

REFERENCE STATE

0 to 2896 K crystal
 2896 to 4951.969 K liquid
 above 4951.969 K ideal monatomic gas

Refer to the individual tables for details.

Molybdenum (Mo)

A_r = 95.94 Molybdenum (Mo)

Mo₁(ref)

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
	C _p ^o	S ^o - [G° - H°(T _r)]/T _r	H° - H°(T _r)	Δ _r H°	
	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	kJ·mol ⁻¹	kJ·mol ⁻¹	
0	0	INFINITE	0	0	0
100	13.495	7.026	-4.585	0	0
200	21.507	19.478	-4.094	0	0
298.15	23.933	28.605	-2.251	0	0
300	23.958	28.606	0	0	0
400	25.080	35.810	0.044	0	0
500	25.850	41.494	2.500	0	0
600	26.460	46.263	5.049	0	0
700	26.980	50.382	7.665	0	0
800	27.440	54.015	10.338	0	0
900	27.850	57.272	13.059	0	0
1000	28.370	60.235	15.825	0	0
1100	28.900	62.963	18.638	0	0
1200	29.490	65.502	21.501	0	0
1300	30.140	67.888	24.419	0	0
1400	30.860	70.148	27.400	0	0
1500	31.650	72.304	30.450	0	0
1600	32.500	74.373	33.575	0	0
1700	33.420	76.371	36.782	0	0
1800	34.420	78.309	40.078	0	0
1900	35.490	80.198	43.469	0	0
2000	36.650	82.048	46.964	0	0
2100	37.900	83.866	50.570	0	0
2200	39.240	85.659	54.297	0	0
2300	40.670	87.435	58.152	0	0
2400	42.210	89.198	62.147	0	0
2500	43.890	90.954	66.290	0	0
2600	45.880	92.713	70.594	0	0
2700	48.370	94.490	75.079	0	0
2800	51.570	96.304	79.786	0	0
2896.000	54.835	98.098	84.777	0	0
2896.000	57.656	110.522	89.885	0	0
2900	57.656	110.522	125.867	0	0
3000	57.656	110.574	126.018	0	0
3100	57.656	111.851	129.784	0	0
3200	57.656	113.086	133.549	0	0
3300	57.656	114.281	137.315	0	0
3400	57.656	115.440	141.080	0	0
3500	57.656	116.564	144.846	0	0
3600	57.656	117.656	148.612	0	0
3700	57.656	118.716	152.377	0	0
3800	57.656	119.748	156.143	0	0
3900	57.656	120.752	159.908	0	0
4000	57.656	121.731	163.674	0	0
4100	57.656	122.684	167.440	0	0
4200	57.656	123.614	171.205	0	0
4300	57.656	124.521	174.971	0	0
4400	57.656	125.407	178.736	0	0
4500	57.656	126.273	182.502	0	0
4600	57.656	127.119	186.268	0	0
4700	57.656	127.947	190.033	0	0
4800	57.656	128.757	193.799	0	0
4900	57.656	129.549	197.564	0	0
4951.969	53.001	130.723	203.287	0	0
4951.969	53.001	249.995	793.918	0	0
5000	53.713	250.510	796.481	0	0
5100	55.185	251.988	801.926	0	0
5200	56.640	253.674	807.517	0	0
5300	58.072	255.766	813.252	0	0
5400	59.483	258.265	819.150	0	0
5500	60.874	261.278	825.148	0	0
5600	62.239	264.811	831.303	0	0
5700	63.577	268.874	837.593	0	0
5800	64.887	273.468	844.015	0	0
5900	66.164	278.604	850.565	0	0
6000	67.413	284.300	857.243	0	0

PREVIOUS: March 1978 (1 atm)

CURRENT: March 1978 (1 bar)

Molybdenum (Mo)

Mo₁(ref)

CRYSTAL

Molybdenum (Mo)

$$S^{\circ}(298.15 \text{ K}) = 28.605 \pm 0.050 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$T_{\text{fus}} = 2896 \pm 8 \text{ K}$$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacities of Mo(cr) have been measured by Clusius and Franzosini¹ between 16 and 256 K (63 measured C_p points). The reported C_p values are smoothed by fitting the data with orthogonal polynomials over selected overlapping temperature intervals. This fitting procedure also includes the smoothed C_p values (275–335 K) reported in the critical evaluation by Dimars *et al.*² so as to provide smoothly varying heat capacity values in the range 256–275 K. The data of Simon and Zeidler,³ 15–238 K, are as much as 2.5% high below 78 K and as much as 1% low above 78 K.

Below 20 K several investigators^{4–7} have determined the heat capacity. Heiniger *et al.*⁸ have summarized and critically reviewed this work as well as other studies. These sources give $S^{\circ}(20 \text{ K})$ values in the range 0.021–0.025 cal·K⁻¹·mol⁻¹. Adopting $S^{\circ}(20 \text{ K}) = 0.024$ cal·K⁻¹·mol⁻¹ and combining this with our analysis of the Clusius and Franzosini work,¹ we calculate $S^{\circ}(298.15 \text{ K}) = 6.836 \pm 0.012$ cal·K⁻¹·mol⁻¹. This result agrees with the review of the heat capacity data ($T < 298.15 \text{ K}$) by Reilly and Furukawa⁹ for Brewer.¹⁰

The high temperature heat capacity values, 273–2800 K, are those selected by Dimars *et al.*² This study reports three recent NBS heat capacity/enthalpy studies covering the 270–2800 K on NBS Standard Reference Material No. 781. In addition, the report contains a bibliography of publications on the high temperature enthalpy and heat capacity of crystalline molybdenum. A graphical comparison of the NBS results with those of all the principal investigators and critical evaluation is also given in the publication. These results are linearly extrapolated from 2800 K to 3300 K. The high temperature heat capacity values adopted by Brewer,¹⁰ based on IPTS–48, are within 0.1% of the NBS results between 298 and 900 K and are 0.2 to 0.3% higher between 1000 and 1400 K. Between 1500 and 1900 K, the difference is less than 0.1%. From 2000 to 2300 K, the values are 0.2 to 0.3% lower and are 0.1% low to 0.2% high between 2400 to 2700 K. The value at 2800 K is 0.5% lower than our adopted value. At 2800 K, the entropy difference is 0.004 cal·K⁻¹·mol⁻¹ with the JANAF value being smaller.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

Eight sublimation studies are discussed on the ideal gas table.

References

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- ⁹M. L. Reilly and G. T. Furukawa, U.S. Natl. Bur. Stand. personal communication to L. Brewer, (February, 1976).
- ¹⁰L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication of preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.

