *et al.*[2] are suspect due to a discontinuity of almost 4% at ~1250 K where the authors switched container materials and temperature sensors. Their data[2] for Ti_2O_3 and TiO_2(rutile) show similar discontinuities and appear to have a bias of about −4% below 1100 K. Their data for Ti_3O_5 do not differ significantly from those of Naylor,[1] so we combine the two sets.

$S°$ is calculated in a manner analogous to that of $\Delta_fH°$. The uncertainty in $S°$ may be as large as ±2.6 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ due to uncertainty in $\Delta_{trs}H°$, if significant fractions of the β–phase failed to revert to the α–phase during drop calorimetry.[1,2] Naylor's data[1] suggest that this may be the case, but Slyusar *et al.*[2] make no mention of the problem (see Transition Data). Excluding this possible uncertainty, we estimate that $S°$ of $Ti_3O_5(\beta)$ is uncertain by ±0.6 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

Transition Data and Phase Data

Ti_3O_5 has been identified in three crystalline structures. Low–temperature α–Ti_3O_5 is monoclinic,[3] high–temperature β–Ti_3O_5 is a pseudobrookite type with slight monoclinic distortion[3] and metastable γ–Ti_3O_5[4] is analogous to V_3O_5.[3 4] Based on its similarity to V_3O_5, γ is the lowest member of the homologous series of phases Ti_nO_{2n-1} with structures related to rutile.[9 10] The magnetic anomaly, observed near 250 K in γ–Ti_3O_5,[4] corresponds to those observed at lower temperatures in Ti_4O_7 and higher homologues. We give the subsequent phase observations because they may have bearing on the anomalous enthalpy data and the discrepancy in $\Delta_fG°$ at high temperatures.

Our designations for the stable phases α and β are reversed from those of Asbrink *et al.*[4] These phases were called M– type (our α), D–type and D'–type (our β) by Iwasaki *et al.*[11] D– and D'–types differed only in their low–temperature oxidation products; D–type gave rutile, while D'–type gave mixtures of anatase and rutile.[11] D–type was obtained by H_2–reduction of anatase and D'–type by action of H_2 on rutile and Ti or CO on either anatase or rutile. D–type presumably is metastable; Iwasaki *et al.*[11] postulated free energy diagrams to explain conversion of D–type to other forms. The observations also can be explained be assuming that conversion of D–type is hindered kinetically, like TiO_2(anatase) → TiO_2(rutile), until gradually activated at elevated temperature. X–ray patterns of D–type, though not well defined, were similar to those of D'–type.[11] Thus, D–type is not the Ti_nO_{2n-1} homologue (γ–Ti_3O_5), as postulated[11] on the basis of oxidation behavior. D– and D'–types may have the same crystal structure but differ in degree of ordering or content of impurities.

Enthalpy data of Naylor[1] gave T_{trs} ~450 K for α → β. X–ray diffraction,[4-6] DTA,[5] magnetic susceptibility,[4,6] and electrical conductivity[5] confirm the transition temperature. The transition is reversible[3,5-7] but exhibits thermal hysteresis of about ±20°.[5,6] More important to interpretation of enthalpy measurements is the observation that the β–phase is stabilized[5, 3] at room temperature by small amounts of impurities such as Fe, W and Mg. Samples doped with 5% Fe did not transform; those with 2% Fe gave a much–reduced endotherm (DTA) at ~75° below the normal T_{trs}.[5] Accidental contamination by W stabilized the β–form.[5]

$\Delta_{trs}H° = 3.17\ kcal{\cdot}mol^{-1}$ is calculated at T_{trs} from the difference in enthalpy between our β–phase curve fit and our adopted α–phase. Alternative enthalpy curves[8] gave $\Delta_{trs}H° = 2.48\ kcal{\cdot}mol^{-1}$. These calculations assume that the β–phase reverted completely to α–phase at room temperature during drop calorimetry.[1 2] Naylor's anomalous enthalpies[1] for the α–phase suggest that part of his sample may have been stabilized in the β–form due to impurities. Other metastable phases may have been present. If the drop–calorimetric samples did not revert completely to α–phase, the true value of $\Delta_{trs}H°$ should be larger than the value calculated on the assumption of complete reversion. $\Delta_fG°$ data (see Ti_3O_5, α) tend to favor an entropy greater than or equal to the adopted value, but DTA data[5] gave $\Delta_{trs}H° = 1.6 \pm 0.4\ kcal{\cdot}mol^{-1}$, opposite to the expected direction. We emphasize this unsatisfactory situation by placing $\Delta_{trs}H°$ in brackets and assigning an uncertainty of ±1.2 $kcal{\cdot}mol^{-1}$. The seeming contradictions should be resolved easily by study of a well–characterized sample in an adiabatic calorimeter or an accurate differential–scanning calorimeter.

Fusion Data and Sublimation Data

Refer to the liquid table for details.

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
0							
100							
200							
298.15	173.962	157.617	157.617	0.000	−2446.189	−2312.759	405.186
300	174.054	158.694	157.621	0.322	−2446.143	−2311.931	402.543
400	179.075	209.454	164.508	17.978	−2443.756	−2267.558	296.113
450	181.586	230.691	170.702	26.995	−2442.604	−2245.602	260.663
500	184.096	249.952	177.679	36.137	−2441 465	−2223.774	232.316
600	189.117	283.961	192.632	54.798	−2439.180	−2180.450	189.825
700	194.138	313.490	207.833	73.960	−2436.818	−2137.514	159.503
800	199.158	339.742	222.710	93.625	−2434.270	−2094.928	136.785
900	204.179	363.489	237.053	113.792	−2431.589	−2052.670	119.134
1000	209.200	385.261	250.800	134.461	−2428.938	−2010.711	105.029
1100	214.221	405.436	263.952	155.632	−2426.485	−1969.009	93.500
1200	219.242	424.291	276.536	177.305	−2436.168	−1927.162	83.887
1300	224.262	442.038	288.591	199.480	−2431.892	−1884.917	75.737
1400	229.283	458.841	300.157	222.158	−2427.425	−1843.008	68.763
1500	234.304	474.831	311.273	245.337	−2422.799	−1801.425	62.731
1600	239.325	490.113	321.976	269.018	−2418.050	−1760.154	57.463
1700	244.346	504.773	332.301	293.202	−2413.214	−1719.183	52.824
1800	249.366	518.881	342.277	317.888	−2408.329	−1678.499	48.709
1900	254.387	532.498	351.932	343.075	−2403.433	−1638.087	45.034
2000	259.408	545.674	361.292	368.765	−2442.627	−1596.570	41.698
2100	264.429	558.452	370.378	394.957	−2440.070	−1554.329	38.662
2200	269.450	570.869	379.210	421.651	−2437.067	−1512.218	35.905
2300	274.470	582.958	387.807	448.847	−2433.619	−1470.256	33.391
2400	279.491	594.745	396.185	476.545	−2429.725	−1428.453	31.089
2500	284.512	606.256	404.358	504.745	−2425.383	−1386.821	28.976

PREVIOUS: March 1967 CURRENT: December 1973

$S°(298.15\ K) = [232.446]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_f H°(298.15\ K) = [-2289.059]\ kJ{\cdot}mol^{-1}$

$T_{fus} = 2050 \pm 20\ K$ $\Delta_{fus}H° = [171.544]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Ti_3O_5,\ l,\ 298.15\ K)$ is calculated from that of $Ti_3O_5(\beta l)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2050\ K)-H°(298.15\ K)$, between the β–phase and liquid.

Heat Capacity and Entropy

$C_p°$ is estimated as 8 $cal{\cdot}K^{-1}$ g $atom^{-1}$. Below the assumed glass transition at 1400 K, $C_p°$ is taken to be the same as that of $Ti_3O_5(\beta)$. $S°(298.15\ K)$ is calculated in a manner analogous to that used for $\Delta_f H°$.

Fusion Data

$Ti_3O_5(\beta)$ melts incongruently at 2047 ± 10 K according to Wahlbeck and Gilles.[1] Their phase diagram[1] suggests that melting starts at 2047 K and completes near 2077 K. The latter value is close to the melting point of 2083 K reported by Slyusar *et al.*,[2] but is almost 90° above the value of ~1990 which may be interpolated from the liquidus curve of Brauer and Littke[3] for the Ti–O system. Conversion of the value of Wahlbeck and Gilles[1] to IPTS 68 yields 2050 K, which is adopted.

Sublimation and Vaporization Data

$Ti_3O_5(\beta)$ is the congruently vaporizing crystalline phase in the Ti–O system according to the studies of Gilles and coworkers.[4-6] Studies of liquid samples[7] showed that the congruently vaporizing composition is between Ti_3O_5 and Ti_4O_7. The principal reaction[4] in congruent vaporization is $Ti_3O_5 \rightarrow TiO(g) + 2\ TiO_2(g)$.

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	173.962	232.446	232.446	0.000	−2289.059	−2177.939	381.566
300	174.054	233.522	232.449	0.322	−2289.013	−2177.250	379.093
400	179.075	284.282	239.336	17.978	−2286.625	−2140.359	279.502
500	184.096	324.781	252.507	36.137	−2284.335	−2104.058	219.809
600	189.117	358.789	267.460	54.798	−2282.050	−2068.217	180.054
700	194.138	388.319	282.661	73.960	−2279.687	−2032.764	151.687
800	199.158	414.570	297.539	93.625	−2277.139	−1997.660	130.434
900	204.179	438.318	311.882	113.792	−2274.459	−1962.886	113.923
1000	209.200	460.090	325.629	134.461	−2271.808	−1928.410	100.730
1100	214.221	480.264	338.781	155.632	−2269.355	−1894.191	89.948
1200	219.242	499.119	351.365	177.305	−2279.038	−1859.826	80.956
1300	224.262	516.866	363.420	199.480	−2274.762	−1825.064	73.332
1400	229.283	533.669	374.985	222.158	−2270.295	−1790.638	66.810
1400.000	229.283	533.669	374.985	222.158	GLASS <--> LIQUID		
1400.000	267.776	533.669	374.985	222.158	TRANSITION		
1500	267.776	552.144	386.187	248.935	−2262.071	−1756.666	61.173
1600	267.776	569.426	397.105	275.713	−2254.226	−1723.230	56.258
1700	267.776	585.660	407.724	302.490	−2246.795	−1690.273	51.936
1800	267 776	600.965	418.039	329.268	−2239.818	−1657.741	48.106
1900	267 776	615.443	428.051	356.046	−2233.333	−1625.582	44.690
2000	267.776	629 178	437.767	382.823	−2271.438	−1592.390	41.589
2050.000	267.776	635.790	442.516	396.212	---- BETA <--> LIQUID ----		
2100	267.776	642.243	447.195	409.601	−2268.296	−1558.516	38.766
2200	267.776	654.700	456.346	436.378	−2265.210	−1524.788	36.203
2300	267.776	666.603	465.231	463.156	−2262.180	−1491.201	33.866
2400	267.776	678.000	473.861	489.934	−2259.206	−1457.745	31.727
2500	267.776	688.931	482.246	516.711	−2256.287	−1424.411	29.761
2600	267.776	699.433	490.399	543.489	−2253.421	−1391.193	27.949
2700	267.776	709.539	498.329	570.266	−2250.608	−1358.083	26.274
2800	267.776	719.278	506.048	597.044	−2247.846	−1325 077	24.720
2900	267.776	728.674	513.563	623.822	−2245.133	−1292.170	23.275
3000	267.776	737.752	520.886	650.599	−2242.470	−1259.354	21.927
3100	267.776	746.533	528.024	677.377	−2239.852	−1226.626	20.669
3200	267.776	755.034	534.986	704.154	−2237.280	−1193.984	19.490
3300	267.776	763.274	541.779	730.932	−2234 751	−1161.421	18.384
3400	267.776	771.268	548.412	757.710	−2232.264	−1128.932	17.344
3500	267.776	779.030	554.891	784.487	−2229.818	−1096.518	16.365
3600	267.776	786.574	561.222	811.265	−2227.409	−1064.171	15.441
3700	267.776	793.910	567.412	838.042	−3452.333	−1008.528	14.238
3800	267.776	801.051	573.467	864.820	−3446.295	−942.558	12.956
3900	267.776	808.007	579.392	891.598	−3440.457	−876.746	11.743
4000	267.776	814.787	585.193	918.375	−3434.815	−811.083	10.592

PREVIOUS: March 1967 CURRENT December 1973

Titanium Oxide (Ti_3O_5) CRYSTAL(α-β)-LIQUID

M_r = 223.6370 Titanium Oxide (Ti_3O_5) $O_5Ti_3(cr,l)$

0	to 450	K	crystal, alpha
450	to 2050	K	crystal, beta
above	2050	K	liquid

Refer to the individual tables for details.

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_fH°$ (kJ·mol⁻¹)	$\Delta_fG°$ (kJ·mol⁻¹)	log K_f
0	0.000	0.000	INFINITE	−23.108	−2446.057	−2446.057	INFINITE
100	46.116	21.062	237.166	−21.610	−2453.501	−2409.803	1258.752
200	114.445	75.659	142.352	−13.339	−2458.258	−2363.911	617.390
298.15	154.808	129.369	129.369	0.000	−2459.146	−2317.293	405.980
300	155 477	130.329	129.372	0.287	−2459.135	−2316.413	403.323
400	182.841	179.228	135.852	17.350	−2457.340	−2269.052	296.308
450	189 954	201.217	141.909	26.688	−2455.868	−2245.602	260.663
450.000	181.586	230.691	141.909	39.952	---- ALPHA <--> BETA ----		
500	184.096	249.952	151.765	49.094	−2441 465	−2223 774	232.316
600	189.117	283.961	171.037	67.754	−2439.180	−2180.450	189.825
700	194.138	313.490	189.323	86.917	−2436.818	−2137.514	159.503
800	199 158	339.742	206.514	106.582	−2434.270	−2094.928	136.785
900	204.179	363.489	222.657	126.749	−2431.589	−2052.670	119.134
1000	209.200	385.261	237.844	147.418	−2428.938	−2010.711	105.029
1100	214.221	405.436	252.173	168.589	−2426.485	−1969.009	93.500
1200	219.242	424.291	265.739	190.262	−2436.168	−1927.162	83.887
1300	224.262	442.038	278.624	212.437	−2431.892	−1884.917	75.737
1400	229.283	458.841	290.902	235.114	−2427.425	−1843.008	68.763
1500	234.304	474.831	302.635	258.294	−2422.799	−1801.425	62.731
1600	239.325	490.113	313.878	281.975	−2418.050	−1760.154	57.463
1700	244.346	504.773	324.679	306.159	−2413.214	−1719.183	52.824
1800	249.366	518.881	335.079	330.844	−2408.329	−1678 499	48.709
1900	254.387	532.498	345.113	356.032	−2403.433	−1638.087	45.034
2000	259.408	545.674	354.813	381.722	−2442.627	−1596.570	41.698
2050.000	261.918	552.111	359.547	394.755	BETA <--> LIQUID TRANSITION		
2050.000	267.776	635.791	359.547	566.299			
2100	267 776	642.243	366.201	579.688	−2268.296	−1558.516	38.766
2200	267 776	654.700	379.034	606.465	−2265.210	−1524.788	36.203
2300	267.776	666.603	391.280	633.243	−2262.180	−1491.201	33.866
2400	267.776	678.000	402.991	660.020	−2259.206	−1457.745	31.727
2500	267.776	688.931	414.212	686.798	−2256.287	−1424.411	29.761
2600	267.776	699.433	424.981	713.576	−2253.421	−1391.193	27.949
2700	267.776	709.539	435.334	740.353	−2250.608	−1358.083	26.274
2800	267 776	719.278	445.302	767.131	−2247.846	−1325.077	24.720
2900	267.776	728.674	454.913	793.908	−2245.133	−1292.170	23.275
3000	267.776	737.752	464.190	820.686	−2242 470	−1259.354	21.927
3100	267.776	746.533	473.157	847.464	−2239.852	−1226.626	20.669
3200	267.776	755.034	481.834	874.241	−2237.280	−1193.984	19.490
3300	267 776	763.274	490.238	901.019	−2234.751	−1161.421	18.384
3400	267 776	771.268	498.387	927.796	−2232.264	−1128.932	17.344
3500	267.776	779.030	506.295	954.574	−2229.818	−1096.518	16.365
3600	267.776	786.574	513.976	981.352	−2227.409	−1064.171	15 441
3700	267.776	793.910	521.443	1008.129	−3452.333	−1008.528	14.238
3800	267.776	801.051	528.708	1034.907	−3446.295	−942.558	12.956
3900	267.776	808.007	535.780	1061.684	−3440.457	−876.746	11.743
4000	267.776	814.787	542.671	1088.462	−3434.815	−811.083	10.592

PREVIOUS.   CURRENT December 1973

Vanadium Oxide (V_2O_5) CRYSTAL $M_r = 181.8800$

$\Delta_f H°(0\ K) = -1541.109 \pm 6.3\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = 130.549 \pm 2.1\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -1550.590 \pm 6.3\ kJ \cdot mol^{-1}$
$T_{fus} = 943 \pm 10\ K$ $\Delta_{fus} H° = 64.517 \pm 3.14\ kJ \cdot mol^{-1}$

Enthalpy of Formation

A review[1] of early experimental studies led to a value of 373 kcal·mol^{-1} for $\Delta_f H°(V_2O_5$, cr, 298.15 K). More recent combustion studies on V(cr) have led to the following $\Delta_f H°$(298.15 K) values for V_2O_5(cr).

Source	Year	$\Delta_f H°(V_2O_5$, cr, 298.15 K), kcal·mol^{-1}
[2]	1969	-376 ± 2
[3]	1960	-370 ± 1
[4]	1961	-370.6 ± 0.5
[5]	1963	-371.9 ± 1.0

We adopt 370.6 ± 1 kcal·mol^{-1} as the enthalpy of formation of V_2O_5(cr) at 298.15 K. This value is the Mah and Kelley result[4] but it is also in good agreement with the results of Golutvin and Kozlovskaya[3] and Volkova and Gel'd.[5] The same value was recently adopted by NBS.[6]

The combustion of vanadium and its oxides, as reported by Mah and Kelley,[4] led to two problems: (1) the oxide products liquefy before the pentoxide composition is obtained and (2) the oxide products are corrosive and cause a container problem. The combustion of vanadium led to varying mixtures of V_2O_4(rutile) and V_2O_5. This was verified by x-ray diffraction. The enthalpy of formation values for V_2O_4 and V_2O_5 were derived from the same set of experiments.[4]

Heat Capacity and Entropy

Using a V_2O_5 sample with a reported purity of 99.5% or better, Anderson[7] measured the heat capacity in the range 56.8–289.5 K. Using the combination of Debye and Einstein functions suggested by Anderson,[7] we calculate $S°(60\ K) = 2.81$ cal·K^{-1}·mol^{-1} and $H°(60\ K)-H°(0\ K) = 130.59$ cal·mol^{-1}. Cook[8] measured the enthalpy of V_2O_5 in the range 372–1513 K. The enthalpy data are fit to a Kelley type equation with the constraint that the data join smoothly with a portion of the integrated data of Anderson.[7] The enthalpy data appear to lie too high in comparison with the integrated data of Anderson.[7] A better fit is obtained by neglecting the 289.5 data point of Anderson. The Anderson data show considerable scatter and deviate from our adopted $C_p°$ values by ±4% below 65 K and ±1.8% between 65 and 280 K. The 289.5 K data point is 2.7% lower than the adopted value. The Cook dauccircIta deviates from the adopted enthalpy values by roughly 8% (200 cal·mol^{-1}) at 371.6 K with the difference decreasing to 2 cal·K^{-1}·mol^{-1} at 754.4 K. In the range 771.1–921.1 K the enthalpy difference ranges from −121 to +139 cal·K^{-1}·mol^{-1}.

Fusion Data

The melting point of V_2O_5 is adopted as $T_{fus} = 943 \pm 10$ K as derived from the enthalpy studies of Cook.[8] The heat of melting is calculated to be $\Delta_{fus}H° = 15.42 \pm 0.75$ kcal·mol^{-1} based on our analyses of Cook's enthalpy data. Refer to the heat capacity discussion for V_2O_5(cr) and V_2O_5(l) for details. By way of comparison, Kohlmuller and Leitner[9] reported $T_{fus} = 937.9$ K and $\Delta_{fus}H° = 14.5$ kcal·mol^{-1} while Pantony and Vasu[10] reported $T_{fus} = 951.12$ K and $\Delta_{fus}H° = 13.8$ kcal·mol^{-1}. The latter two succirctudies[9,10] involved cryoscopic techniques. Murphy and West[11] reported $T_{fus} = 943$ K based on DTA measurements and Holtzberg *et al.*[12] determined $T_{fus} = 947 \pm 5$ K in their study of the phases in the K_2O V_2O_5 system.

The variance in the reported T_{fus} values is probably attributable to the presence of V_2O_4(cr). Refer to the discussion in the section on Sublimation Data in the V_2O_5(cr) table and Decomposition Data in the V_2O_5(l) table.

Sublimation Data

Using the combination of Knudsen effusion and mass spectrometric techniques, Berkowitz *et al.*[13] concluded that V_2O_5(cr) did not "vaporize" invariantly. The temperature range investigated was not reported. Their conclusion was based on two observations: (1) some reduced vanadium oxide species were present in the gas phase, and (2) oxygen was also found to be effusing from the Knudsen cell. Chizhikov *et al.*[14] studied the dissociation of V_2O_5 at temperatures below T_{fus} using mass spectrometry. They assumed reduced vanadium oxides, in addition to V_4O_{10}, were present in the vapor upon dissociation of V_2O_5(cr) in vacuum. We conclude that there is no invariant sublimation process for V_2O_5(cr) and thus we do not calculate a $\Delta_{sub}H°$(298.15 K) value. For related discussion refer to V_2O_5(l) table.

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Continued on page 1816

Vanadium Oxide (V_2O_5) O_5V_2(cr)

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0	0.000	0.000	INFINITE	−21.506	−1541.109	−1541.109	INFINITE
100	52.647	31.564	238.170	−20.661	−1548.502	−1506.895	787.121
200	101.123	84.203	141.649	−11.489	−1550.281	−1462.556	381.980
298.15	130.599	130.549	130.549	0.000	−1550.590	−1419.348	248.664
300	131.027	131.358	130.552	0.242	−1550.577	−1418.533	246.989
400	150.950	171.988	135.954	14.414	−1548.962	−1374.719	179.520
500	161.753	206.948	146.747	30.100	−1546.243	−1331.458	139.096
600	168.314	237.044	159.348	46.617	−1543.068	−1288.795	112.200
700	173.234	263.370	172.367	63.702	−1539.671	−1246.682	93.029
800	177.251	286.771	185.232	81.231	−1536.152	−1205.066	78.683
900	180.749	307.858	197.705	99 138	−1532.562	−1163.895	67.551
943.000	182.004	316.323	202.922	106.937	--- CRYSTAL <--> LIQUID ---		
1000	183.678	327.054	209.694	117.359	−1528.939	−1123.126	58.666
1100	186.606	344.697	221.176	135.874	−1525.292	−1082.721	51.414
1200	189.535	361.060	232.159	154.681	−1521.624	−1042.649	45.385
1300	192.464	376.346	242.669	173.781	−1517.934	−1002.884	40.296
1400	195.393	390.717	252.736	193.173	−1514.230	−963.403	35.945
1500	198.322	404.297	262.391	212.859	−1510.509	−924.189	32.183

PREVIOUS: CURRENT: June 1973

Vanadium Oxide (V_2O_5) LIQUID $M_r = 181.8880$ Vanadium Oxide (V_2O_5) $O_5V_2(l)$

$S°(298.15\ K) = [191.956]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 943 \pm 10\ K$
$T_{dcm} = 1963\ K$

$\Delta_fH°(298.15\ K) = [-1491.209]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 64.517 \pm 3.14\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(V_2O_5, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(943\ K)-H°(298.15\ K)$, between $V_2O_5(cr)$ and $V_2O_5(l)$.

Heat Capacity and Entropy

Cook[1] measured the enthalpy of V_2O_5 in the range 372–1513 K. In the liquid region ($T > 943$ K), Cook[1] represented his data by a straight line with a slope of $C_p° = 45.60\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. We adopt this value of $V_2O_5(l)$. A glass transition is assumed at 600 K. The heat capacity values used below 600 K are those of $V_2O_5(cr)$. The entropy at 298.15 K is calculated in a manner analogous to that used in calculating the enthalpy of formation.

Decomposition Data

Polyakov[2] measured the weight loss of molten V_2O_5 in the range 700–1200°C for various oxygen flows. The oxygen pressure was greater than the dissociation pressure of V_2O_5. The vapor pressure was calculated by extrapolating to zero oxygen flow and assuming the vapor was monomeric $V_2O_5(g)$. Polyakov[2] assumed no loss of oxygen. Pak[3] proposed a method of calculating vapor pressures from experimental results obtained by the entrainment method with allowance for diffusion. Using Polystov's data and assuming that the vapor phase is the dimeric molecule $V_4O_{10}(g)$, Pak[3] calculated a heat of vaporization $\Delta_{vap}H°(298.15\ K)$ which is 1.4 $kcal{\cdot}mol^{-1}$ more positive than Polyakov's reported value of 32.3 $kcal{\cdot}mol^{-1}$ V_2O_5. Semenov *et al.*[4] determined the vapor pressure of $V_4O_{10}(g)$ over $V_2O_5(l)$ at 1215–1530 K by an improved transfer technique in an oxygen carrier stream. The reported heat of vaporization was calculated to be 3.5 $kcal{\cdot}mol^{-1}$ more positive than Polyakov's value.

Pantony and Vasu[5] stated that molten V_2O_5 attains a constant weight under fixed oxygen pressure and temperature in a reasonably short length of time while in pure nitrogen it is converted into $V_2O_4(cr)$. Pantony and Vasu[5] studied gravimetrically the dissociation equilibrium of $V_2O_5(l)$ and confirmed its existence by cryoscopic methods. They concluded that the vapor pressure ascribed to $V_2O_5(g)$ or $V_4O_{10}(g)$ and measured by a transpiration weight loss method is due to the loss of oxygen arising from the following dissociation $V_2O_5(soln) = V_2O_4(soln) + 1/2\ O_2(g)$.

An effusion mass spectrometric investigation of the vapor in equilibrium with V_2O_5 in the range 1000–1200 K led Farber *et al.*[6] to the conclusion that the vapor contained not only $V_4O_{10}(g)$, significant amounts of $V_4O_8(g)$, but also other vanadium oxides. We conclude that there is decomposition upon heating $V_2O_5(l)$ in an inert atmosphere or in vacuo. The use of an oxygen atmosphere suppresses decomposition but in the transpiration weight loss experiment it has not been verified that the weight loss is indeed $V_4O_{10}(g)$. We calculate a decomposition temperature, T_{dcm}, as that temperature at which the free energy approaches zero for the reaction $V_2O_5(l) = V_2O_4(l) + 1/2\ O_2(g)$.

References

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	130.599	191.956	191.956	0.000	−1491.209	−1378.274	241.468
300	131.027	192.765	191.959	0.242	−1491.195	−1377.574	239.857
400	150.950	233.396	197.362	14.414	−1489.580	−1339.900	174.973
500	161.753	268.355	208.154	30.100	−1486.861	−1302.780	136.100
600	168.314	298.477	220.757	46.632	−1483.672	−1266.258	110.238
600.000	168.314	298.477	220.757	46.632	GLASS <--> LIQUID TRANSITION		
600.000	190.790	298.477	220.757	46.632			
700	190.790	327.887	234.015	65.711	−1478.280	−1230.454	91.818
800	190.790	353.364	247.377	84 790	−1473.211	−1195.400	78.052
900	190.790	375.836	260.426	103.869	−1468.449	−1160.962	67.381
943.000	190.790	384.740	265.893	112.073	--- CRYSTAL <--> LIQUID ---		
1000	190.790	395.938	272.990	122.948	−1463.969	−1127.040	58.871
1100	190.790	414.122	285.006	142.027	−1459.757	−1093.553	51.928
1200	190.790	430.723	296.468	161.106	−1455.817	−1060.437	46.160
1300	190.790	445.994	307.390	180.185	−1452.148	−1027.640	41.291
1400	190.790	460.133	317.802	199.264	−1448.758	−995.114	37.128
1500	190.790	473.296	327.734	218.343	−1445.643	−962.822	33.528
1600	190.790	485.610	337.221	237.422	−1442.797	−930.728	30.385
1700	190.790	497.176	346.293	256.501	−1440.236	−898.804	27.617
1800	190.790	508.082	354.981	275.580	−1437.966	−867.023	25.160
1900	190.790	518.397	363.313	294.659	−1436.009	−835.358	22.966
2000	190.790	528.183	371.314	313.738	−1434.379	−803.788	20.993
2100	190.790	537.492	379.008	332.817	−1433.097	−772.292	19.210
2200	190.790	546.368	386.415	351.896	−1477.943	−740.637	17.585
2300	190.790	554.849	393.555	370.975	−1477.681	−707.130	16.059
2400	190.790	562.969	400.446	390.054	−1477.475	−673.634	14.661
2500	190.790	570.757	407.104	409.133	−1477.324	−640.143	13.375
2600	190.790	578.240	413.543	428.212	−1477.227	−606.658	12.188
2700	190.790	585.440	419.777	447.292	−1477.182	−573.175	11.089
2800	190.790	592.379	425.818	466.371	−1477.188	−539.693	10.068
2900	190.790	599.074	431.678	485.450	−1477.243	−506.212	9.118
3000	190.790	605.542	437.366	504.529	−1477.348	−472.725	8.231

PREVIOUS: CURRENT June 1973

Vanadium Oxide (V_2O_5) $O_5V_2(l)$

Vanadium Oxide (V_2O_5) CRYSTAL-LIQUID

0 to 943 K crystal
above 943 K liquid

Refer to the individual tables for details.