Molybdenum (Mo)

A₁ = 95.94

Molybdenum (Mo)

Mo₁(cr)

T/K	C _p ^a	S ^b - [G ^c - HF(T)]/T	H ^d - HF(T)	ΔH ^e	ΔG ^f	Standard State Pressure = p ^o = 0.1 MPa	
						kJ·mol ⁻¹	log K _r
0	0	INFINITE	-4.585	0	0	0	0
100	13.495	7.026	-4.094	0	0	0	0
200	21.507	30.735	-2.251	0	0	0	0
250	23.074	24.462	-1.133	0	0	0	0
298.15	23.933	28.605	0	0	0	0	0
300	23.938	28.753	0.044	0	0	0	0
350	24.580	32.494	28.900	0	0	0	0
400	25.080	35.810	29.560	0	0	0	0
450	25.500	38.789	30.423	0	0	0	0
500	25.850	41.494	31.597	0	0	0	0
600	26.460	46.263	33.487	0	0	0	0
700	26.980	50.382	35.613	0	0	0	0
800	27.440	54.015	38.059	0	0	0	0
900	27.850	57.272	39.689	0	0	0	0
1000	28.370	60.235	41.597	0	0	0	0
1100	28.900	62.963	43.417	0	0	0	0
1200	29.490	65.502	45.153	0	0	0	0
1300	30.140	67.888	46.811	0	0	0	0
1400	30.860	70.148	48.398	0	0	0	0
1500	31.650	72.304	49.970	0	0	0	0
1600	32.500	74.373	51.384	0	0	0	0
1700	33.420	76.371	52.796	0	0	0	0
1800	34.400	78.309	54.160	0	0	0	0
1900	35.480	80.198	55.481	0	0	0	0
2000	36.650	82.048	56.763	0	0	0	0
2100	37.900	83.866	58.010	0	0	0	0
2200	39.240	85.659	59.226	0	0	0	0
2300	40.670	87.435	60.414	0	0	0	0
2400	42.210	89.198	61.577	0	0	0	0
2500	43.890	90.954	62.717	0	0	0	0
2600	45.880	92.713	63.837	0	0	0	0
2700	48.370	94.490	64.939	0	0	0	0
2800	51.570	96.304	66.077	0	0	0	0
2896.000	54.835	98.098	67.060	89.885	0	0	0
2900	54.970	98.173	67.103	90.104	0.050	-0.001	-0.001
3000	58.370	100.094	68.170	95.771	-34.012	1.258	-0.072
3100	61.770	102.064	69.232	101.778	-31.771	2.398	-0.040
3200	65.170	104.078	70.289	108.125	-29.189	3.460	-0.056
3300	68.570	106.136	71.344	114.812	-26.268	4.436	-0.070

CRYSTAL ← LIQUID

PREVIOUS: December 1966

CURRENT March 1978

Molybdenum (Mo)

Mo₁(cr)

Mo₁(cr,l)

A_r = 95.94 Molybdenum (Mo)

CRYSTAL-LIQUID

0 to 2896 K crystal
above 2896 K liquid

Refer to the individual tables for details.

Molybdenum (Mo)

T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K		H ^o - H ^o (T _r)/J	Standard State Pressure = P ^o = 0.1 MPa	log K _f
		S ^o - [G ^o - H ^o (T _r)]/T	Δ _f H ^o / J·mol ⁻¹			
0	0	0	INFINITE	-4.585	0	0
100	13.495	7.026	47.961	-4.094	0	0
200	21.507	19.478	30.735	-2.251	0	0
250	23.074	24.462	28.995	-1.133	0	0
298.15	23.933	28.605	28.605	0	0	0
300	23.958	28.753	28.606	0.044	0	0
350	24.580	32.494	28.900	1.208	0	0
400	25.080	35.810	29.560	2.090	0	0
450	25.500	38.789	30.423	2.765	0	0
500	25.850	41.494	31.397	3.169	0	0
600	26.460	46.263	33.487	4.665	0	0
700	26.980	50.382	35.613	6.338	0	0
800	27.440	54.015	37.691	8.159	0	0
900	27.890	57.272	39.689	10.075	0	0
1000	28.370	60.235	41.597	12.038	0	0
1100	28.900	62.963	43.417	14.041	0	0
1200	29.480	65.482	45.155	16.076	0	0
1300	30.110	67.888	46.811	18.140	0	0
1400	30.860	70.186	48.398	20.225	0	0
1500	31.650	72.304	49.920	22.325	0	0
1600	32.500	74.373	51.384	24.435	0	0
1700	33.420	76.371	52.796	26.550	0	0
1800	34.420	78.309	54.160	28.665	0	0
1900	35.490	80.198	55.481	30.775	0	0
2000	36.650	82.048	56.763	32.875	0	0
2100	37.900	83.866	58.010	34.960	0	0
2200	39.240	85.659	59.226	37.025	0	0
2300	40.670	87.435	60.414	39.065	0	0
2400	42.210	89.198	61.577	41.080	0	0
2500	43.890	90.954	62.717	43.065	0	0
2600	45.880	92.713	63.837	45.015	0	0
2700	48.370	94.490	64.939	46.935	0	0
2800	51.570	96.304	66.027	48.815	0	0
2896.000	54.835	98.098	67.060	50.650	0	0
2896.000	37.656	110.522	67.060	89.885	CRYSTAL → LIQUID	0
2900	37.656	110.574	67.120	125.867	CRYSTAL → LIQUID	0
3000	37.656	111.851	68.590	126.018	CRYSTAL → LIQUID	0
3100	37.656	113.086	70.005	129.784	CRYSTAL → LIQUID	0
3200	37.656	114.281	71.370	133.549	CRYSTAL → LIQUID	0
3300	37.656	115.440	72.688	137.315	CRYSTAL → LIQUID	0
3400	37.656	116.564	73.962	141.080	CRYSTAL → LIQUID	0
3500	37.656	117.656	75.195	144.846	CRYSTAL → LIQUID	0
3600	37.656	118.716	76.389	148.612	CRYSTAL → LIQUID	0
3700	37.656	119.748	77.547	152.377	CRYSTAL → LIQUID	0
3800	37.656	120.752	78.671	156.143	CRYSTAL → LIQUID	0
3900	37.656	121.731	79.763	159.908	CRYSTAL → LIQUID	0
4000	37.656	122.684	80.824	163.674	CRYSTAL → LIQUID	0
4100	37.656	123.614	81.856	167.440	CRYSTAL → LIQUID	0
4200	37.656	124.521	82.861	171.205	CRYSTAL → LIQUID	0
4300	37.656	125.407	83.841	174.971	CRYSTAL → LIQUID	0
4400	37.656	126.273	84.795	178.736	CRYSTAL → LIQUID	0
4500	37.656	127.119	85.726	182.502	CRYSTAL → LIQUID	0
4600	37.656	127.947	86.635	186.268	CRYSTAL → LIQUID	0
4700	37.656	128.757	87.523	190.033	CRYSTAL → LIQUID	0
4800	37.656	129.549	88.390	193.799	CRYSTAL → LIQUID	0
4900	37.656	130.326	89.238	197.564	CRYSTAL → LIQUID	0
4951.969	37.656	130.723	89.671	201.330	CRYSTAL → LIQUID	0
5000	37.656	131.087	90.068	203.287	FUGACITY = 1 bar	0
5100	37.656	131.832	90.879	205.096	5.731	-0.060
5200	37.656	132.564	91.674	208.861	17.690	-0.181
5300	37.656	133.281	92.452	212.627	29.683	-0.298
5400	37.656	133.985	93.215	216.392	41.713	-0.411
5500	37.656	134.676	93.962	220.158	53.781	-0.520
5600	37.656	135.354	94.695	223.924	65.889	-0.626
5800	37.656	136.676	96.120	227.689	603.614	-0.728
6000	37.656	137.952	97.494	235.220	608.795	-0.923
				242.752	614.491	-1.106

PREVIOUS:

CURRENT: March 1978

Molybdenum (Mo)

Mo₁(cr,l)

Molybdenum (Mo)

IDEAL GAS

Molybdenum (Mo)

Mo(g)

IP(Mo, g) = 57260 ± 50 cm⁻¹
S°(298.15 K) = 181.951 ± 0.04 J·K⁻¹·mol⁻¹

Table with 2 columns: State, g.; and 2 columns: Electronic Levels and Quantum Weights. Rows include 7s, 7s2, 7p, 7p2, 7d, 7d2, 7f, 7f2, 7f3, 7f4, 7f5, 7f6, 7f7, 7f8, 7f9, 7f10, 7f11, 7f12, 7f13, 7f14, 7f15, 7f16, 7f17, 7f18, 7f19, 7f20.