M_r = 181.8800 Vanadium Oxide (V_2O_5) $O_5V_2(cr,l)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−21.506	−1541.109	−1541 109	INFINITE
100	52.647	31.564	238 170	−20.661	−1548.502	−1506.895	787.121
200	101.123	84.203	141.649	−11.489	−1550.281	−1462.556	381.980
298.15	130.599	130.549	130.549	0 000	−1550.590	−1419.348	248.664
300	131.027	131.358	130.552	0.242	−1550.577	−1418.533	246.989
400	150.950	171.988	135.954	14.414	−1548.962	−1374.719	179.520
500	161.753	206.948	146 747	30 100	−1546.243	−1331.458	139.096
600	168.314	237.044	159.348	46.617	−1543.068	−1288.795	112.200
700	173.234	263.370	172.367	63.702	−1539.671	−1246.682	93.029
800	177.251	286.771	185.232	81.231	−1536.152	−1205.066	78.683
900	180.749	307.858	197.705	99.138	−1532.562	−1163.895	67.551
943.000	182.004	316.323	202.922	106.937	CRYSTAL <--> LIQUID TRANSITION		
943.000	190.790	384.740	202.922	171.455			
1000	190.790	395.938	213.608	182.330	−1463.969	−1127.040	58.871
1100	190.790	414.122	231.023	201.409	−1459.757	−1093.553	51.928
1200	190.790	430.723	246.983	220.488	−1455.817	−1060.437	46.160
1300	190.790	445.994	261 712	239.567	−1452.148	−1027.640	41.291
1400	190 790	460.133	275.386	258.646	−1448.758	−995.114	37.128
1500	190.790	473.296	288.146	277.725	−1445.643	−962.822	33.528
1600	190.790	485.610	300.107	296.804	−1442.797	−930.728	30.385
1700	190 790	497.176	311.363	315.883	−1440.236	−898.804	27.617
1800	190.790	508.082	321.992	334.962	−1437.966	−867.023	25.160
1900	190.790	518.397	332.060	354.041	−1436.009	−835.358	22.966
2000	190.790	528.183	341.623	373.120	−1434.379	−803.788	20.993
2100	190.790	537.492	350.731	392.199	−1433.097	−772.292	19.210
2200	190.790	546.368	359.423	411.278	−1477.943	−740.637	17.585
2300	190.790	554.849	367.737	430.357	−1477.681	−707.130	16.059
2400	190.790	562.969	375.703	449 436	−1477.475	−673.634	14.661
2500	190.790	570.757	383.351	468.515	−1477.324	−640.143	13.375
2600	190.790	578.240	390.704	487.594	−1477.227	−606.658	12.188
2700	190.790	585.440	397.784	506.673	−1477.182	−573.175	11.089
2800	190.790	592.379	404.610	525.752	−1477.188	−539.693	10.068
2900	190.790	599.074	411.201	544.831	−1477.243	−506.212	9.118
3000	190.790	605.542	417.572	563.910	−1477.348	−472.725	8.231

PREVIOUS: CURRENT: June 1973

Vanadium Oxide (V_2O_5) $O_5V_2(cr,l)$

Phosphorus Oxide ($(P_2O_3)_2$) IDEAL GAS M_r = 219.89144 Phosphorus Oxide ($(P_2O_3)_2$) $O_6P_4(g)$

$S°(298.15 K) = 345.641 \pm 33.5 J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0 K) = -2189.97 \pm 3.35 kJ \cdot mol^{-1}$
$\Delta_f H°(298.15 K) = -2214.31 \pm 33.5 kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}
613 (1)	465 (2)
613 (1)	643 (3)
302 (3)	919 (3)
370 (3)	1029 (2)
407 (3)	636 (3)

Ground State Quantum Weight: 1 $\sigma = 12$
Point Group: T_d
Bond Distances: P–O = 1.65 ± 0.02 Å
Bond Angles: P–O–P = 127.5 ± 1.0° O–P–O = 99° ± 1°
Product of the Moments of Inertia: $I_A I_B I_C = 4.838017 \times 10^{-112} g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(P_4O_6, l, 298.15 K)$ was measured by Koerner and Daniels.[1] The measurement was made by burning samples of red phosphorus in nitric oxide in a flow calorimeter. Calculation of the enthalpy of formation of the gas was made using $\Delta_{vap}H°(298.15 K) = 11.46 kcal \cdot mol^{-1}$ as reported by Farr.[2]

Heat Capacity and Entropy

The vibrational levels are from the Raman data of Gerding *et al.*[3] and infrared spectra data of Sidorov and Sobolev.[4] Bond distances and angles are from electron diffraction data by Hampson and Stosick.[5]

References

[1] W. E. Koerner and F. Daniels, J. Chem. Phys. 20, 113 (1952).
[2] T. D. Farr, Tenn. Valley Authority, Chem. Engr. Report No. 8 (1950).
[3] H. Gerding, H. van Brederode and H. C. J. de Decker, Rec. Trav. Chim. 61, 549 (1942).
[4] T. A. Sidorov and N. N. Sobolev, Optics and Spect. 2, 710 (1957).
[5] G. C. Hampson and A. J. Stosick, J. Amer. Chem. Soc. 60, 1814 (1938).

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−23.153	−2189.970	−2189.970	INFINITE
100	47.025	247.701	443.275	−19.557	−2198.637	−2164.340	1130.535
200	101.296	296.685	357.555	−12.174	−2209.040	−2126.586	555.407
250	125.151	321.933	347.911	−6.494	−2212.101	−2105.599	439.941
298.15	143.937	345.641	345.641	0.	−2214.307	−2084.877	365.262
300	144.581	346.534	345.644	0.267	−2214.379	−2084.074	362.870
350	160.035	370.028	347.464	7.897	−2218.922	−2061.933	307.727
400	172.246	392.227	351.686	16.216	−2220.352	−2039.401	266.319
450	181.911	413.094	357.362	25.080	−2221.305	−2016.721	234.095
500	189.609	432.674	363.925	34.375	−2221.900	−1993.955	208.307
600	200.809	468.305	378.414	53.935	−2222.349	−1948.310	169.615
700	208.312	499.860	393.554	74 414	−2222.164	−1902.645	141.977
800	213.527	528.037	408.635	95.521	−2221.598	−1857.035	121.252
900	217.274	553.414	423.335	117.071	−2220.794	−1811.511	105.137
1000	220.045	576.457	437.513	138.944	−2219.838	−1766.085	92.251
1100	222.147	597.533	451.116	161.058	−2218.781	−1720 759	81.712
1200	223.776	616.935	464.137	183.358	−2471.947	−1671.220	72.746
1300	225.062	634.899	476.590	205.802	−2467.683	−1604.666	64.476
1400	226.095	651.617	488.502	228.362	−2463.415	−1538.440	57.400
1500	226.935	667.246	499.903	251.014	−2459.153	−1472.520	51.278
1600	227.628	681.914	510.825	273.744	−2454.906	−1406.883	45.930
1700	228.206	695.732	521.299	296.536	−2450.683	−1341.511	41.220
1800	228.693	708.790	531.356	319.382	−2446.490	−1276.387	37.040
1900	229.107	721.166	541.023	342.272	−2442.334	−1211.495	33.306
2000	229.462	732.927	550.327	365.201	−2438.217	−1146.820	29.952
2100	229.768	744.130	559.291	388.163	−2434.145	−1082.351	26.922
2200	230.034	754.825	567.937	411.154	−2430.121	−1018.072	24.172
2300	230.267	765.056	576.287	434.169	−2426.148	−953.979	21.666
2400	230.471	774.861	584.358	457.206	−2422.226	−890.057	19.372
2500	230.652	784.273	592.168	480.262	−2418.358	−826.296	17.265
2600	230.813	793.322	599.732	503.336	−2414.543	−762.689	15.323
2700	230.957	802.036	607.064	526.424	−2410.783	−699.227	13.527
2800	231.085	810.438	614.178	549.527	−2407.077	−635.903	11.863
2900	231.201	818.549	621.086	572.641	−2403.425	−572.714	10.316
3000	231.305	826.389	627.800	595.766	−2399.825	−509.646	8.874
3100	231.399	833.975	634.329	618.902	−2396.278	−446.697	7.527
3200	231.485	841.323	640.683	642.046	−2392.781	−383.865	6.266
3300	231.564	848.447	646.872	665.199	−2389.333	−321.141	5.083
3400	231.635	855.361	652.903	688.358	−2385.933	−258.518	3.972
3500	231.700	862.076	658.784	711.525	−2382.581	−195.997	2.925
3600	231.761	868.605	664.522	734.698	−2379.273	−133.570	1.938
3700	231.816	874.955	670.124	757.877	−2376.009	−71.235	1.006
3800	231.867	881.138	675.596	781.061	−2372.789	−8.985	0.124
3900	231.914	887.162	680.943	804.251	−2369.609	53.180	−0.712
4000	231.958	893.034	686.173	827.444	−2366.471	115.261	−1.505
4100	231.999	898.762	691.288	850.642	−2363.372	177.266	−2.258
4200	232.036	904.353	696.295	873.844	−2360.312	239.195	−2.975
4300	232.071	909.813	701.197	897.049	−2357.291	301.054	−3.657
4400	232.104	915.149	705.999	920.258	−2354.308	362.840	−4.307
4500	232.135	920.365	710.705	943.470	−2351.363	424.559	−4.928
4600	232.163	925.468	715.319	966.685	−2348.457	486.213	−5.521
4700	232.190	930.461	719.843	989.903	−2345.590	547.806	−6.088
4800	232.216	935.350	724.282	1013.123	−2342.762	609.338	−6.631
4900	232.239	940.138	728.639	1036.346	−2339.975	670.813	−7.151
5000	232.262	944.830	732.916	1059.571	−2337.229	732.230	−7.650
5100	232.283	949.430	737.116	1082.798	−2334.527	793.593	−8.128
5200	232.302	953.940	741.243	1106.027	−2331.869	854.900	−8.588
5300	232.321	958.365	745.298	1129.258	−2329.258	916.161	−9.029
5400	232.339	962.708	749.284	1152.491	−2326.696	977.370	−9.454
5500	232.355	966.971	753.203	1175.726	−2324.185	1038.532	−9.863
5600	232.371	971.158	757.058	1198.962	−2321.727	1099.653	−10.257
5700	232.386	975.271	760.850	1222.200	−2319.326	1160.726	−10.637
5800	232.400	979.313	764.582	1245.440	−2316.984	1221.761	−11.003
5900	232.414	983.286	768.255	1268.680	−2314.704	1282.749	−11.357
6000	232.427	987.192	771.872	1291.922	−2312.491	1343.707	−11.698

PREVIOUS: December 1962 CURRENT· December 1962 (1 bar)

Tungsten Oxide ((WO$_3$)$_2$) IDEAL GAS $M_r = 463.6964$ Tungsten Oxide ((WO$_3$)$_2$) O$_6$W$_2$(g)

$S°(298.15 \text{ K}) = [415.601] \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = -1157.96 \text{ kJ·mol}^{-1}$

$\Delta_f H°(298.15 \text{ K}) = -1163.99 \pm 41.8 \text{ kJ·mol}^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[600] (4)
[300] (8)
[172] (6)

Ground State Quantum Weight: [1] $\sigma = [4]$

Point Group: [D_{2h}]

Bond Distance: W–O = [1.81] Å

Bond Angles: O–W–O = [109.47]° W–O$_{\text{bridge}}$–W = [70.53]°

Product of the Moments of Inertia: $I_A I_B I_C = [5.918184 \times 10^{-112}]$ g^3·cm^6

Enthalpy of Formation

The adopted value, $\Delta_f H°(W_2O_6, g, 298.15 \text{ K}) = -278.2$ kcal·mol^{-1}, was reduced from $\Delta_f H°(1450 \text{ K}) = -272.5$ kcal mol^{-1}, reported by Ackermann and Rauh.[1] They have studied the sublimation behavior of the tungsten–oxygen system over the temperature range from 1300 to 1600 K by mass spectrometry, mass effusion, and X-ray diffraction, and also have determined $\Delta_f G°(W_2O_6, g) = 272{,}500 + 54.98T$ cal·K^{-1}·mol^{-1} from partial pressure measurements over the W–WO$_2$(cr) system.

Battles[2] has also studied the same system in the temperature range from 1418 to 1527 K. Third law calculation of the partial pressure data gives $\Delta_r H°(298.15 \text{ K}) = 144.0$ kcal·mol^{-1} for 3 WO$_2$(cr) = W$_2$O$_6$(g) + W(cr) which yields $\Delta_f H°(W_2O_6, g, 298.15 \text{ K}) = -278.8$ kcal·mol^{-1} using all JANAF functions. This value is in good agreement with the value adopted.

Norman and Staley[3] have obtained $\Delta_r H°(1800 \text{ K}) = -127$ kcal·mol^{-1} for 2 WO$_3$(g) = W$_2$O$_6$(g) by mass spectrometric study of the vapor over WO$_3$ dissolved in CaO–Al$_2$O$_3$–SiO$_2$. The value of $\Delta_r H°$ was determined by the 2nd law method from ion intensities and leads to $\Delta_f H°(W_2O_6, g, 298.15 \text{ K}) = -275$ kcal·mol^{-1}, using all JANAF functions (dated Sept. 30, 1966). The absolute pressure values reported by Norman and Staley appear to be quite inconsistent with the JANAF functions since they lead to $\Delta_f H°(W_2O_6, g, 298.15 \text{ K}) = -246$ kcal·mol^{-1} by the 3rd law method.

Source	Reaction	T/K	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15K) kcal·mol^{-1}
1	3 WO$_2$(cr) = W$_2$O$_6$(g) + W(cr)	1300–1600	144.54	144.63	0.01	−278.2*
2	3 WO$_2$(cr) = W$_2$O$_6$(g) + W(cr)	1418–1527	142.66	143.97	0.85 ± 0.40	−278.8*
3	2 WO$_3$(g) = W$_2$O$_6$(g)	1700–1900	−135	−106		−275**

*3rd law value adopted in calculation **2nd law value adopted in calculation

Heat Capacity and Entropy

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 600 cm^{-1} (4), 300 cm^{-1} (8), and 172 cm^{-1} (6) in order to give the entropy at 1450 K, $S°(1450 \text{ K}) = 164.66$ cal·K^{-1}·mol^{-1}, corresponding to $\Delta_r S°(1450 \text{ K}) = 54.98$ cal·K^{-1}·mol^{-1} which was reported by Ackermann and Rauh.[1] The adopted value, $S°(W_2O_6, g, 298.15 \text{ K}) = 99.3$ cal·K^{-1}·mol^{-1}, was reduced from the entropy at 1450 K, using JANAF functions. Second law calculation of the partial pressure data of Battles gives $\Delta_r S°(1470 \text{ K}) = 63.5$ cal·K^{-1}·mol^{-1} for 3 WO$_2$(cr) = W$_2$O$_6$(g) + W(cr). This yields $S°(W_2O_6, g, 298.15 \text{ K}) = 97.9$ cal·K^{-1}·mol^{-1}.