ΔHf°(0 K) = 657.37 ± 3.8 kJ·mol⁻¹
ΔHf°(298.15 K) = 658.98 ± 3.8 kJ·mol⁻¹

Main thermodynamic data table with columns: T/K, Cp°, S°, S°(T) - S°(298.15 K), H° - H°(T), ΔHf°, ΔG°, log Kf. Rows correspond to temperatures from 100 to 6000 K.

Enthalpy of Formation
The enthalpy of formation at 298.15 K for Mo(g) is simply the enthalpy of sublimation at 298.15 K, i.e. Mo(cr) → Mo(g). The following table summarizes the analysis of the numerous sublimation studies by a 2nd and 3rd law calculation. All temperatures have been corrected to IPTS-68. All studies are based on the Langmuir effusion method.

Data table with columns: Source, Points, eqn, T/K, ΔsubHf°(298.15 K), kcal·mol⁻¹, 2nd law, 3rd law, Draft. Rows 1-7 list various studies and their calculated values.

A mass spectrometric study of the enthalpy of sublimation of molybdenum⁹ yielded, ΔsubHf°(2500 K) = 144.1 ± 2.2 kcal·mol⁻¹; correcting to 298.15 K, we calculate ΔsubHf°(298.15 K) = 149.8 kcal·mol⁻¹. We adopt ΔsubHf°(298.15 K) = 157.5 ± 0.9 kcal·mol⁻¹ from a consideration of five studies.^{1-6,7} Brewer¹² has adopted a value 0.2 kcal·mol⁻¹ less positive, however his vapor pressure analysis is based on the 1948 temperature scale.

Heat Capacity and Entropy

The electronic energy levels are given in the compilations by Moore.^{9,10} Although we have only listed the ground state, first excited state, highest observed excited state, and the ionization limit for Mo(g), all levels listed by Moore,^{9,10} as well as estimated levels, are used in our calculations. The observed levels are too numerous to list completely. An examination of the estimates for missing levels suggests that they all lie above 20000 cm⁻¹. Our calculations indicate that for Mo(g) the thermochemical functions are independent of the estimated missing levels (for n = 5, 6, 7), the cut-off procedure, and the inclusion of n = 6, 7 levels up to 3000 K. The Gibbs energy function is essentially unaffected up to 4000 K. The reported uncertainty in S°(298.15 K) is due to uncertainties in the relative atomic gas and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut-off procedures.¹¹ In fact, the inclusion of some higher states (n = 5, 6, 7) and consideration of various cut-off procedures leads to calculational differences in the Gibbs energy function of roughly 0.1 cal·K⁻¹·mol⁻¹ or greater at temperatures in excess of 7600 K. The thermal functions adopted here are the same as those of Brewer.¹²

References

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2. H. Z. Jones, I. Langmuir, and G. M. J. Mackay, Phys. Rev. 30, 201 (1927).
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PREVIOUS: March 1978 (1 atm)

CURRENT: March 1978 (1 bar)

IDEAL GAS

Molybdenum, Ion (Mo⁺)

EA(Mo, g) = 0.746 ± 0.010 eV
 S°(298.15 K) = 180.669 ± 0.003 J·K⁻¹·mol⁻¹

Electronic Level and Quantum State	Weight g _i
6S _{3/2}	6

Enthalpy of Formation

Δ_fH°(Mo⁺, g, 0 K) is calculated from Δ_fH°(Mo, g, 0 K) using the adopted electron affinity of EA(Mo) = 0.746 ± 0.010 eV (71.978 ± 0.965 kJ·mol⁻¹). This value, recommended by Hotop and Lineberger,² is based on a laser photodetachment electron spectroscopy study.³ Additional information on Mo⁺(g) may be obtained in the critical discussions of Hotop and Lineberger,^{2,4} Rosenstock *et al.*,⁵ and Massey.⁶

Δ_fH°(Mo⁺, g, 298.15 K) is obtained from Δ_fH°(Mo, g, 0 K) by using EA(Mo) with JANAF¹ enthalpies, H°(0 K) - H°(298.15 K), or Mo⁺(g), Mo(g), and e⁻ (ref) Δ_fH°(Mo⁺ → Mo + 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 Δ_fH°(298.15 K) should be changed by +6.197 kJ·mol⁻¹ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for Mo⁺(g) is given by Hotop and Lineberger^{2,4} and Rosenstock *et al.*⁵ Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

References

- ¹JANAF Thermochemical Tables: Mo(g), 3-31-78; e⁻ (ref), 3-31-82.
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M_r = 95.94055 Molybdenum, Ion (Mo⁺)

Δ_fH°(0 K) = 585.390 ± 1.5 kJ·mol⁻¹
 Δ_fH°(298.15 K) = [580.805] kJ·mol⁻¹

T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
		S ^o - [C _p ^o - F(T _r)]/T	INFINITE	H° - F(T)	Δ _f H°	
0	0	0	INFINITE	-6.197	585.390	
100	20.786	157.962	199.149	-4.119		-94.907
200	20.786	172.370	182.570	-2.040		-84.280
250	20.786	177.008	181.011	-1.001		-79.849
298.15	20.786	180.669	180.669	0	580.805	-69.068
300	20.786	180.798	180.669	0.038		-60.666
350	20.786	184.002	180.925	1.078		-53.971
400	20.786	186.777	181.483	2.117		-49.951
450	20.786	189.226	182.112	3.136		-36.859
500	20.786	191.416	183.024	4.196		-31.500
600	20.786	195.205	184.748	6.274		-24.170
700	20.786	198.410	186.477	8.353		-21.507
800	20.786	201.185	188.146	10.431		-19.299
900	20.786	203.633	189.733	12.510		-17.441
1000	20.786	205.823	191.235	14.589		-15.851
1100	20.786	207.805	192.653	16.667		-14.492
1200	20.786	209.613	193.992	18.746		-13.304
1300	20.786	211.277	195.258	20.824		-12.662
1400	20.786	212.817	196.438	22.903		-12.142
1500	20.786	214.251	197.597	24.982		-11.342
1600	20.786	215.593	198.680	27.060		-10.524
1700	20.786	216.853	199.713	29.139		-9.793
1800	20.786	218.041	200.698	31.217		-9.136
1900	20.786	219.165	201.641	33.296		-8.542
2000	20.786	220.231	202.544	35.375		-8.005
2100	20.786	221.245	203.410	37.453		-7.516
2200	20.786	222.212	204.243	39.532		-6.662
2300	20.786	223.136	205.045	41.610		-5.934
2400	20.786	224.021	205.817	43.689		-5.354
2500	20.786	224.869	206.562	45.768		-4.824
2600	20.786	225.685	207.282	47.846		-4.354
2700	20.786	226.469	207.979	49.925		-3.934
2800	20.786	227.225	208.652	52.004		-3.554
2900	20.786	227.955	209.306	54.082		-3.214
3000	20.786	228.659	209.939	56.161		-2.914
3100	20.786	229.341	210.554	58.239		-2.649
3200	20.786	230.001	211.151	60.318		-2.419
3300	20.786	230.640	211.732	62.397		-2.219
3400	20.786	231.261	212.298	64.475		-2.049
3500	20.786	231.863	212.848	66.554		-1.909
3600	20.786	232.449	213.384	68.632		-1.799
3700	20.786	233.018	213.907	70.711		-1.709
3800	20.786	233.573	214.418	72.790		-1.634
3900	20.786	234.113	214.916	74.868		-1.574
4000	20.786	234.639	215.402	76.947		-1.524
4100	20.786	235.157	215.878	79.025		-1.484
4200	20.786	235.653	216.343	81.104		-1.454
4300	20.786	236.142	216.797	83.183		-1.434
4400	20.786	236.620	217.243	85.261		-1.424
4500	20.786	237.087	217.678	87.340		-1.424
4600	20.786	237.544	218.105	89.418		-1.434
4700	20.786	237.991	218.524	91.497		-1.454
4800	20.786	238.429	218.934	93.576		-1.484
4900	20.786	238.857	219.336	95.654		-1.524
5000	20.786	239.277	219.731	97.733		-1.574
5100	20.786	239.689	220.118	99.811		-1.634
5200	20.786	240.093	220.498	101.890		-1.704
5300	20.786	240.488	220.872	103.969		-1.784
5400	20.786	240.877	221.239	106.047		-1.874
5500	20.786	241.258	221.599	108.126		-1.974
5600	20.786	241.633	221.954	110.204		-2.084
5700	20.786	242.001	222.302	112.283		-2.204
5800	20.786	242.362	222.645	114.362		-2.334
5900	20.786	242.718	222.982	116.440		-2.474
6000	20.786	243.067	223.314	118.519		-2.624

PREVIOUS: March 1978 (1 atm)

CURRENT: March 1984 (1 bar)

Molybdenum, Ion (Mo⁺)

Mo⁺(g)

Mo₂O₃(cr)

M₁ = 127.9388 Molybdenum Oxide (MoO₂)

CRYSTAL

Molybdenum Oxide (MoO₂)

T/K	C _p ^o	S ^o - [G ^o - F ^o (T)]/T	H ^o - F ^o (T)	ΔH ^o	log K _r
0	0	INFINITE	-8.319	-582.903	INFINITE
100	16.175	85.470	-7.801	-585.780	296.951
200	41.363	26.960	-4.841	-587.574	143.743
298.15	55.898	46.459	0	-587.852	93.206
300	56.095	46.806	0.104	-587.847	92.571
400	63.551	64.076	6.125	-587.253	66.992
500	67.936	78.758	12.713	-586.272	51.666
600	71.174	91.441	19.674	-585.087	41.468
700	73.935	102.623	26.932	-583.757	34.199
800	76.488	112.664	34.434	-582.293	28.760
900	78.965	121.816	42.227	-580.692	24.541
1000	81.437	130.264	50.247	-578.946	21.176
1100	83.948	138.143	58.515	-577.049	18.431
1200	86.513	145.557	67.038	-574.994	16.151
1300	89.148	152.585	75.820	-572.776	14.230
1400	91.872	159.291	84.870	-570.389	12.589
1500	94.680	165.725	94.197	-567.829	11.173
1600	97.588	171.927	103.810	-565.090	9.940
1700	100.588	177.933	113.718	-562.170	8.858
1800	103.688	183.770	123.931	-559.064	7.901
1900	106.893	189.461	134.459	-555.770	7.049
2000	110.198	195.028	145.313	-552.285	6.288
2100	113.608	200.487	156.502	-548.608	5.603
2200	117.123	205.852	168.038	-544.736	4.985
2300	120.742	211.138	179.930	-540.669	4.425
2400	124.470	216.355	192.190	-536.405	3.915
2500	128.302	221.514	204.827	-531.946	3.450
2600	132.244	226.622	217.854	-527.301	3.024
2700	136.290	231.689	231.280	-522.500	2.634
2800	140.440	236.720	245.115	-517.593	2.274
2900	144.704	241.722	259.371	-512.535	1.942
3000	149.072	246.701	274.059	-507.272	1.615

Pearson Notation: mP12
 S^o(298.15 K) = 46.459 ± 0.42 J·K⁻¹·mol⁻¹
 ΔH^o(0 K) = -582.90 ± 2.1 kJ·mol⁻¹
 ΔH^o(298.15 K) = -587.85 ± 2.9 kJ·mol⁻¹

Enthalpy of Formation
 The adopted enthalpy of formation of MoO₂(cr) at 298.15 K is -140.5 ± 0.2 kcal·mol⁻¹. This value is chosen so as to be in agreement with Brewer¹ who has performed a critical analysis of all data pertaining to the molybdenum-oxygen system. However, Brewer¹ chose to adopt the value previously used by JANAF,¹⁴ a value which was derived as a weighted average of two calorimetric determinations and seven equilibrium studies, the latter results based on S^o(298.15 K) = 11.954 cal·K⁻¹·mol⁻¹. In revising the S^o(298.15 K) value to 11.04 cal·K⁻¹·mol⁻¹ in this tabulation, the enthalpy of formation should also have been revised. With the exception of the data from Barbi⁵ the following equilibrium studies suggest ΔH^o(298.15 K) = -141.20 kcal·mol⁻¹ in comparison with the calorimetric mean of ΔH^o(298.15 K) = -140.8 kcal·mol⁻¹ for MoO₂(cr). In addition, eight recent emf studies (published since the analysis by Brewer) also yield a value of ΔH^o(298.15 K) = -141.2 kcal·mol⁻¹. Although there is some overlap in the values for ΔH^o derived from equilibrium and calorimetric studies, the equilibrium studies appear to be more negative by 0.4 kcal·mol⁻¹. Brewer¹ noted (in reference to ΔH^o(298.15 K) = -140.5 kcal·mol⁻¹, however, that a better overall fit of all Mo-O data would be obtained if the enthalpy of formation of MoO₂(cr) were made more negative by 0.5 kcal·mol⁻¹ with a corresponding decrease of 0.5 kcal·mol⁻¹ for MoO₂(g) and MoO(g) and 0.8 kcal·mol⁻¹ for MoO₃(g). Such a change could be accommodated in the MoO₂ tables.

Ignition of the bomb products from the calorimetric studies of Staskiewicz *et al.*² indicated that oxidation was only about 70 percent complete. The authors also digested the products with NH₄OH to remove the trioxide. The residue was the dioxide, as indicated by both oxidation and reduction. This evidence does not necessarily eliminate the possibility of known intermediate oxides in the combustion products. Mah³ found 72-75 percent conversion to trioxide by weighing the total combustion products; no additional analysis was performed.