The molecular configuration for W$_2$O$_6$(g) was estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, and two of these tetrahedra share a common oxygen edge to form a planar four-member ring. The bond distance W–O was estimated as 1.81 Å and the bond angle O–W–O = 109.47° and W–O$_{\text{bridge}}$–W = 70.53°. The principal moments of inertia are. $I_A = 34.8158 \times 10^{-39}$, $I_B = 124.7049 \times 10^{-39}$, and $I_C = 136.3101 \times 10^{-39}$ g·cm^2.

References

[1] R. J. Ackermann and E. G. Rauh, J. Phys. Chem. 67, 2596 (1963).

[2] J. E. Battles, Ph.D. dissertation, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide," the Ohio State University, (1964).

[3] J. H. Norman and H. G. Staley, J. Chem. Phys. 43, 3804 (1965).

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

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0	0.	0.	INFINITE	−29.966	−1157.958	−1157.958	INFINITE
100	81.358	284.301	535.415	−25.111	−1163.122	−1137.638	594.241
200	131.491	358.417	429.062	−14.129	−1164.889	−1111.172	290.208
250	144.838	389.289	418.085	−7.199	−1164.646	−1097.760	229.364
298.15	153.665	415.601	415.601	0.	−1163.989	−1084.931	190.075
300	153.946	416.552	415.604	0.285	−1163.957	−1084.441	188.818
350	160.314	440.789	417.503	8.150	−1162.969	−1071.263	159.877
400	164.881	462.511	421.795	16.286	−1161.796	−1058.240	138.192
450	168.240	482.134	427.427	24.618	−1160.519	−1045.372	121.344
500	170 768	499.997	433.805	33.096	−1159.192	−1032.649	107.880
600	174 231	531.464	447.530	50.360	−1156.521	−1007.592	87.719
700	176.420	558.498	461.497	67.901	−1153 947	−982.975	73.351
800	177.883	582.157	475.132	85.620	−1151.527	−958.718	62.598
900	178.907	603.171	488.213	103.463	−1149.279	−934.754	54.252
1000	179.649	622.061	500.669	121.392	−1147.203	−911.031	47.587
1100	180.205	639.211	512.496	139.386	−1145.294	−887.507	42.144
1200	180.630	654.910	523.719	157.429	−1143.547	−864.150	37.615
1300	180.963	669.382	534.374	175.509	−1141.956	−840.932	33.789
1400	181.229	682.802	544.503	193.619	−1140.519	−817.832	30.514
1500	181.444	695.314	554.145	211.753	−1139.234	−794.829	27.678
1600	181.621	707.029	563.338	229.907	−1138.101	−771.906	25.200
1700	181.767	718.045	572.117	248.077	−1137.121	−749.050	23.015
1800	181.890	728.438	580.516	266.260	−1136.295	−726.248	21.075
1900	181.995	738.275	588.562	284.454	−1135.623	−703.486	19.340
2000	182.084	747.612	596.283	302.658	−1135.109	−680.756	17.780
2100	182.161	756.498	603.703	320.870	−1134.753	−658.047	16.368
2200	182.228	764.974	610.842	339.090	−1134.556	−635.351	15.085
2300	182.286	773.076	617.721	357.316	−1134.519	−612.662	13.914
2400	182.338	780.835	624.357	375.547	−1134.644	−589.972	12.840
2500	182.383	788.279	630.766	393.783	−1134.929	−567.271	11.852
2600	182.423	795.433	636.963	412.023	−1135.368	−544.557	10.940
2700	182.459	802.319	642.960	430.268	−1136.015	−521.821	10.095
2800	182.491	808.955	648.771	448.515	−1136.937	−499.056	9.310
2900	182.520	815.359	654.405	466.766	−1138.213	−476.256	8.578
3000	182.546	821.547	659.874	485.019	−1139.894	−453.401	7.894
3100	182.569	827.533	665.187	503.275	−1142.066	−430.482	7.254
3200	182.590	833.330	670.351	521.533	−1144.789	−407.488	6.652
3300	182.610	838.949	675.375	539.793	−1148.112	−384.399	6.085
3400	182.628	844 401	680.267	558.055	−1152.105	−361.196	5.549
3500	182.644	849.695	685.032	576.318	−1156.894	−337.868	5.042
3600	182.659	854.840	689.678	594.583	−1162.669	−314.387	4.562
3700	182.673	859.845	694.210	612.850	−1239.161	−290.351	4.099
3800	182.685	864.717	698.633	631.118	−1240.331	−264.689	3.638
3900	182.697	869.462	702.953	649.387	−1241.541	−238.998	3.201
4000	182.708	874.088	707.174	667.657	−1242.790	−213.277	2.785
4100	182.718	878.599	711.300	685.928	−1244.078	−187.524	2.389
4200	182.727	883.003	715.336	704.201	−1245.402	−161.738	2.012
4300	182.736	887.302	719.285	722.474	−1246.762	−135.919	1.651
4400	182.744	891.504	723.152	740.748	−1248.159	−110.072	1.307
4500	182.752	895.610	726.939	759.023	−1249.591	−84.191	0.977
4600	182.759	899.627	730.649	777.298	−1251.059	−58.278	0.662
4700	182.765	903.558	734.287	795.574	−1252.563	−32.331	0.359
4800	182.772	907.406	737.853	813.851	−1254.104	−6.352	0.069
4900	182.778	911.174	741.352	832.129	−1255.683	19.661	−0.210
5000	182.783	914.867	744.786	850.407	−1257.300	45.705	−0.477
5100	182.788	918.487	748.156	868.685	−1258.958	71.782	−0.735
5200	182.793	922.036	751.466	886.964	−1260.656	97.888	−0.983
5300	182.798	925.518	754.717	905.244	−1262.398	124.034	−1.222
5400	182.802	928.935	757.912	923.524	−1264.187	150.208	−1.453
5500	182.806	932.289	761.052	941.804	−1266.022	176.416	−1.675
5600	182.810	935.583	764.139	960.085	−1267.907	202.662	−1.890
5700	182.814	938.819	767.176	978.366	−1269.846	228.937	−2.098
5800	182.817	941.998	770.162	996.648	−1271.840	255.252	−2.299
5900	182.821	945.123	773.101	1014.930	−1273.892	281.593	−2.493
6000	182.824	948.196	775.994	1033.212	−1276.007	307.978	−2.681

PREVIOUS: September 1966 (1 atm) CURRENT· September 1966 (1 bar)

Tungsten Oxide ((WO$_3$)$_2$) O$_6$W$_2$(g)

Titanium Oxide (Ti_4O_7) CRYSTAL $M_r = 303.5158$ Titanium Oxide (Ti_4O_7) $O_7Ti_4(cr)$

$\Delta_fH°(0\ K)$ = Unknown
$S°(298.15\ K) = 198.740 \pm 12.6\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = -3404.521 \pm 6.3\ kJ{\cdot}mol^{-1}$
$T_{trs1} = 130 \pm 8\ K$ $\Delta_{trs1}H° = 95 \pm 5\ kJ{\cdot}mol^{-1}$
$T_{trs2} = 150 \pm 3\ K$ $\Delta_{trs2}H° = 468 \pm 5\ kJ{\cdot}mol^{-1}$
$T_{fus} = 1950 \pm 20\ K$ $\Delta_{fus}H° = [225.936]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_fH°$ is calculated from that of $Ti_3O_5(\beta)$ using $\Delta_rH°(298.15\ K) = -34.16\ kcal{\cdot}mol^{-1}$ for $4/3\ Ti_3O_5(\beta) + 1/6\ O_2(g) + Ti_4O_7(cr)$. $\Delta_fH°$ is derived by the 3rd law method from two concordant studies[1,2] of high temperature equilibria. Merritt *et al.*[1] obtained isothermal gravimetric equilibrium over the two phase system Ti_3O_5–Ti_4O_7 using ($H_2 + H_2O$) gas mixtures of known oxygen potential. Integration yields $\Delta_rG°(1304\ K) = -20.29 \pm 0.16\ kcal{\cdot}mol^{-1}$. Suzuki and Sambongi[2] reported solid state emf data relative to the couple Cr/Cr_2O_3 over a range of ~500°. We convert their (graphical) emf data[2] to oxygen potentials, using the authors' self consistent data for Cr/Cr_2O_3, and integrate to get $\Delta_rG°$. Vasil'eva and Shaulova[3] reported an equation for the oxygen potential based on their emf data relative to $Fe/Fe_{0.95}O$ over a range of ~90°. Equilibration data of Porter[4] are not considered because of the likelihood of oxidation during quenching of the composition.[1]

3rd law analyses of the equilibria for $4/3\ Ti_3O_5(\beta) + 1/6\ O_2(g) \rightarrow Ti_4O_7(cr)$ are summarized below. Merritt *et al.*[1] agree closely with Suzuki and Sambongi[2] but the earlier emf study[3] yields a $\Delta_rH°$ which is 1.9 kcal·mol⁻¹ less negative. All three studies agree with the earlier conclusion of Wahlbeck and Gilles[5] that Ti_4O_7 is stable with respect to disproportionation into $Ti_3O_5(\beta)$ and TiO_2(rutile). We dismiss the $\Delta_fH°$ derived from Vasil'eva[3] since it implies the contrary when combined with our adopted $S°$ and $C_p°$. We adopt $\Delta_fH° = -813.7 \pm 1.5\ kcal{\cdot}mol^{-1}$, where the uncertainty includes the possibility that $\Delta_{trs}H°$ and $S°$ of $Ti_3O_5(\beta)$ are biased.[6]

Source	Method	T/K	δS cal·K⁻¹·mol⁻¹	$\Delta_rH°$(298.15 K), kcal·mol⁻¹ 2nd law	 3rd law	$\Delta_fH°$(298.15 K) kcal·mol⁻¹
1	Gravimetric	1304	–	–	−34.10	−813.63
2	emf	~1273–1773	0.1	−34.0	−34.20	−813.74
3	emf	1168–1257	2.0	−29.8	−32.31	−811.84

Heat Capacity and Entropy

$C_p°$ is based on constrained fitting of enthalpy data (679–1937 K) of Slyusar et al.[6] The constraints required that the enthalpy be zero at the reference temperature (298.15 K) and that $C_p° = 50\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ and $dC_p°/dT \sim 0.09\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ at 300 K. The latter values are estimated by comparison with TiO_2, Ti_3O_5, Ti_2O_3 and TiO[6]. Deviations of the data from the resulting fit have a pattern[6] similar to that found with the authors' data[7] for $Ti_3O_5(\beta)$. The enthalpies of Slyusar *et al.*[7] for TiO_2, Ti_2O_3, Ti_3O_5 and Ti_4O_7 are less than satisfactory due to inconsistencies in H near 1200 K and in the reported values of T_{fus}.[6] Our constraints for Ti_4O_7 are an attempt to minimize the effects of the inconsistencies. They lead to a reasonable variation of $C_p°$ with temperature. We assume that there are no phase transitions above 298 K.

$S°(298.15\ K) = 47.5 \pm 3\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ is derived from the emf data of Suzuki and Sambongi.[2] The uncertainty includes the possibility that $\Delta_{trs}H°$ and $S°$ of $Ti_3O_5(\beta)$ are biased;[6] excluding this possibility, we estimate an uncertainty of ±1.5 cal·K⁻¹·mol⁻¹. $S°(298.15\ K) = 49.5\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ can be derived from the less reliable data of Vasil'eva and Shaulova.[3] These authors[3] derived $S°(298.15\ K) = 42\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ which is clearly too low. Unfortunately, the entropy derived form $C_p°$ data (12–300 K) of Berezovskii *et al.*[11] is unpublished and not yet available. These workers also measured $C_p°$ of the higher monologues Ti_5O_9, Ti_6O_{11} and Ti_9O_{17}.

Transition Data and Phase Data

Transition temperatures near 130 K and 150 K were found by use of DTA,[8] elecrical conductivity,[8] magnetic susceptibility[9] and x-ray diffraction.[8, 10] The three crystalline phases are triclinic, the two transitions involve no change in symmetry but only rearrangements of atoms within the unit cell.[10] There is obvious thermal hysteresis in the transition near 130 K. DTA endotherms[8] suggest that $\Delta_{trs}H°$ (150 K) is considerably larger than $\Delta_{trs}H°$(130 K). $\Delta_{trs}H°$ values presumably were obtained with the $C_p°$ data,[11] but these are not yet available.

Ti_4O_7 is the lowest stable phase in the homologous series of structures Ti_nO_{2n-1} related to rutile. Phases exist with n = 4,5,6,7,8,9 and certain higher integer values. These were reviewed in detail by Bursill and Hyde[12] in terms of the persistent structural phenomenon crystallographic shear. Equilibrium data[1 2] emphasize that $\Delta_rG°$ is negative, but were small in magnitude, for formation of Ti_nO_{2n-1} from its two nearest neighbors. Kinetic limitations can cause hysteresis in measured properties.[1]

FusionData

Refer to the liquid table for details.

Sublimation Data

Ti_4O_7(cr) vaporizes incongruently such that the residue approaches the congruently vaporizing composition of $Ti_3O_5(\beta)$.

References

[1] R. R. Merritt, B. G. Hyde, L. A. Bursill and D. K. Philp, Phil. Trans. Roy. Soc. London, Ser. A 274, (1245), 627 (1973)
[2] K. Suzuki and K. Sambongi, Tetsu To Hagane 58, 1579 (1972).

Continued on page 1816

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	208.489	198.740	198.740	0.000	−3404.521	−3213.016	562.907
300	209.200	200.032	198.744	0.386	−3404.512	−3211.828	559.229
400	239.911	264.765	207.361	22.961	−3402.790	−3147.798	411.060
500	258.864	320.495	224.551	47 972	−3399.447	−3084.414	322.226
600	271 165	368.848	244.663	74.511	−3395.268	−3021.790	263 070
700	279.659	411.321	265.500	102.075	−3390.647	−2959.904	220.871
800	285.976	449.097	286.132	130.372	−3385.729	−2898.703	189.266
900	290.830	483.070	306.158	159.221	−3380.763	−2838.124	164.720
1000	294.805	513.923	325.416	188.508	−3376.077	−2778.086	145.112
1100	298.152	542.182	343.855	218.159	−3371.968	−2718.492	129.090
1200	301.081	568.252	361.483	248.123	−3384.403	−2658.763	115.733
1300	303.675	592.456	378.330	278.363	−3378.626	−2598.529	104.410
1400	306.018	615.047	394.441	308.849	−3373.023	−2538.733	94.721
1500	308.235	636.236	409.861	339.563	−3367.654	−2479.330	86.338
1600	310.285	656.196	424.639	370.490	−3362.581	−2420.276	79.014
1700	312.210	675.065	438.820	401.615	−3357.867	−2361.528	72.561
1800	314.051	692.962	452.446	432.929	−3353.574	−2303.047	66.833
1900	315.850	709.991	465.557	464.424	−3349.758	−2244.790	61.714
1950.000	316.729	718.207	471.930	480.239	--- CRYSTAL <--> LIQUID ---		
2000	317.607	726.237	478.188	496.097	−3405.222	−2184.907	57.064
2100	319.281	741.773	490.372	527.942	−3405.522	−2123.883	52.829
2200	320.913	756.664	502.140	559.952	−3405.736	−2062.845	48.978
2300	322.545	770.965	513.520	592.125	−3405.865	−2001.803	45.462
2400	324.134	784.726	524.535	624.459	−3405.911	−1940.757	42.239

PREVIOUS: CURRENT: December 1973

Titanium Oxide (Ti_4O_7) LIQUID $M_r = 303.5158$

$S°(298.15\ K) = [291.066]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 1950 \pm 20\ K$

$\Delta_fH°(298.15\ K) = [-3216.035]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = [225\ 936]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(Ti_4O_7,\ l,\ 298\ 15\ K)$ is calculated from that of $Ti_4O_7(cr)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1950\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is estimated as 8 $cal{\cdot}K^{-1}$ $g\text{–}atoms^{-1}$ Below the assumed glass transition at 1300 K, $C_p°$ is taken to be the same as that of the crystal. $S°(298.15\ K)$ is calculated in a manner analogous to that used for $\Delta_fH°$.

Fusion Data

Hampson and Gilles[1] reported that $T_{fus} < 1943$ K, which is in reasonable agreement with $T_{fus} \sim 1955$ K obtained from the liquidus curve of Brauer and Littke.[2] The value of 1993 K reported by Slyusar *et al.*[3] is over 40° higher than our adopted value of 1950 ± 20 K. Ti_4O_7 probably melts incongruently, but the data[2] are not completely conclusive on this point.

Vaporization Data

Studies of liquid samples[4] showed that the congruently vaporizing composition is between Ti_3O_5 and Ti_4O_7. The principal products[1] of vaporization are $TiO_2(g)$ and $TiO(g)$.

References

[1] P. J. Hampson and P. W Gilles, J Chem Phys. **55**, 3712 (1971).
[2] G. Brauer and W. Littke, J. Inorg. Nucl. Chem. **16**, 67 (1960).
[3] N. P. Slyusar, A. D. Krivorotenko, E. N. Fomichev, A. A. Kalashnik and V. P. Bondarenko, Teplofiz. Vys. Temp. **11**, 213 (1973).
[4] *P. W. Gilles, H. F. Franzen, G. D. Stone and P. G Wahlbeck, J. Chem. Phys.* **48**, *1938 (1968).*

Titanium Oxide (Ti_4O_7) $O_7Ti_4(l)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298 15	208.489	291.066	291.066	0.000	−3216.035	−3052.056	534.708
300	209.200	292.358	291.070	0.386	−3216.026	−3051 039	531.233
400	239.911	357.091	299.687	22.961	−3214.304	−2996.243	391.269
500	258.864	412.821	316.877	47.972	−3210.960	−2942.090	307.358
600	271.165	461.174	336.989	74.511	−3206.781	−2888.699	251 484
700	279.659	503.647	357.826	102 075	−3202.160	−2836.046	211.628
800	285.976	541.423	378.458	130.372	−3197.242	−2784.078	181.782
900	290.830	575.396	398.484	159.221	−3192.277	−2732.732	158.604
1000	294.805	606.249	417.742	188.508	−3187.591	−2681.926	140.089
1100	298.152	634.508	436.181	218.159	−3183.482	−2631.564	124.963
1200	301.081	660.578	453.809	248.123	−3195.917	−2581.068	112.351
1300	303 675	684.782	470.656	278.364	−3190.139	−2530.066	101.659
1300.000	303.675	684.782	470.656	278.364	GLASS <−−> LIQUID TRANSITION		
1300 000	368.192	684.782	470.656	278.364			
1400	368.192	712.068	486.937	315.183	−3178.202	−2479.742	92.520
1500	368.192	737.471	502.803	352.002	−3166.728	−2430.256	84.629
1600	368.192	761.233	518.220	388.821	−3155.763	−2381.518	77.749
1700	368.192	783.555	533.178	425.641	−3145.356	−2333.450	71.698
1800	368.192	804.600	547.678	462.460	−3135.557	−2285.977	66 337
1900	368.192	824.507	561.729	499.279	−3126 417	−2239.030	61.555
1950.000	368.192	834.071	568.590	517.689	−−− CRYSTAL <−−> LIQUID −−−		
2000	368.192	843.393	575.344	536.098	−3176.735	−2190.733	57.216
2100	368.192	861.357	588.539	572.917	−3172.060	−2141.548	53.268
2200	368.192	878.485	601.332	609.737	−3167.465	−2092.582	49 684
2300	368.192	894.852	613.741	646.556	−3162.948	−2043.826	46.417
2400	368.192	910.522	625.783	683.375	−3158.509	−1995.265	43.426
2500	368 192	925.553	637.475	720.194	−3154 147	−1946 887	40.678
2600	368.192	939.993	648.834	757.013	−3149.859	−1898.681	38.145
2700	368.192	953.889	659.877	793.833	−3145.645	−1850.638	35.803
2800	368.192	967.279	670.618	830.652	−3141.503	−1802.750	33.631
2900	368.192	980.200	681.072	867.471	−3137.430	−1755.012	31.611
3000	368.192	992.682	691.252	904.290	−3133.426	−1707.410	29.729
3100	368.192	1004.755	701.171	941.109	−3129.486	−1659.939	27.970
3200	368.192	1016.445	710.842	977.929	−3125.610	−1612.599	26.323
3300	368.192	1027.774	720.275	1014.748	−3121.795	−1565.377	24.778
3400	368.192	1038.766	729.482	1051.567	−3118.037	−1518.268	23.325
3500	368.192	1049.439	738.472	1088.386	−3114.337	−1471.271	21.958
3600	368.192	1059.811	747.254	1125.205	−3110.690	−1424.377	20.667
3700	368.192	1069.899	755.839	1162.025	−4743.489	−1346.433	19.008
3800	368.192	1079.718	764.233	1198.844	−4735.007	−1254.732	17.247
3900	368.192	1089.282	772.446	1235.663	−4726.794	−1163.252	15.580
4000	368.192	1098.604	780.484	1272.482	−4718.845	−1071.983	13.999

PREVIOUS: CURRENT: December 1973

Titanium Oxide (Ti_4O_7) $O_7Ti_4(l)$

CRYSTAL(I–II–III)-LIQUID

0	to	130	K	crystal, I
130	to	150	K	crystal, II
150	to	1950	K	crystal, III
above		1950	K	liquid

Refer to the individual tables for details.

$M_r = 303.5158$ Titanium Oxide (Ti_4O_7)

Enthalpy Reference Temperature = T_r = 298.15 K

Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	208.489	198.740	198.740	0.000	−3404.521	−3213.016	562.907
300	209.200	200.032	198.744	0.386	−3404.512	−3211.828	559.229
400	239.911	264.765	207.361	22.961	−3402.790	−3147.798	411.060
500	258.864	320.495	224.551	47.972	−3399.447	−3084.414	322.226
600	271.165	368.848	244.663	74.511	−3395.268	−3021.790	263.070
700	279.659	411.321	265.500	102.075	−3390.647	−2959.904	220.871
800	285.976	449.097	286.132	130.372	−3385.729	−2898.703	189.266
900	290.830	483.070	306.158	159.221	−3380.763	−2838.124	164.720
1000	294.805	513.923	325.416	188.508	−3376.077	−2778.086	145.112
1100	298.152	542.182	343.855	218.159	−3371.968	−2718.492	129.090
1200	301.081	568.252	361.483	248.123	−3384.403	−2658.763	115.733
1300	303.675	592.456	378.330	278.363	−3378.626	−2598.529	104.410
1400	306.018	615.047	394.441	308.849	−3373.023	−2538.733	94.721
1500	308.235	636.236	409.861	339.563	−3367.654	−2479.330	86.338
1600	310.285	656.196	424.639	370.490	−3362.581	−2420.276	79.014
1700	312.210	675.065	438.820	401.615	−3357.867	−2361.528	72.561
1800	314.051	692.962	452.446	432.929	−3353.574	−2303.047	66.833
1900	315.850	709.991	465.557	464.424	−3349.758	−2244.790	61.714
1950.000	316.729	718.207	471.930	480.239	CRYSTAL <− −> LIQUID TRANSITION		
1950.000	368 .192	834.071	471.930	706.175			
2000	368.192	843.393	481.101	724.584	−3176.735	−2190.732	57.216
2100	368.192	861.357	498.784	761.404	−3172.060	−2141.548	53.268
2200	368.192	878.485	515.657	798.223	−3167.465	−2092.582	49.684
2300	368.192	894.852	531.790	835.042	−3162.948	−2043.826	46.417
2400	368.192	910.522	547.247	871.861	−3158.509	−1995.265	43.426
2500	368.192	925.553	562.080	908.680	−3154.147	−1946.887	40.678
2600	368.192	939.993	576.340	945.500	−3149.859	−1898.681	38.145
2700	368.192	953.889	590.067	982.319	−3145.645	−1850.638	35.803
2800	368.192	967.279	603.301	1019.138	−3141.503	−1802.750	33.631
2900	368.192	980.200	616.076	1055.957	−3137.430	−1755.012	31.611
3000	368.192	992.682	628.423	1092.776	−3133.426	−1707.410	29.729
3100	368.192	1004.755	640.369	1129.596	−3129.486	−1659.939	27.970
3200	368.192	1016.445	651.940	1166.415	−3125.610	−1612.599	26.323
3300	368.192	1027.774	663.158	1203.234	−3121.795	−1565.377	24.778
3400	368.192	1038.766	674.044	1240.053	−3118.037	−1518.268	23.325
3500	368.192	1049.439	684.618	1276.872	−3114.337	−1471.271	21.958
3600	368.192	1059.811	694.897	1313.692	−3110.690	−1424.377	20.667
3700	368.192	1069.899	704.896	1350.511	−4743.489	−1346.433	19.008
3800	368.192	1079.718	714.632	1387.330	−4735.007	−1254.732	17.247
3900	368.192	1089.282	724.116	1424.149	−4726.794	−1163.252	15.580
4000	368.192	1098.604	733.362	1460.968	−4718.845	−1071.983	13.999

PREVIOUS:

CURRENT: December 1973

Tungsten Oxide (W_3O_8) **IDEAL GAS** **$M_r = 679.5452$** **Tungsten Oxide (W_3O_8)** **$O_8W_3(g)$**

$S°(298.15\ K) = [494.013]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -1700.31\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -1710.00 \pm 41\ 8\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	 ν, cm^{-1}
[800] (6)	[199] (3)
[350] (4)	[150] (6)
[242] (8)	

Ground State Quantum Weight: [1] $\sigma = [4]$
Point Group: [D_{2d}]
Bond Distance: W–O = [1.81] Å
Bond Angle: O–W–O = [109.47]°
Product of the Moments of Inertia: $I_AI_BI_C = [7.651013 \times 10^{-111}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

Ackermann and Rauh[1] have studied the sublimation behavior of the tungsten–oxygen system over the temperature range from 1300 to 1600 K by mass spectrometry, mass effusion and x–ray diffracton, and also have determined the $\Delta_fG°(W_3O_8, g) = -400{,}900 + 9054\ T$ $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ from partial pressure measurements over W–WO_2(cr). The adopted value, $\Delta_fH°(W_3O_8, g, 298.15\ K) = -408.7\ kcal{\cdot}mol^{-1}$ was reduced from $\Delta_fH°(W_3O_8, g, 1450\ K) = -400.9\ kcal{\cdot}mol^{-1}$, using JANAF functions.

Source	Reaction	T/K	$\Delta_fH°$(298.15 K), $kcal{\cdot}mol^{-1}$ 2nd law	 3rd law	Drift $cal^{-1}{\cdot}mol^{-1}$	$\Delta_fH°$(298.15K) $kcal{\cdot}mol^{-1}$
1	$4\ WO_2(cr) = W_3O_8(g) + W(cr)$	1300−1600	155.05	155.09	−0.04	−408.7

Heat Capacity and Entropy

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 800 cm^{-1}(6), 350 cm^{-1}(4), 242 cm^{-1}(8), 199 cm^{-1}(3) and 150 cm^{-1}(6) in order to give the entropy at 1450 K, $S°(1450\ K) = 208.18\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, corresponding to $\Delta_fS°(1450\ K) = -90.54\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, which was reported by Ackermann and Rauh.[1]

The molecular configuration for W_3O_8(g) was estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, the three tetrahedra are connected by two common edges, and also the three tungsten atoms are in the same axis. The bond distance W−O was estimated as 1.81 Å and the bond angle < OWO = 109.47°. The principal moments of inertia are: $I_A = 46.4211 \times 10^{-39}$ and $I_B = I_C = 405.9772 \times 10^{-39}\ g{\cdot}cm^2$.

Reference

[1] R. J. Ackermann and E. G. Rauh, J. Phys. Chem. 67, 2596 (1963).