Source	Method	Reaction	T/K	Data Points	2nd law	3rd law	Drift	ΔH ^o (298.15 K)
Staskiewicz <i>et al.</i> ²	Calorimetric	A	-	-	-37.12	-	-	-140.86 ± 0.13**
Mah ³	Calorimetric	A	-	-	-37.52	-	-	-140.64 ± 0.13**
Rapp ⁴	emf	B	1023-1323	35	-13.26	-14.18	-0.8 ± 0.1	-141.46
Barbi ⁵	emf	C	1023-1273	22	-25.64	-26.65	-0.9 ± 0.1	-141.25
Gleiser and Chipman ⁶	emf	F	873-1073	Eqn.	-140.4	-139.45	0.9	-139.45
Gokcen ⁷	Equilibrium	D	1296-1341	9	+3.02	-6.57	-3.6 ± 1.5	-141.84
Collins ⁸	Equilibrium	E	949-1344	Eqn.	-19.88	-25.50	-3.4	-141.11
Tonosaki ⁹	Equilibrium	E	973-1173	Eqn.	-22.18	-25.46	-1.5	-141.07
	Equilibrium	E	981-1096	Eqn.	-18.86	-25.86	-3.0	-140.47

**Auxiliary data for MoO₂(cr) are taken from corresponding measurements of the same authors. See also JANAF.¹³

- Reaction:
 A. MoO₂(cr) + 1/2 O₂(g) = MoO₃(cr)
 B. 2 Fe₃O₄(cr) + Mo(cr) = MoO₂(cr) + 2 xFe(cr)
 C. 2 NiO(cr) + Mo(cr) = MoO₂(cr) + 2 Ni(cr)
 D. Mo(cr) + 2 CO₂(g) = MoO₂(cr) + 2 CO(g)
 E. Mo(cr) + 2 H₂O(g) = MoO₂(cr) + 2 H₂(g)
 F. Mo(cr) + O₂(g) = MoO₂(cr) derived by the author from the cell reaction 2 Fe₃O₄(cr) + Mo(cr) = MoO₂(cr) + 2 xFe(cr) using ΔG^o data for Fe₃O₄(cr)

Heat Capacity and Entropy

King¹⁰ measured low temperature heat capacities from 53.3 to 296 K. King *et al.*¹¹ measured the high temperature enthalpy changes from 399 to 1801 K by drop calorimetry. The adopted heat capacities are derived from these two sets of data, subject to the constraint that they join smoothly at 298.15 K. Deviations of the enthalpy data from the adopted values are -1.3 to +0.7%, excluding the point at 1801 K. This point at the highest temperature deviates by +2.3%, which suggests that the apparent heat capacity is rising very rapidly. No explanation for this rapid rise is available.

The entropy S^o(298.15 K) = 11.104 cal·K⁻¹·mol⁻¹ is obtained from the low temperature heat capacity data, based on S^o(51 K) = 0.36 cal·K⁻¹·mol⁻¹. As discussed by Brewer,¹ Ghose *et al.*¹² used neutron diffraction measurements to demonstrate the absence of a permanent magnetic moment. Thus no additional heat capacity or entropy contribution below 50 K due to a possible antiferromagnetic effect is necessary.

References

1. Brewer, Materials and Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, personal communication, September 29, 1978, preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
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CRYSTAL

Molybdenum Oxide (MoO_{2.750})

Molybdenum Oxide (MoO_{2.750})

Mo₂O_{7.50}(cr)

Pearson Notation: mP60
 $S^\circ(298.15\text{ K}) = [69.936 \pm 1.7] \text{ J K}^{-1} \text{ mol}^{-1}$
 $T_m = 875 \pm 50 \text{ K}$
 $\Delta H_f^\circ(0\text{ K}) = \text{Unknown}$
 $\Delta H_f^\circ(298.15\text{ K}) = -708.41 \pm 3.3 \text{ kJ mol}^{-1}$
 $\Delta_m H_f^\circ = 0 \text{ kJ mol}^{-1}$

Enthalpy of Formation

For this oxide, the atomic ratio of oxygen to molybdenum is 2.750 or 11/4. The formula MoO_{2.750} (upon which this tabulation is based) is more indicative of the oxygen content relative to MoO₂ and MoO₃, as opposed to Mo₂O₁₁. The thermochemical values describing MoO_{2.750} are numerically 1/4 those of Mo₂O₁₁.

The high temperature emf measurements^{1,2,3} on compositions between MoO₂ and MoO₃ gave widely divergent results, some of which are contradicted by the Mo-O phase diagram recommended by Brewer.⁴ Brewer⁴ found that it was more practical to determine a $\Delta H_f^\circ(298.15\text{ K})$ value for Mo₂O₁₁(cr) by fixing the thermodynamic properties from the peritectic equilibrium together with the thermodynamic data for the liquid. From the phase diagram,⁴ MoO₂ and Mo₂O₁₁ solids are in equilibrium with the peritectic liquid of 74.2 ± 0.1 atomic % oxygen at 1091 \pm 7 K. For Mo₂O₁₁(cr) + 3 MoO₃(l), Brewer⁴ obtained $\Delta_r G^\circ/RT = 0.863 \pm 0.05$ at 1091 K. This yielded, using auxiliary data,⁵ $\Delta_r H^\circ/R = 1280 \pm 400 \text{ K}$ for the disproportionation of Mo₂O₁₁ to crystalline MoO₂ and MoO₃ at 298.15 K. This heat of reaction yields $\Delta H_f^\circ(298.15\text{ K})/R = -85203 \pm 200 \text{ K}$ for Mo₂O₁₁, from which we calculate $\Delta H_f^\circ(\text{MoO}_{2.750}, \text{cr}, 298.15\text{ K}) = -169.315 \pm 0.4 \text{ kcal mol}^{-1}$. We increase the uncertainty in ΔH_f° to $\pm 0.8 \text{ kcal mol}^{-1}$, which better represents the effect of errors in reducing a $\Delta_r G^\circ$ value at 1091 K to a $\Delta_r H_f^\circ$ value at 298.15 K.

Heat Capacity and Entropy

Bousquet *et al.*⁶ used differential enthalpy analysis to obtain enthalpies between 379 and 971 K for Mo₂O₁₁(cr), Mo₂O₇(cr), and Mo₂O₆(cr). Brewer⁴ compared their values of MoO₂(cr) and MoO₃(cr) mixtures with the same composition. For Mo₂O₁₁(cr), the enthalpies were higher by 3% at 400 K, decreasing to 1.5% at 700 K. As these differences were within the scatter of the experimental measurements, Brewer⁴ assumed $\Delta_r C_p^\circ = 0$ and $\Delta_r S^\circ = 0$ for the formation of Mo₂O₁₁ from 3 MoO₃(cr) and MoO₂(cr). Bousquet *et al.*⁶ also measured the high temperature enthalpy data of MoO₃ from 379 to 971 K. Their values agree with the adopted JANAF values for MoO₃, within 2% below 500 K, but the deviations increase rapidly at higher temperatures becoming 10% high at 950 K. Thus, the adopted heat capacity values for Mo₂O₁₁(cr), based on the assumption $\Delta_r C_p^\circ = 0$ as discussed in the preceding paragraph, may be less reliable at higher temperatures.

Phase Data

Mo₂O₁₁(oP60) disproportionates to MoO₂ and liquid at 1091 \pm 7 K, according to the phase diagram of Phillips and Chang.^{7a} Mo₂O₁₁(oP60) transforms on cooling below 875 \pm 50 K to Mo₂O₁₁(mP60). Bousquet *et al.*⁶ did not interpret their enthalpy data to include a transition at 875 K. However, a graphical examination of their data suggests two comments. First, the data point at 670 K may be a typographical error; perhaps 62.58 cal g⁻¹ should be 52.58 cal g⁻¹. Second, a transition at approximately 850 K with a corresponding heat of 0.7 kcal mol⁻¹ could be easily derived. To be consistent with Brewer,⁴ we assume a transition at 875 \pm 50 K with a corresponding zero heat of transition.

In addition to the discussion of the molybdenum oxygen system by Brewer,⁴ Gemlin Handbuch der Anorganischen Chemie⁸ has recently presented a thorough summary of the literature dealing with the phase diagram and properties of the oxide phases. Ekstrom and Tilley¹⁰ have reviewed the work of Ekstrom as well as the earlier work of Kihlborg¹¹ on the phases in the Mo-O system.