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

T/K	$C_p°$ $J{\cdot}K^{-1}mol^{-1}$	S°	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ $kJ{\cdot}mol^{-1}$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−39 964	−1700.312	−1700.312	INFINITE
100	112.720	315.859	655.406	−33.955	−1707.878	−1667.258	870.886
200	177.022	417.309	512.062	−18.951	−1710.541	−1625.251	424.472
250	194.050	458.740	497.345	−9.651	−1710.544	−1603.915	335.120
298.15	206.277	494.013	494.013	0.	−1710.001	−1583.420	277.409
300	206.684	495.291	494.017	0.382	−1709 971	−1582.635	275.561
350	216.267	527.904	496.571	10.967	−1708.965	−1561.487	233.039
400	223.618	557.284	502.354	21.972	−1707.657	−1540.504	201.169
450	229.316	583.965	509.963	33.301	−1706.151	−1519.699	176.402
500	233.784	608.366	518.601	44.883	−1704.524	−1499.068	156.607
600	240.175	651.597	537.257	68.604	−1701.114	−1458.296	126.956
700	244.386	688.958	556.321	92.846	−1697.693	−1418.098	105.820
800	247.281	721.792	574.995	117.438	−1694.384	−1378.384	89.999
900	249.344	751.043	592.960	142.275	−1691.235	−1339.074	77.718
1000	250.861	777.396	610.108	167.288	−1688.271	−1300 106	67.911
1100	252.006	801.362	626.422	192.434	−1685 499	−1261.424	59.900
1200	252.891	823.329	641.928	217.681	−1682.920	−1222.988	53.235
1300	253.588	843.600	656.672	243.006	−1680.538	−1184.758	47.604
1400	254.146	862.414	670.704	268.394	−1678.352	−1146.704	42.784
1500	254.599	879.964	684.076	293.832	−1676.367	−1108.801	38.612
1600	254.973	896.408	696.838	319.311	−1674.586	−1071.022	34.965
1700	255.284	911.875	709.037	344.824	−1673.011	−1033.348	31.751
1800	255.546	926.474	720.715	370.366	−1671.646	−995.763	28.896
1900	255.768	940.297	731.911	395.932	−1670.495	−958.246	26.344
2000	255.958	953.421	742.662	421.519	−1669.561	−920.784	24.048
2100	256.123	965.913	752.998	447.123	−1668.849	−883.363	21.972
2200	256.265	977.831	762.948	472.743	−1668.359	−845.969	20.086
2300	256.390	989.226	772.541	498.376	−1668.095	−808.596	18.364
2400	256.500	1000.140	781.798	524.020	−1668.057	−771.230	16.785
2500	256.597	1010.613	790.743	549.675	−1668.247	−733.859	15.333
2600	256.683	1020.678	799.394	575.339	−1668.654	−696.476	13.992
2700	256.760	1030.367	807.770	601.011	−1669.359	−659.071	12.750
2800	256.829	1039.706	815.888	626.691	−1670.466	−621.633	11.597
2900	256.890	1048.720	823.762	652.377	−1672.090	−584.151	10.522
3000	256.946	1057.430	831.407	678.069	−1674.311	−546.598	9.517
3100	256.997	1065.856	838.834	703.766	−1677.257	−508.959	8.576
3200	257.043	1074.016	846.057	729.468	−1681.020	−471.217	7.692
3300	257.084	1081.926	853.085	755.174	−1685.674	−433.343	6.859
3400	257.123	1089.601	859.929	780.885	−1691.321	−395.309	6.073
3500	257.158	1097.055	866.598	806.599	−1698.154	−357.096	5.329
3600	257.190	1104.300	873.101	832.316	−1706.457	−318.666	4.624
3700	257.219	1111.347	879.445	858.037	−1820.827	−279.412	3.945
3800	257.247	1118.207	885.639	883.760	−1822.207	−237.730	3.268
3900	257.272	1124.890	891.688	909.486	−1823.639	−196.013	2.625
4000	257.295	1131.403	897.600	935.214	−1825.122	−154.263	2.014
4100	257.317	1137.757	903.380	960.945	−1826.655	−112.472	1.433
4200	257.337	1143.958	909.035	986.678	−1828.236	−70.644	0.879
4300	257.356	1150.013	914.569	1012.412	−1829.865	−28.776	0.350
4400	257.373	1155.930	919.987	1038.149	−1831.542	13.127	−0.156
4500	257.390	1161.714	925.295	1063.887	−1833.265	55.069	−0.639
4600	257.405	1167.372	930.496	1089.627	−1835.035	97.050	−1.102
4700	257 419	1172.908	935.595	1115.368	−1836.854	139.073	−1.546
4800	257.433	1178.327	940.596	1141.111	−1838.720	181.134	−1.971
4900	257.446	1183.635	945.502	1166.854	−1840.637	223.236	−2.380
5000	257.457	1188.837	950.317	1192.600	−1842.604	265.376	−2.772
5100	257.469	1193.935	955.044	1218.346	−1844.625	307.557	−3.150
5200	257.479	1198.935	959.686	1244.093	−1846.700	349.773	−3.514
5300	257.489	1203.839	964.247	1269.842	−1848.832	392.037	−3.864
5400	257.499	1208.652	968.728	1295.591	−1851.026	434.335	−4.201
5500	257.508	1213.377	973.134	1321.341	−1853.281	476.676	−4.527
5600	257.516	1218.017	977.465	1347.093	−1855.605	519.063	−4.842
5700	257.524	1222.575	981.725	1372.845	−1857.998	561.487	−5.145
5800	257.532	1227.054	985.917	1398.597	−1860.464	603.959	−5.439
5900	257.539	1231 457	990.041	1424.351	−1863.009	646.464	−5.723
6000	257.546	1235.785	994.101	1450.105	−1865.636	689.023	−5.998

PREVIOUS: September 1966 (1 atm) CURRENT· September 1966 (1 bar)

Tungsten Oxide (W_3O_8) **$O_8W_3(g)$**

Tungsten Oxide ($(WO_3)_3$) IDEAL GAS $M_r = 695.5446$ Tungsten Oxide ($(WO_3)_3$) $O_9W_3(g)$

$S°(298.15 K) = [504.674]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0 K) = -2011.05\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15 K) = -2023.38 \pm 41.8\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}
[800](6)	[200](6)
[396](3)	[150](6)
[330](9)	

Ground State Quantum Weight: [1] $\sigma = [6]$
Point Group: [D_{3h}]
Bond Distance: W–O = [1.81] Å
Bond Angles: O–W–O = [109.47]° $W{-}O_{bridge} - W = [130.53]°$
Product of the Moments of Inertia: $I_AI_BI_C = [3.865176 \times 10^{-110}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

The adopted value, $\Delta_f H°(W_3O_9, g, 298.15 K) = -483.6\ kcal{\cdot}mol^{-1}$, was reduced from $\Delta_f H°(W_3O_9, g, 1450 K) = -474.1\ kcal{\cdot}mol^{-1}$ of Ackermann and Rauh,[1] who studied the sublimation behavior of the tungsten–oxygen system over the temperature range from 1300 to 16000 K by mass spectrometry, mass effusion and x–ray diffraction, and determined $\Delta_f G°(W_3O_9, g) = -474{,}100 + 110.26T\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$from partial pressure measurements over $W{-}WO_2(cr)$. They reviewed the previous determinations[1-4] of the thermodynamic properties of sublimation of WO_3 and also pointed out that it was not possible to make quantitative observations on stoichiometric WO_3 in vacuo since it is a "bivariant" system and the ion current is not constant until the composition of the sample reaches $WO_{2.96}$. This is probably the cause of previous discrepancies in sublimation studies.

Battles[2] has also studied that the partial pressure of $W_3O_9(g)$ over $W{-}WO_2(cr)$ *in the temperature range from* 1389 to 1527 K. 3rd law calculation of the partial pressure data gives $\Delta_r H°(298.15 K) = 148.2\ kcal{\cdot}mol^{-1}$ for $4.5\ WO_2(cr) = W_3O_9(g) + 1.5\ W(cr)$ which yields $\Delta_f H°(W_3O_9, g, 298.15 K) = -486.0\ kcal{\cdot}mol^{-1}$, using all JANAF functions.

Normand and Staley[3] have obtained $\Delta_r H°(1800 K) = -240\ kcal{\cdot}mol^{-1}$ for $3\ WO_3(g) = W_3O_9(g)$ by mass spectrometric study of the vapor over WO_3 dissolved in $CaO{-}Al_2O_3{-}SiO_2$. The value of $\Delta_r H°$ was determined by the 2nd law method from ion intensities and leads to $\Delta_f H°(W_3O_9, g) = -463.4\ kcal{\cdot}mol^{-1}$. Using all JANAF functions (dated September 30, 1966). The absolute pressure values reported by Norman and Staley also appear to be quite inconsistent with the JANAF functions since they lead to $-443\ kcal{\cdot}mol^{-1}$ by the 3rd law method.

Source	Reaction	T/K	$\Delta_r H°(298.15 K)$, $kcal{\cdot}mol^{-1}$ 2nd law	3rd law	Drift $cal{\cdot}K^{-1}{\cdot}mol^{-1}$	$\Delta_f H°(298.15 K)$ $kcal{\cdot}mol^{-1}$
1	$4.5\ WO_2(cr) = W_3O_9(g) + 1.5\ W(cr)$	1300–1600	150.61	150.64	−0.05	−483.6*
2	$4.5\ WO_2(cr) = W_3O_9(g) + 1.5\ W(cr)$	1389–1527	148.20	148.20	−1.91 ± 0.24	−486.0*
3	$3\ WO_3(g) = W_3O_9(g)$	1700–1900	−253.4	−233		−463.4**

*3rd law value adopted in calculation** 2nd law value adopted in calculation

Heat Capacity and Entropy

The heat capacity was approximated by making a tenative choice of the vibrational frequencies of 800 cm^{-1}(6), 396 cm^{-1}(3), 330 cm^{-1}(9), 200 cm^{-1}(6), and 150 cm^{-1}(6) in order to give the entropy at 1450 K. $S°(1450 = 219.14\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, corresponding to $\Delta_f S°(1450 K) = 110.26\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, reported by Ackermann and Rauh.[1] The adopted value, $S°(W_3O_9, g, 298.15 K) = 120.6\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, was reduced from the entropy at 1450 K, using JANAF functions. 2nd law calculation of the partial pressure data of Battles[2] gives $\Delta_r S°(1455 K) = 71.7\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ for $4.5\ WO_2(cr) = W_3O_9(g) + 1.5\ W(cr)$. This yields $S°(W_3O_9, g, 298.15 K) = 122.4\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

The molecular configuration for $W_3O_9(g)$ is estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, and that each tetrahedra shares two oxygen atoms to form a planar six–member ring. The bond distance W–O is estimated as 1.81 Å and the bond angles O–W–O = 109.47° and $W{-}O_{bridge}{-}W = 130.53°$. The principal moments of inertia are: $I_A = I_B = 280.4787 \times 10^{-39}$ and $I_C = 491.3257 \times 10^{-39}\ g{\cdot}cm^2$.

References

[1] R. J. Ackermann and E. G. Rauh, J. Phys. Chem. 67, 2596 (1963).
[2] J. E. Battles, Ph.D. dissertation, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide," the Ohio State University, (1964).
[3] J. H. Norman and H. G. Staley, J. Chem. Phys. 43, 3804 (1965).
[4] K. Ueno, J. Chem. Soc. Japan 62, 990 (1941).
[5] J. Berkowitz, W. A. Chupka and M. G. Inghram, J. Chem. Phys. 27, 85 (1957).
[6] P. E. Blackburn, J. Hoch and H. L. Johnston, J. Phys. Chem. 62, 769 (1958); P. E. Blackburn, WADC TR 59-575, part 1, March 1960; and part 2, (December 1960).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	S°	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−41.659	−2011.047	−2011.047	INFINITE
100	111.355	318.753	675.866	−35.711	−2020.127	−1971.131	1029.613
200	186.893	422.590	524.066	−20.295	−2023.834	−1920.252	501.518
250	208.026	466.694	508.266	−10.393	−2023.962	−1894.323	395.797
298.15	222.942	504 674	504.674	0.	−2023.382	−1869.398	327.511
300	223.433	506.055	504.678	0 413	−2023.349	−1868.443	325.325
350	234.911	541.401	507.443	11.885	−2022.194	−1842.710	275.009
400	243.591	573.362	513.718	23.858	−2020.665	−1817.170	237.298
450	250.250	602.454	521.986	36.211	−2018.894	−1791.837	207.991
500	255.430	629 100	531.384	48.858	−2016.973	−1766.710	184.567
600	262.784	676.370	551.710	74.796	−2012.925	−1717.036	149.481
700	267.594	717.264	572.506	101.331	−2008.839	−1668.045	124.471
800	270.884	753.225	592.894	128.265	−2004.856	−1619.634	105.751
900	273.223	785.273	612.521	155.476	−2001.036	−1571.712	91.220
1000	274.939	814.153	631.264	182.889	−1997.404	−1524.206	79.616
1100	276.232	840.421	649.102	210.450	−1993.970	−1477.053	70.139
1200	277.230	864.501	666.063	238.125	−1990.738	−1430.205	62.255
1300	278.015	886.723	682.193	265.889	−1987.708	−1383.619	55.594
1400	278.644	907.350	697.548	293.723	−1984.883	−1337.257	49.894
1500	279.154	926.592	712.183	321.614	−1982.266	−1291.092	44.960
1600	279.575	944.622	726.153	349.551	−1979.861	−1245.093	40.648
1700	279.924	961.582	739.508	377.526	−1977.669	−1199.238	36.848
1800	280.219	977.591	752.294	405.534	−1975.697	−1153.508	33.474
1900	280.469	992.749	764.554	433.569	−1973.946	−1107.879	30.458
2000	280.683	1007.140	776.327	461.627	−1972.423	−1062.336	27.745
2100	280.867	1020.839	787.647	489.704	−1971.130	−1016.865	25.293
2200	281.028	1033.909	798.546	517.799	−1970.069	−971.447	23.065
2300	281.168	1046.404	809.053	545.909	−1969.243	−926.076	21.032
2400	281.291	1058.374	819.193	574.032	−1968.653	−880.736	19.169
2500	281.400	1069.859	828.992	602.167	−1968.301	−835.414	17.455
2600	281.496	1080.897	838.470	630.312	−1968.175	−790.102	15.873
2700	281.583	1091.523	847.646	658.466	−1968.357	−744 787	14.409
2800	281.660	1101.765	856.540	686.628	−1968.949	−699.459	13.049
2900	281.729	1111.650	865.168	714.798	−1970.069	−654.106	11.782
3000	281.792	1121.202	873.544	742.974	−1971.795	−608.699	10.598
3100	281.849	1130.443	881.683	771.156	−1974.254	−563.221	9.490
3200	281.900	1139.392	889.597	799.343	−1977.538	−517.657	8.450
3300	281.947	1148.067	897.299	827.536	−1981.721	−471.975	7.471
3400	281.990	1156.485	904.799	855.732	−1986.906	−426.148	6.547
3500	282.029	1164.659	912.107	883.933	−1993.284	−380.155	5.674
3600	282.065	1172.605	919.233	912.138	−2001.139	−333.958	4.846
3700	282.098	1180.334	926.186	940.346	−2115.069	−286.949	4.051
3800	282.129	1187.857	932.974	968.558	−2116.015	−237.524	3.265
3900	282.157	1195.186	939.603	996.772	−2117.019	−188.075	2.519
4000	282.184	1202.330	946.083	1024.989	−2118.081	−138.604	1.810
4100	282.208	1209.298	952.418	1053.209	−2119.200	−89.104	1.135
4200	282.231	1216.099	958.615	1081.431	−2120.372	−39.575	0.492
4300	282.252	1222.740	964.681	1109.655	−2121.599	9.984	−0.121
4400	282.271	1229.229	970.620	1137.881	−2122.879	59.568	−0.707
4500	282.290	1235.573	976.437	1166.109	−2124.210	109.182	−1.267
4600	282.307	1241.777	982.139	1194.339	−2125.596	158.827	−1.804
4700	282.323	1247.849	987.728	1222.570	−2127.035	208.505	−2.317
4800	282.338	1253.793	993.209	1250.803	−2128.529	258.213	−2.810
4900	282.352	1259.615	998.587	1279.038	−2130.079	307.956	−3.283
5000	282.366	1265.319	1003.864	1307.274	−2131.686	357.728	−3.737
5100	282.378	1270.911	1009.046	1335.511	−2133.353	407.534	−4.174
5200	282.390	1276.394	1014.135	1363.749	−2135.081	457.367	−4.594
5300	282.401	1281.773	1019.134	1391.989	−2136.873	507.244	−4.999
5400	282.412	1287.052	1024.047	1420.230	−2138.735	557.147	−5.389
5500	282.422	1292.234	1028.876	1448.471	−2140.667	607.087	−5.766
5600	282.431	1297.323	1033.624	1476.714	−2142.674	657.068	−6.129
5700	282.440	1302.322	1038.294	1504.958	−2144.760	707.079	−6.480
5800	282.449	1307.234	1042.889	1533.202	−2146.929	757.134	−6.819
5900	282.457	1312.063	1047.411	1561.447	−2149.185	807.216	−7.147
6000	282.465	1316.810	1051.861	1589.693	−2151.535	857.349	−7.464

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

Tungsten Oxide ($(WO_3)_3$) $O_9W_3(g)$

Phosphorus Oxide ($(P_2O_5)_2$) CRYSTAL $M_r = 283.88904$ Phosphorus Oxide ($(P_2O_5)_2$) $O_{10}P_4(cr)$

$\Delta_f H°(0\ K) = -2979.041 \pm 8.9\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = 228.781 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298\ 15\ K) = -3009\ 936 \pm 8.9\ kJ \cdot mol^{-1}$
$T_{sub} = 631\ K$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(298.15\ K)$ of $P_4O_{10}(cr)$ has been reported by many investigators. The most recent value, $\Delta_f H°(298.15\ K) = -719.4 \pm 2.0\ kcal \cdot mol^{-1}$ for the reaction $P_4(\alpha, white, cr) + 5\ O_2(g) = P_4O_{10}(hex, cr)$ was determined by Egan and Luff.[1] This $\Delta_f H°(298.15\ K)$ value was derived from energy of combustion, $\Delta_c E = -716.397\ kcal \cdot mol^{-1}$, which is an average value of many measurements using three different sample forms, i.e , uncoated phosphorus, lucite coated phosphorus and cellulose acetate coated phosphorus. The adopted $\Delta_f H°(P_4O_{10}$, cr, 298.15 K) value was recalculated based on the P(red, V, cr) as reference state.

The enthalpy of combustion of white phosphorus was determined as 713.2 ± 1.0 $kcal \cdot mol^{-1}$ by Holmes[2] yielding $\Delta_f H°(P_4O_{10}$, cr, 298.15 K) = $-696.5 \pm 1.3\ kcal\ mol^{-1}$, based on P(red, V, cr) as reference state The enthalpy of formation of P_2O_5 from red phosphorus was reported to be 355 ± 2 $kcal\ mol^{-1}$ by Koerner and Daniels.[3] The product, P_2O_5, was considered to be a mixture of two forms, i e., crystalline and amorphous. The other $\Delta_f H°(P_4O_{10}$, cr, 298.15 K) values reported by early investigators were reviewed by Egan and Luff.[1]

Heat Capacity and Entropy

The heat capacities (12–324 K) and $S°(298.15\ K)$ adopted were taken from Andon *et al.*[4] The $C_p°$ values above 324 K were obtained by graphical extrapolation. The $S°(298.15\ K)$ value was calculated based on $S°(10\ K) = 0.36\ cal \cdot K^{-1} \cdot mol^{-1}$.

Low temperature (15–310 K) and high temperature (298.15–623.15 K) heat capacities were also measured by Thermal Laboratory[5] and Frandsen,[6] respectively. The low temperature data were not adopted because they are less satisfactory than the data of Andon *et al.*[4] The high temperature data were not used because the sample employed for enthalpy measurements was not explicitly reported as pure hexagonal form.

Sublimation Data

The value of $\Delta_{sub}H°(298.15\ K)$ was derived from the vapor pressure data by both the 2nd and 3rd law analyses. See the $P_4O_{10}(g)$ table for details. T_{sub} is the temperature at which the Gibbs energy change of the reaction $P_4O_{10}(hex, cr) = P_4O_{10}(g)$ approaches zero. Sublimation temperature for $P_4O_{10}(cr)$ was derived to be 632 K, 636 K (average of three determinations) and 623.7 K (average of two determinations) by Frandsen[6] from the vapor pressure data reported by Hoeflake and Scheffer,[7] Smits[8] and Smits and Rutgers,[9] respectively.

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−33.962	−2979.041	−2979.041	INFINITE
100	77.613	77.530	376.309	−29 878	−2993.030	−2907.054	1518.489
200	154.557	155.896	246.521	−18.125	−3004.886	−2816.879	735.693
298 15	211.710	228.781	228.781	0.000	−3009.936	−2723.335	477.117
300	212.673	230 094	228.785	0.393	−3009.992	−2721.557	473.865
400	260.245	297.978	237 719	24 104	−3014 145	−2624.398	342.711
500	299.993	360.390	256.096	52.147	−3011.926	−2527.145	264.009
600	335.975	418.323	278.362	83.977	−3006.425	−2430.655	211.607
700	368 192	472.581	302.272	119.216	−2997.988	−2335.322	174.264
800	396 643	523.641	326 783	157.486	−2986 933	−2241.381	146.347
900	421.747	571.849	351.360	198.440	−2973.536	−2148.968	124 723
1000	442.667	617.389	375 707	241.682	−2958 135	−2058 158	107.507
1100	461 077	660.477	399.655	286.904	−2940.989	−1968.976	93.499
1200	475.302	701.230	423.104	333.751	−3176.705	−1877.108	81.708
1300	486.181	739 718	445.993	381.843	−3153.960	−1769.725	71 108
1400	494 967	776 080	468.284	430.914	−3130 407	−1664.124	62.089
1500	502.080	810.481	489.961	480.780	−3106.213	−1560.231	54.332

PREVIOUS. December 1962 CURRENT: December 1965

Phosphorus Oxide ($(P_2O_5)_2$) $O_{10}P_4(cr)$

Phosphorus Oxide ($(P_2O_5)_2$) IDEAL GAS $M_r = 283.88904$ Phosphorus Oxide ($(P_2O_5)_2$) $O_{10}P_4(g)$

$S°(298.15\ K) = [403.964]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -2870.18 \pm 8.9\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -2904.08 \pm 8.9\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
424(1)	650 (2)	750(3)	764(3)
721(1)	952 (2)	257(3)	1015(3)
1417(1)	[170](3)	329(3)	1390(3)
278(2)	[470](3)	573(3)	

Ground State Quantum Weight: [1] $\sigma = 12$
Point Group: T_d
Bond Distances: $P{-}O_{apical} = 1.40 \pm 0.03$ Å $P{-}O = 1.60 \pm 0.01$ Å $P{-}P = 2.83 \pm 0.03$ Å
Bond Angles: $O_{apical}{-}P{-}O = 117 \pm 1°$ $O{-}P{-}O = 101 \pm 1°$ $P{-}O{-}P = 124°30' \pm 1°$
Product of the Moments of Inertia: $I_AI_BI_C = 2.939188 \times 10^{-111}\ g^3{\cdot}cm^6$

Enthalpy of Formation

$\Delta_fH°(P_4O_{10}, g, 298.15\ K)$ was calculated from the enthalpies of formation and sublimation for P_4O_{10}(hex, cr). The enthalpy of sublimation, $\Delta_{sub}H°(298.15\ K)$, was derived from vapor pressure data by the second and third law methods. The results obtained are presented as follows.

Source	T/K	$\Delta_{sub}H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
1	260.0–401.0	25.42 ± 0.07	25.33	−0.39 ± 0.13
2	216.2–300.4	25.59 ± 0.06	25.35	−0.18 ± 0.14
	283.6–389.3	25.45 ± 0.07	25.35	−0.10 ± 0.07

The value of $\Delta_{sub}H°(298.15\ K)$ adopted was $25.34 + 0.08\ kcal{\cdot}mol^{-1}$. There are many vapor pressure measurements reported but only the above two over P_4O_{10}(hex, cr).

It has been shown that P_4O_{10} has three solid phases and two liquid phases. The three solid phases are hexagonal, orthorhombic and tetragonal. As temperature increases, the thermal stability of P_4O_{10} follows the same order. The metastable liquid, according to data of Hoeflake and Scheffer[1] is from hexagonal form. The stable liquid is from tetragonal form. Hill *et al.*[3] reported that molecules of P_4O_{10} having the same structure as in the vapor are present in the hexagonal form of the solid. The vapor pressures of P_4O_{10} over different condensed phases have been measured by many investigators and reviewed by Farr.[4] The complexity of the solid state of P_4O_{10} has also been discussed by Smits and Rutgers,[5] Smits,[6] Smits *et al.*[7] and Smits.[8]

Heat Capacity and Entropy

The molecular structure and constants were obtained from Akishin *et al.*[9] The molecular structure of $P_4O_{10}(g)$ has also been studied by the electron diffraction method by Maxwell *et al.*[10] and Hampson and Stosick.[11] The model of the P_4O_{10} molecule was later confirmed by the x–ray method reported by Decker and MacGillavry[12] and spectroscopic studies reported by Gerding and DeDecker[13] and Sidorov and Sobolev.[14] All vibrational frequencies were obtained from Egan[15] except nine frequencies, i.e. 170(3), 470(3), and 750(3) cm^{-1} which were estimated in order to make the second and third law values of $\Delta_{sub}H°(298.15\ K)$ agree. The principal moments of inertia are: $I_A = I_B = I_C = 143.2430 \times 10^{-39}\ g{\cdot}cm^2$. The heat capacities (549–1098°C or 822–1371 K) of $P_4O_{10}(g)$ have been determined by Frandsen.[16] His results are in fair agreement with the calculated ones.

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Continued on page 1816

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

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_fH°$	$\Delta_fG°$	log K$_f$
0	0.	0.	INFINITE	−30.951	−2870.176	−2870.176	INFINITE
100	70.439	269.420	534.866	−26.545	−2883.841	−2817.054	1471.478
200	136.770	339.152	419.662	−16.102	−2897.007	−2745.652	717.091
250	165.183	372.796	406.944	−8.537	−2901.099	−2707.317	565.663
298.15	188.804	403.964	403.964	0.	−2904.081	−2669.711	467.722
300	189.639	405.134	403.967	0.350	−2904.179	−2668.257	464.585
350	210.273	435.963	406.355	10.363	−2909.292	−2628.464	392.277
400	227.511	465.202	411.900	21.321	−2911.072	−2588.215	337.986
450	241.860	492.853	419.373	33.066	−2912.178	−2547.785	295.739
500	253.807	518.973	428.039	45.467	−2912.751	−2507.262	261.932
600	272.134	566.965	447.269	71.818	−2912.729	−2426.144	211.215
700	285.128	609.946	467.494	99.717	−2911.633	−2345.122	174.995
800	294.543	648.667	487.761	128.724	−2909.840	−2264.308	147.844
900	301.519	683.781	507.621	158.544	−2907.577	−2183.748	126.741
1000	306.801	715.835	526.863	188.972	−2904.990	−2103 459	109.873
1100	310.877	745.276	545.399	219.864	−2902.173	−2023.439	96.085
1200	314.081	772.469	563.203	251.119	−3153.482	−1939.372	84.419
1300	316.638	797.713	580.283	282.659	−3147.288	−1838.447	73.870
1400	318.708	821.257	596.664	314.430	−3141.035	−1738.001	64.846
1500	320.406	843.305	612.380	346.388	−3134.750	−1638.004	57.040
1600	321.814	864.030	627.467	378.501	−3128.454	−1538.426	50.224
1700	322.995	883.576	641.962	410.744	−3122.165	−1439.242	44.223
1800	323.993	902.067	655.904	443.094	−3115.899	−1340.429	38.898
1900	324.845	919.608	669.325	475.537	−3109.669	−1241.961	34 144
2000	325.577	936.290	682.260	508.059	−3103.484	−1143.821	29.874
2100	326.211	952.190	694.738	540.650	−3097.355	−1045.988	26.018
2200	326.763	967.379	706.788	573.299	−3091.289	−948.444	22.519
2300	327.246	981.915	718.436	606.000	−3085.291	−851.178	19.331
2400	327.672	995.851	729.707	638.746	−3079.366	−754.172	16.414
2500	328.050	1009.235	740.622	671.533	−3073.517	−657.409	13.736
2600	328.385	1022.108	751.203	704.355	−3067.746	−560.879	11.268
2700	328.685	1034.507	761.467	737.208	−3062.056	−464.568	8.988
2800	328.954	1046.466	771.434	770.091	−3056.445	−368.466	6.874
2900	329.196	1058.014	781.118	802.998	−3050.914	−272.569	4.909
3000	329.415	1069.178	790.535	835.929	−3045.464	−176.855	3.079
3100	329.613	1079.982	799.698	868.881	−3040.091	−81.321	1.370
3200	329.793	1090.450	808.622	901.851	−3034.796	14.035	−0.229
3300	329.957	1100.601	817.316	934.839	−3029.575	109.229	−1.729
3400	330.108	1110.453	825 794	967.842	−3024.427	204.269	−3 138
3500	330.245	1120.024	834.064	1000.860	−3019.352	299.155	−4.465
3600	330.372	1129.329	842.138	1033.891	−3014.344	393.899	−5.715
3700	330 488	1138.383	850.022	1066.934	−3009.405	488.502	−6.896
3800	330.596	1147.198	857.727	1099.988	−3004.531	582.980	−8.014
3900	330.695	1155.787	865.260	1133.053	−2999.720	677.326	−9.072
4000	330.788	1164.160	872.629	1166.127	−2994.972	771.546	−10 075
4100	330.873	1172.329	879.839	1199.210	−2990.286	865.651	−11.029
4200	330.953	1180.304	886.898	1232.301	−2985.658	959.642	−11.935
4300	331 027	1188.092	893.813	1265.400	−2981.091	1053.526	−12.798
4400	331.096	1195.703	900.588	1298.507	−2976.583	1147.299	−13.620
4500	331.161	1203.144	907.229	1331 620	−2972.132	1240 972	−14.405
4600	331.221	1210.423	913.741	1364.739	−2967.742	1334.546	−15.154
4700	331.278	1217.547	920.130	1397.864	−2963.413	1428.029	−15.871
4800	331.331	1224.523	926.399	1430.994	−2959.145	1521.419	−16.556
4900	331.381	1231.355	932.553	1464.130	−2954.941	1614.724	−17.213
5000	331.429	1238.050	938.596	1497.270	−2950.801	1707.940	−17.843
5100	331.473	1244.614	944.532	1530.416	−2946.730	1801.076	−18.447
5200	331.515	1251.051	950.365	1563.565	−2942.728	1894.126	−19.027
5300	331.554	1257.366	956.098	1596.718	−2938.801	1987.109	−19.584
5400	331.592	1263.564	961.735	1629.876	−2934.952	2080.012	−20.120
5500	331.627	1269.648	967.278	1663.037	−2931.182	2172.844	−20.636
5600	331.660	1275.624	972.731	1696.201	−2927.500	2265.616	−21.133
5700	331.692	1281.495	978.097	1729.369	−2923.907	2358.316	−21.612
5800	331.722	1287.264	983.378	1762.539	−2920.408	2450 960	−22.073
5900	331.751	1292.934	988.576	1795.713	−2917.010	2543.532	−22.519
6000	331.778	1298.510	993.696	1828.890	−2913.718	2636.061	−22.949

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

Tungsten Oxide ((WO$_3$)$_4$) IDEAL GAS $M_r = 927.3928$ Tungsten Oxide ((WO$_3$)$_4$) O$_{12}$W$_4$(g)

$\Delta_f H°(0\ K) = -2789.53 \pm 41.8\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = [605.272]\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -2804.12 \pm 41.8\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}
[800](8)	[240](8)
[300](8)	[200](18)

Ground State Quantum Weight: [1] $\sigma = [8]$
Point Group: [D$_{4h}$]
Bond Distance: W–O = [1.81] Å
Bond Angles: O–W–O = [109.47]° W–O$_{bridge}$–W = [160.53]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.854 \times 10^{-109}]\ g^3\cdot cm^6$

Enthalpy of Formation

The adopted value, $\Delta_f H°(W_4O_{12}, g, 298.15\ K) = -670.2\ kcal\cdot mol^{-1}$, was reduced from $\Delta_f H°(W_4O_{12}, g, 1450\ K) = -655.6\ kcal\cdot mol^{-1}$ of Ackermann and Rauh[1] who studied the sublimation behavior of the tungsten–oxygen system over the temperature range from 1300 to 1600 K by mass spectrometry, mass effusion and x–ray diffraction, and determined $\Delta_f G°(W_4O_{12}, g) = -655{,}600 + 160.29\,T\ cal\cdot K^{-1} mol^{-1}$ from partial pressure measurements over the W–WO$_2$(cr). They reviewed the previous determinations[1-4] of the thermodynamic properties of sublimation of WO$_3$ and also pointed out that it was not possible to make quantitative observations of stoichiometric WO$_3$ in vacuo since it is a "bivariant" system and the ion current is not constant until the composition of the sample reaches WO$_{2.96}$. This is probably the cause of previous discrepancies in sublimation studies.