References

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T/K	Enthalpy Reference Temperature = T, = 298.15 K		Standard State Pressure = P° = 0.1 MPa	
	C _p ^o	S° - (G° - H°(T))/T	H° - H°(T)	Δ _r H°
0				
100				
200				
298.15	70.135	69.936	0	-708.412
300	70.354	69.937	0.130	-708.401
400	78.208	72.800	7.583	-707.487
500	82.797	78.438	15.642	-706.185
600	86.626	84.968	24.114	-704.674
700	90.344	91.701	32.962	-702.973
800	94.145	98.369	42.185	-701.059
900	98.072	104.864	51.795	-698.899
1000	102.139	111.152	61.804	-696.462
1100	106.331	117.226	72.227	-693.777
1200	110.638	123.094	83.074	-690.878
1300	115.050	128.769	94.358	-687.802
1400	119.553	134.266	106.087	-684.591
1500	124.139	139.599	118.271	-679.539

log K,

Δ_rG°

Δ_rH°

H° - H°(T)

S° - (G° - H°(T))/T

C_p^o

PREVIOUS:

CURRENT: September 1978

Molybdenum Oxide (MoO_{2.750})

Mo₂O_{7.50}(cr)

Molybdenum Oxide (MoO_{2.875}) (cr)Molybdenum Oxide (MoO_{2.875})M_r = 141.9383

CRYSTAL

Molybdenum Oxide (MoO_{2.875})

Pearson Notation. mP62

$$S^{\circ}(298.15 \text{ K}) = [73.849 \pm 1.7] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

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

$$\Delta_f H^{\circ}(298.15 \text{ K}) = -727.13 \pm 2.5 \text{ kJ} \cdot \text{mol}^{-1}$$

Enthalpy of Formation

For this oxide, the atomic ratio of oxygen to molybdenum is 2.875 or 23/8. The formula MoO_{2.875} (upon which this tabulation is based) is more indicative of the oxygen content relative to MoO₂ and MoO₃, as opposed to Mo₄O₁₁. The thermochemical values describing MoO_{2.875} are numerically 1/8 those of Mo₄O₁₁.

The high temperature emf measurements^{1,2,3} on compositions between MoO₂ and MoO₃ gave widely divergent results, some of which are contradicted by the Mo-O phase diagram recommended by Brewer.⁴ Brewer⁴ found that it was more practical to determine a $\Delta_f H^{\circ}(298.15 \text{ K})$ value for MoO_{2.875} by fixing the thermodynamic properties from the peritectic equilibria together with the thermodynamic data for the liquid. From the Mo-O phase diagram,⁴ MoO₂ and MoO₃ solids are in equilibrium with the peritectic liquid of 74.45 ± 0.1 atomic % oxygen at 1058 ± 5 K. For the equilibrium MoO_{2.875}(cr) = MoO₂(cr) + 4 MoO₃(l), Brewer⁴ calculated a $\Delta_f G^{\circ}/RT$ value at 1058 K. This yielded, using auxiliary data,⁵ $\Delta_f H^{\circ}/R = 380 \pm 200 \text{ K}$ for the disproportionation of MoO_{2.875} to crystalline MoO₂ and MoO₃ at 298.15 K. This enthalpy of reaction yields $\Delta_f H^{\circ}(298.15 \text{ K})/R = -87454 \pm 150 \text{ K}$ from which we calculate $\Delta_f H^{\circ}(\text{MoO}_{2.875}, \text{cr}, 298.15 \text{ K}) = -173,788 \pm 0.3 \text{ kcal} \cdot \text{mol}^{-1}$. We increase the uncertainty in $\Delta_f H^{\circ}$ to ± 0.6 kcal·mol⁻¹, a value which better represents the effect of uncertainties in reducing a $\Delta_f G^{\circ}$ value at 1058 K to a $\Delta_f H^{\circ}$ value at 298.15 K.

Heat Capacity and Entropy

Bousquet *et al.*⁶ used differential enthalpy analysis to obtain enthalpies between 379 and 971 K for Mo₄O₁₁(cr), Mo₄O₁₁(cr), and Mo₄O₁₁(cr). Brewer⁴ compared their values with values of MoO₂(cr) and MoO₃(cr) mixtures with the same composition. For MoO_{2.875}(cr), the enthalpies were lower by 15% at 400 K, lower by 3% at 500 K, and higher at higher temperatures, becoming 6% high at 700 K. As these differences were within the scatter of the experimental measurements, Brewer⁴ assumed $\Delta C_p^{\circ} = 0$ and $\Delta S^{\circ} = 0$ for the formation of MoO₂(cr) from 3MoO₂(cr) and MoO₃(cr).

Bousquet *et al.*⁶ also measured high temperature enthalpy data of MoO₃ from 379 to 971 K. Their values agree with the adopted JANAF values⁷ for MoO₃(cr) within 2% below 500 K, but the deviations increase rapidly at higher temperatures becoming 10% high at 950 K. Thus, the adopted heat capacity values for MoO_{2.875}(cr), based on the assumption $\Delta C_p^{\circ} = 0$ as discussed in the preceding paragraph, may be less reliable at higher temperatures.

Phase Data

The phase Mo₄O₁₁(mP62) was found by Kihlberg⁸ and Bousquet and Guillon⁹ at temperatures up to 1058–1063 K. Bousquet and Guillon⁹ observed MoO_{2.875} to disproportionate to MoO₂(cr) and MoO₃(g) at 1053 K by differential thermal analysis. Brewer⁴ adopted MoO_{2.875} as a stable phase which disproportionates to MoO₂(cr) and liquid at a temperature, $T_{\text{dis}} = 1058 \pm 5 \text{ K}$, which is slightly above the disproportionation temperature of Mo₃O₈.

In addition to the discussion of the molybdenum-oxygen system by Brewer,⁴ Gmelin Handbuch der Anorganischen Chemie¹⁰ has recently presented a thorough summary of the literature dealing with the phase diagram and properties of the oxide phases. Ekstrom and Tilley¹⁰ have reviewed the work of Ekstrom as well as the earlier work of Kihlberg¹¹ on the phases in the Mo-O system.

References

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T/K	Enthalpy Reference		Temperature = T, = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
	C _p ^o	S ^o	-(G°-H°(T))/T	H°-H°(T)	Δ _f H°	Δ _f G°	
0				0.			
100	298.15	72.508	73.849	73.849	-727.128	-652.662	114.344
200		72.730	74.298	73.850	-727.116	-652.200	113.558
300		80.651	96.385	76.807	-726.147	-627.358	81.925
400		85.274	114.891	82.625	-724.793	-602.813	62.975
500		89.201	130.786	89.358	-723.229	-578.561	50.368
600		93.079	144.826	96.297	-721.468	-554.586	41.384
700		97.088	157.515	103.169	-719.481	-530.878	34.663
800		101.256	169.189	109.864	-717.229	-507.435	29.451
900		105.589	180.081	116.347	-714.679	-484.259	25.295
1000		110.062	190.353	122.612	-711.806	-461.353	21.908
1200		114.638	200.126	128.667	-708.592	-438.723	19.097
1300		119.366	209.489	134.527	-705.025	-416.376	16.730
1400		124.166	218.510	140.203	-701.096	-394.318	14.712
1500		129.049	227.243	145.718	-696.797	-372.553	12.973

PREVIOUS.

CURRENT: September 1978

Molybdenum Oxide (MoO_{2.875})MoO_{2.875} (cr)

Molybdenum Oxide (MoO_{2.889}) **CRYSTAL** M_r = 142.1623 Molybdenum Oxide (MoO_{2.889}) Mo₁₀O_{28.89}(cr)

Pearson Notation: mP70
 $S^{\circ}(298.15\text{ K}) = [74.281 \pm 1.7] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $\Delta_f H^{\circ}(0\text{ K}) = \text{Unknown}$
 $\Delta_f H^{\circ}(298.15\text{ K}) = -729.16 \pm 2.5 \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^{\circ}(298.15\text{ K}) = -729.16 \pm 2.5 \text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation
 For this oxide, the atomic ratio of oxygen to molybdenum is 2.889 or, more exactly, 26/9. The formula MoO_{2.889} (upon which this tabulation is based) is more indicative of the oxygen content relative to MoO₂ and MoO₃, as opposed to Mo₅O₁₄. The thermochemical values describing MoO_{2.889} are numerically 1/9 those of Mo₅O₁₄.

The high temperature emf measurements^{2,3} on compositions between MoO₂ and MoO₃ gave widely divergent results, some of which are contradicted by the Mo-O phase diagram recommended by Brewer.⁴ Brewer⁴ found that it was more practical to determine a $\Delta_f H^{\circ}(298.15\text{ K})$ value for MoO_{2.889} by fixing the thermodynamic properties from the peritectic equilibria together with the thermodynamic data for the liquid. From the Mo-O phase diagram,⁴ Mo₅O₁₄ and Mo₅O₁₃ solids are in equilibrium with the peritectic liquid of 74.6 ± 0.1 atomic % oxygen at 1053 ± 5 K. For the equilibrium Mo₅O₁₄(cr) + MoO₂(l) = Mo₅O₁₃(cr) + MoO₂(l), Brewer⁴ calculated a $\Delta_f G^{\circ}/RT$ value at 1053 K. This yielded, using auxiliary data,⁵ $\Delta_f H^{\circ}/R = 50 \pm 50 \text{ K}$ for the disproportionation of Mo₅O₁₄ to crystalline Mo₅O₁₃ and MoO₂ at 298.15 K. This enthalpy of reaction yields $\Delta_f H^{\circ}(298.15\text{ K})/R = -87699 \pm 150 \text{ K}$ from which we calculate $\Delta_f H^{\circ}(\text{MoO}_{2.889}, \text{cr}, 298.15\text{ K}) = -174.275 \pm 0.3 \text{ kcal}\cdot\text{mol}^{-1}$. We increase the uncertainty in $\Delta_f H^{\circ}$ to ± 0.6 kcal·mol⁻¹, a value which better represents the effects of uncertainties in reducing a $\Delta_f G^{\circ}$ value of 1053 K to a $\Delta_f H^{\circ}$ value at 298.15 K.

Heat Capacity and Entropy
 Bousquet *et al.*⁶ used differential enthalpy analysis to obtain enthalpies between 379 and 971 K for Mo₅O₁₁(cr), Mo₅O₁₃(cr), and Mo₅O₁₄(cr). Brewer⁴ compared their values with values of MoO₂(cr) and MoO₃(cr) mixtures with the same composition. For Mo₅O₁₄(cr), the enthalpies were lower by 10% at 400 K but crossed over between 500 and 600 K and were 3% higher at 700 K. As these differences were within the scatter of the experimental measurements, Brewer⁴ assumed $\Delta C_p^{\circ} = 0$ and $\Delta S^{\circ} = 0$ for the formation of Mo₅O₁₃(cr) from MoO₂(cr) and 8 MoO₃(cr).
 Bousquet *et al.*⁶ also measured high temperature enthalpy data of MoO₃ from 379 to 971 K. Their values agree with the adopted JANAF values⁷ for MoO₃(cr) within 2% below 500 K, but the deviations increase rapidly at higher temperatures becoming 10% high at 950 K. Thus, the adopted heat capacity values for Mo₅O₁₄(cr), based on the assumption $\Delta C_p^{\circ} = 0$ as discussed in the preceding paragraph, may be less reliable at higher temperatures.

Phase Data
 Mo₅O₁₄ (mP70) disproportionates at 1053 ± 5 K to Mo₅O₁₁ and liquid according to the phase diagram of Phillips and Chang.¹⁴ Brewer⁴ adopted a phase diagram which included Mo₅O₁₃ which Phillips and Chang¹⁴ did not have.
 In addition to the discussion of the molybdenum-oxygen system by Brewer,⁴ Gmelin Handbuch der Anorganischen Chemie⁹ has recently presented a thorough summary of the literature dealing with the phase diagram and properties of the oxide phases. Ekstrom and Tilley¹⁰ have reviewed the work of Ekstrom as well as the earlier work of Kihlberg¹¹ on the phases in the Mo-O system.

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T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa	
	C _p ^o J·K ⁻¹ ·mol ⁻¹	S° - [C _p ° - H°(T _r)]/T _r J·K ⁻¹ ·mol ⁻¹	H° - H°(T _r) kJ·mol ⁻¹	Δ _f G° kJ·mol ⁻¹
0				
100				
200				
298.15	72.772	74.281	0	-654.461
300	72.995	74.282	0.135	-653.998
400	80.923	77.250	7.858	-629.078
500	85.550	83.088	16.188	-604.456
600	89.487	89.843	24.940	-580.129
700	93.383	96.806	34.082	-556.082
800	97.415	103.700	43.621	-532.303
900	101.611	109.940	53.571	-508.790
1000	105.973	165.922	63.949	-485.545
1100	110.476	191.181	74.770	-462.573
1200	115.105	200.991	86.048	-439.879
1300	119.846	210.391	97.795	-417.470
1400	124.679	219.449	110.021	-395.351
1500	129.595	228.218	122.734	-373.528

PREVIOUS: CURRENT: September 1978

Molybdenum Oxide (MoO_{2.889}) Mo₁₀O_{28.89}(cr)

Molybdenum Oxide (MoO₃)

Pearson Notation: oP16

 $S^{\circ}(298.15\text{ K}) = 77.760 \pm 1.3\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ $T_{\text{fus}} = 1074 \pm 5\text{ K}$

Enthalpy of Formation

The adopted enthalpy of formation, $-178.1\text{ kcal}\cdot\text{mol}^{-1}$, is the weighted average of two calorimetric determinations.^{1,2} The result of these and other calorimetric determinations, all for the reaction $\text{Mo}(\text{cr}) + 3/2\text{ O}_2(\text{g}) \rightarrow \text{MoO}_3(\text{cr})$, are given below. Staskiewicz *et al.*¹ found that oxidation was only about 80% complete and tentatively attributed this to formation of $\text{MoO}_3(\text{cr})$. Using their analytical results and their value of enthalpy of combustion for the dioxide, we obtain $\Delta H_f^{\circ}(\text{MoO}_3, \text{cr}, 298.15\text{ K}) = -177.98\text{ kcal}\cdot\text{mol}^{-1}$. Subsequent discovery of oxides intermediate between MoO_3 and MoO_2 raises a possible uncertainty concerning the incomplete oxidation. Mah² also reported that combustion of the $\text{Mo}(\text{cr})$ sample ranged from 84 to 93 percent complete, as determined only by weight gain of the total combustion products upon prolonged low temperature ignition. In contrast, the earlier workers reported almost complete combustion. Neumann *et al.*³ found about 97% completion using a wet analysis involving aqua regia. Moose and Parr⁴ found that in several combustions, they obtained over 99% completion, based on the weight of the oxide formed.