Battles[2] has also studied the partial pressure of W$_4$O$_{12}$(g) over W–WO$_2$(cr) in the temperature range from 1449 to 1527 K. 3rd law calculation of the partial pressure data gives $\Delta_r H°(298.15\ K) = 172.0\ kcal\cdot mol^{-1}$ for 6 WO$_2$(cr) = W$_4$O$_{12}$(g) + 2 W(cr) which yields $\Delta_f H°(W_4O_{12}, g, 298.15\ K) = -673\ 6\ kcal\cdot mol^{-1}$, using all JANAF functions.

Source	Reaction	T/K	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$,(298.15 K) kcal mol^{-1}
1	6 WO$_2$(cr) = W$_4$O$_{12}$(g) + 2 W(cr)	1300–1600	175.41	175.55	0.01	−670.2
2	6 WO$_2$(cr) = W$_4$O$_{12}$(g) + 2 W(cr)	1449–1257	176.16	172.01	−2.90 ± 0.39	−673.6

Heat Capacity and Entropy

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 800 cm^{-1}(8), 300 cm^{-1}(8), 240 cm^{-1}(8), and 200 cm^{-1}(18) in order to give the entropy at 1450 K, $S°(1450\ K) = 278.9\ cal\cdot K^{-1}\cdot mol^{-1}$, corresponding to $\Delta_f S°(1450\ K) = -160.29\ cal\cdot K^{-1}\cdot mol^{-1}$, reported by Ackermann and Rauh.[1] The adopted value, $S°(W_4O_{12}, g, 298.15\ K) = 144.6\ cal\cdot K^{-1}\cdot mol^{-1}$, was reduced from the entropy at 1450 K, using JANAF functions. 2nd law calculation of the partial pressure data of Battles gives $\Delta_r S°(1487\ K) = 82.3\ cal\cdot K^{-1}\cdot mol^{-1}$ for 6 WO$_2$(cr) = W$_4$O$_{12}$(g) + 2 W(cr) This yields $S°(W_4O_{12}, g, 298.15\ K) = 147.4\ cal\cdot K^{-1}\cdot mol^{-1}$.

The molecular configuration for W$_4$O$_{12}$(g) is estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, and that each tetrahedra shares two oxygen atoms to form a planar eight–member ring. The bond distance W–O is estimated as 1.81 Å and the bond angles O–W–O = 109.47° and W–O$_{bridge}$–W = 160.53°. The principal moments of inertia are: $I_A = I_B = 5.935 \times 10^{-37}$ and $I_C = 1.094 \times 10^{-36}\ g\cdot cm^2$.

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−57.403	−2789.527	−2789.527	INFINITE
100	155.404	342.363	846.055	−50.369	−2802.530	−2728.938	1425.451
200	264.535	490.351	632.324	−28.395	−2806.053	−2653.323	692.977
250	290.904	552.391	610.266	−14.469	−2805.502	−2615.182	546.412
298.15	309.177	605.272	605.272	0.	−2804.117	−2578.641	451.767
300	309.778	607.186	605.277	0.573	−2804.051	−2577.242	448.738
350	323.782	656.042	609.104	16.428	−2801.950	−2539.600	379.015
400	334.379	700.000	617.765	32.894	−2799.410	−2502.290	326.766
450	342.521	739.875	629.152	49.825	−2796.588	−2465.317	286.167
500	348.867	776.305	642.072	67.117	−2793.598	−2428.668	253.721
600	357.895	840.770	669.957	102.488	−2787.414	−2356.261	205 131
700	363.813	896.414	698.424	138.593	−2781.241	−2284.891	170.501
800	367.868	945.276	726.289	175.189	−2775.246	−2214.397	144.585
900	370.754	988.780	753.082	212.128	−2769.495	−2144.639	124.472
1000	372.873	1027.958	778.644	249.314	−2764.016	−2075.507	108.413
1100	374.471	1063.575	802.952	286.685	−2758.816	−2006.909	95.300
1200	375 705	1096.213	826.049	324.197	−2753.895	−1938.773	84.393
1300	376.676	1126.326	848.004	361.817	−2749.253	−1871.037	75.179
1400	377.453	1154.270	868.895	399.525	−2744.890	−1803.647	67.295
1500	378.085	1180.334	888.798	437.303	−2740.810	−1736.560	60.472
1600	378.605	1204.752	907.790	475.138	−2737.017	−1669.735	54.511
1700	379.038	1227.718	925.941	513.021	−2733.513	−1603.139	49.258
1800	379.402	1249.394	943.314	550.944	−2730.304	−1536.742	44.595
1900	379 712	1269.915	959.968	588.900	−2727.394	−1470.513	40.427
2000	379.976	1289.399	975.957	626.885	−2724.788	−1404.430	36.680
2100	380.205	1307.944	991.328	664.894	−2722.491	−1338.470	33.293
2200	380.404	1325.636	1006.124	702.925	−2720.506	−1272.608	30.216
2300	380.577	1342.549	1020.387	740.974	−2718.836	−1206.836	27.408
2400	380.730	1358.750	1034.150	779.039	−2717 481	−1141.129	24.836
2500	380.864	1374.294	1047.447	817 119	−2716.444	−1075.470	22.471
2600	380.984	1389.235	1060.307	855.212	−2715.711	−1009.846	20.288
2700	381.091	1403.615	1072.758	893.316	−2715.388	−944.241	18.267
2800	381.187	1417.476	1084.823	931.430	−2715.614	−878.640	16.391
2900	381.273	1430.854	1096.526	969.553	−2716.543	−813.024	14.644
3000	381.350	1443.781	1107.887	1007.684	−2718.281	−747.356	13.013
3100	381.420	1456.287	1118.925	1045.822	−2720.997	−681.614	11.485
3200	381.484	1468.397	1129.658	1083.968	−2724.814	−615.773	10.051
3300	381.542	1480.137	1140.101	1122.119	−2729.830	−549.794	8.703
3400	381.596	1491.528	1150.271	1160.276	−2736.182	−483.637	7.430
3500	381.644	1502.590	1160.180	1198.438	−2744.126	−417.277	6.228
3600	381.689	1513.342	1169.841	1236.605	−2754.039	−350.659	5.088
3700	381.730	1523.801	1179.267	1274.776	−2905.385	−282.975	3.995
3800	381.768	1533.981	1188.468	1312.951	−2906.086	−212.085	2.915
3900	381.803	1543.898	1197.455	1351.129	−2906.866	−141.178	1.891
4000	381.835	1553.565	1206.237	1389.311	−2907.723	−70.256	0.917
4100	381.866	1562.994	1214.824	1427.496	−2908.655	0.693	−0.009
4200	381.894	1572.196	1223.224	1465.684	−2909.660	71.664	−0.891
4300	381.920	1581.183	1231.445	1503.875	−2910.737	142.663	−1.733
4400	381.944	1589.963	1239.493	1542.068	−2911.885	213.682	−2.537
4500	381.967	1598.547	1247.377	1580.264	−2913.103	284.729	−3.305
4600	381.988	1606.942	1255.103	1618.461	−2914.392	355.804	−4 040
4700	382.008	1615.158	1262.677	1656.661	−2915.754	426.912	−4.745
4800	382.027	1623.201	1270.104	1694.863	−2917.187	498.048	−5.420
4900	382.044	1631.078	1277.391	1733.066	−2918.696	569.218	−6.068
5000	382.061	1638.796	1284.542	1771.272	−2920.281	640.416	−6.690
5100	382.076	1646.362	1291.563	1809.479	−2921.947	711.648	−7.289
5200	382 091	1653.782	1298.457	1847.687	−2923.694	782.906	−7.864
5300	382.105	1661.060	1305.230	1885.897	−2925.527	854.210	−8.419
5400	382.118	1668.202	1311.886	1924.108	−2927.452	925.540	−8.953
5500	382.131	1675.214	1318.429	1962.320	−2929.471	996.907	−9.468
5600	382.142	1682.100	1324.861	2000.534	−2931.590	1068.320	−9.965
5700	382.153	1688.863	1331.188	2038.749	−2933.815	1139.764	−10.445
5800	382.164	1695.510	1337.413	2076.965	−2936.150	1211.255	−10.909
5900	382.174	1702.043	1343.537	2115.182	−2938.602	1282.773	−11.357
6000	382.184	1708.466	1349.566	2153.399	−2941.178	1354.349	−11.791

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

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Continued from page 1733

Due to the large scatter in the mass spectrometric results, we prefer not to average the resulting $\Delta_f H°$ values but to rely on correlations with VO(g) and NbO(g). There has been good agreement for VO(g) and NbO(g) between the adopted JANAF $\Delta_f H°$(298.15 K) value and the value derived from the Birge–Sponer result corrected for ionicity.[2] Thus we adopt $\Delta_f H°$(TaO, g, 298.15 K) = 46.0 ± 15.0 kcal·mol^{-1}, which is a rounded value based on the adjusted Birge–Sponer result. This corresponds to $D_0^\circ = 8.65 \pm 0.65$ eV.

Heat Capacity and Entropy

The band spectrum attributable to TaO(g) has been observed by many investigators.[8–13] Weltner and McLeod[14] studied TaO spectroscopically in the infrared, visible, and near–ultraviolet regions by means of matrix isolation techniques. Sixteen electronic transitions were observed from the $X^2\Delta_{3/2}$ state, determined to be the ground state. Cheetham and Barrow[15] characterized nineteen electronic states from a rotational analysis of the emission spectrum of TaO in the region 2740–9500 Å. The combination of the results of these latter two studies as given by Cheetham and Barrow[15] provides the adopted vibrational and rotational constants as well as the electronic levels. Cheetham and Barrow[15] indicated the possibility of other low lying states based on the early work by Kiess and Stowell.[8]

The electronic states listed by Cheetham and Barrow[15] are actually sublevels as indicated by the value. The quantum weight of 2 is assigned if the two sublevels which are part of the same state are present (i.e. similar ω_e and $\omega_e x_e$ values of rthe same Δ state but different value). If the two sublevels of a particular Δ state are not accounted for, then a quantum weight of 4 is assigned to that sublevel which is tabulated.

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Recent C_p° data (60–298 K) for $TiO_{1.01}$[15] are larger at all temperatures with deviations of 2–3% at 110–250 K increasing to 5% at 298 K and 7% at 60 K. The new data yield $S°$(298.15 K) = 8.55 cal·K^{-1}·mol^{-1} of TiO. We know nothing about the TiO sample,[15] but it also may have been used to obtain enthalpies (700–2300 K) which are not yet published.[16] Shomate,[12] Naylor[13] and later Humphrey,[3] (see $\Delta_f H°$) all used the same sample, 99.2% pure with Si and C as impurities. The (O/Ti) ratio was 0.994.[17] Vacancy concentration is unknown and the phase is uncertain.

Transition Data and Phase Data – Refer to the β-crystal table for details.

Sublimation Data – This is the difference in $\Delta_f H°$ for TiO(g) and TiO(α).

References – References are listed on liquid table.

Continued from page 1738

Heat Capacity and Entropy

Electronic levels (T_0) and vibrational–rotational constants are from Rosen[1] as supplemented[4] by extensive new data.[2,3,5,8,9] Additional states near 32000 cm^{-1} [10, 3] are omitted since their effect is negligible. We estimate unknown spectroscopic constants from known values for states arising from like molecular–orbital configurations.[11] Although $^3\Delta$ is the ground state,[6] several authors[1–3, 12] noted that energy levels of all singlet states are approximate due to uncertainty in the low–lying $a^1\Delta$. We revise $a^1\Delta$ from 581 cm^{-1}[6] to 1000 ± 400 cm^{-1} based on the temperature dependence of band intensities,[6,7] the requirement that $b^1\Pi$ lie above $E^3\Pi$ observed at 11894 cm^{-1} in a Ne–matrix,[3] and the assumption that $f^1\Delta$[8,4] is the perturber of $C^3\Delta$[5]. The new E and f states confirm empirical predictions[11] which suggest additional unobserved levels at ~13000 ($^3\Sigma$) and 15000 cm^{-1}Σ). We omit these states since their predicted energies are less well established and their contributions to C_p° and $S°$ would be quite small. The functions are calculated using first–order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \Sigma Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$.

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The bending frequency is estimated as 270 ± 80 $\mathrm{cm^{-1}}$ from the following information. A value of 272 $\mathrm{cm^{-1}}$ derived from the three-constant valence–force field[17] using ν_1, ν_3 and $(k\delta/l^2)/k_1 = 0.040$ transferred from isoelectronic CaF_2.[18] The resulting value of k_{12}/k_1 is similar to that of CaF_2. The inferior two–constant central–force field gives $\nu_2 = 325$ $\mathrm{cm^{-1}}$. Bending modes have been observed[19] for electronic states of TaO_2 (285 and 281 $\mathrm{cm^{-1}}$) and WO_2 (300 $\mathrm{cm^{-1}}$). These molecules have stretching frequencies similar to TiO_2, but the excited states may be linear rather than bent as are the ground states. We estimate that $S°(298.15\ \mathrm{K})$ is uncertain by about 0.7 and 0.3 $\mathrm{cal\cdot K^{-1}\cdot mol^{-1}}$ due to uncertainties in ν_2 and the geometry, respectively.

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