Source	Year	$\Delta H_f^{\circ}(298.15\text{ K}), \text{kcal}\cdot\text{mol}^{-1}$
1	1955	-177.98
2	1957	-178.16
3	1934	-180.4
4	1924	-175.6

Heat Capacity and Entropy

Smith *et al.*⁵ measured low temperature heat capacities from 18.3 to 299.8 K. King *et al.*⁶ measured high temperature enthalpy data from 399.3 to 1063.9 K by drop calorimetry. The adopted heat capacities are derived from these two sets of data, subject to the constraint that they join smoothly near 300 K. Deviations of the enthalpy data from the adopted values are -0.65% to $+0.17\%$. Seltz *et al.*⁷ have also measured low temperature heat capacities from 70 to 298.7 K which are not in agreement with the values adopted, the discrepancy has been discussed by Smith. Cosgrove and Snyder⁸ measured high temperature enthalpy data from 273 to 1068 K by drop calorimetry. Their smooth values are about 2% higher than the values adopted in the tabulation. Bousquet *et al.*⁹ also measured high temperature enthalpy data from 379 to 971 K. Their values agree with the adopted values within 2% below 500 K, but the deviations increase rapidly at higher temperature becoming $+10\%$ at 930 K.

The entropy, $S^{\circ}(298.15\text{ K}) = 18.585\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, is obtained from the low temperature heat capacity data of Smith *et al.*⁵ based on $S^{\circ}(20\text{ K}) = 0.197\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. This starting entropy was obtained by the authors from a T^2 extrapolation of the data. Recently, McBride and Westrum¹⁰ have shown that the T^2 limiting law is inappropriate for MoO_3 and a T^3 law is suggested for this and other compounds with lamellar lattices. They have also shown that the heat capacity data of Smith *et al.* for MoO_3 was positively biased by $\sim 0.07\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ below 100 K. If the same bias is present in the C_p° data of Smith *et al.* for MoO_3 , and a T^3 extrapolation is used, our analysis suggests a reduction of $\sim 0.12\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ in $S^{\circ}(298.15\text{ K})$. Other treatments result in estimated decreases in $S^{\circ}(298.15\text{ K})$ ranging from 0.08 to 0.17 $\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The increasing scatter in the C_p° data below 40 K (indicative of a loss of calorimeter sensitivity) coupled with uncertainty due to bias suggests an uncertainty of $\pm 0.3\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for $S^{\circ}(298.15\text{ K})$. Therefore, we adopt the author's original interpretation while recognizing the need for new low temperature C_p° measurements. It is surprising that the entropy of $\text{MoO}_3(\text{cr})$ is larger than that of $\text{WO}_3(\text{cr})$ by about $0.4\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. This may be due to the difference in the crystal structures, MoO_3 being orthorhombic (oP16) and WO_3 monoclinic, and also to uncertainty in the entropy extrapolation below 50 K for $\text{WO}_3(\text{cr})$.

Fusion Data

The adopted melting point, $1074 \pm 5\text{ K}$, is obtained from King *et al.*⁶ The enthalpy of fusion is calculated from the adopted enthalpies of the crystal and liquid based on the enthalpy data of King, Cosgrove and Snyder⁸ found the melting point 1068 K by the cooling curve method and derived $\Delta_{\text{fus}}H^{\circ} = 12.54\text{ kcal}\cdot\text{mol}^{-1}$ from their smooth enthalpy values at the melting point.

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Molybdenum Oxide (MoO₃)Mo₂O₇(cr)

T/K	Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$		Standard State Pressure = $p^{\circ} = 0.1\text{ MPa}$		log K _f
	C_p°	$S^{\circ} - [G^{\circ} - H^{\circ}(T_r)]/T$	$H^{\circ} - H^{\circ}(T_r)$	$\Delta_r H^{\circ}$	
0	0	0	INFINITE	-740.150	INFINITE
100	31.648	19.553	132.814	-743.735	375.563
200	59.279	50.977	84.136	-745.249	181.125
298.15	74.881	77.760	77.760	-745.170	117.045
300	75.107	78.224	77.761	-745.158	116.240
400	83.094	101.065	80.821	-744.111	83.872
500	87.751	120.130	86.830	-742.696	64.405
600	91.776	136.487	93.775	-741.074	51.486
700	95.814	150.936	100.927	-739.250	42.280
800	100.031	164.003	108.007	-737.186	35.394
900	104.441	176.037	114.906	-734.839	30.054
1000	109.039	187.278	121.587	-732.172	25.796
1074.000	112.562	195.186	126.387	CRYSTAL \leftarrow LIQUID	---
1100	113.792	197.894	128.046	-729.156	22.376
1200	118.679	208.004	134.291	-725.775	19.447
1300	123.683	217.700	140.336	-722.014	17.023
1400	128.779	227.052	146.198	-717.862	14.956
1500	133.959	236.113	151.892	-713.312	13.176

PREVIOUS: June, 1967

CURRENT: September, 1978

Molybdenum Oxide (MoO₃)Mo₂O₇(cr)

Mo₂O₃(l)

Molybdenum Oxide (MoO₃)

LIQUID

Molybdenum Oxide (MoO₃)

$M_r = 143.9382$

$\Delta_f H^\circ(298.15 \text{ K}) = [-703.727] \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{liq}} H^\circ = 48.534 \pm 4.2 \text{ kJ}\cdot\text{mol}^{-1}$

$S^\circ(298.15 \text{ K}) = [114.935] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fus}} = 1074 \pm 5 \text{ K}$

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$ Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$
 $\text{kJ}\cdot\text{mol}^{-1}$ log K_r

T/K	C _p ^o	S ^o - [C _p ^o - F(T _r)]/T	H ^o - H ^o (T _r)	Δ _f H ^o	Δ _g G ^o	log K _r
0			0.	-703.727	-637.719	111.726
100	74.881	114.935	0.139	-703.714	-637.310	110.966
200	75.107	115.399	8.098	-702.668	-615.317	80.352
298.15	83.094	138.240	17.996	-701.252	-593.638	62.017
300	87.751	157.305	124.005	-699.631	-572.264	49.820
400	91.776	173.661	130.949	-697.807	-551.178	41.129
500	95.814	188.110	138.102			
700	97.898	194.791	141.660			
750.000	126.951	194.791	141.660			
800	126.951	202.985	145.240	-694.343	-530.415	34.633
900	126.951	217.937	152.503	-689.523	-510.214	29.612
1000	126.951	231.313	159.727	-684.833	-490.544	25.623
1074.000	126.951	240.376	164.975			
1100	126.951	243.413	166.794			
1200	126.951	254.459	173.645	-680.265	-471.337	22.382
1300	126.951	264.620	180.258	-675.511	-452.541	19.699
1400	126.951	274.028	186.624	-671.472	-434.112	17.443
1500	126.951	282.787	192.746	-667.247	-416.012	15.322
1600	126.951	290.980	198.633	-663.139	-398.212	13.867
1700	126.951	298.677	204.293	-659.152	-380.680	12.428
1800	126.951	305.933	209.740	-655.290	-363.393	11.166
1900	126.951	312.797	214.985	-651.560	-346.333	10.050
2000	126.951	319.309	220.040	-647.968	-329.475	9.058
				-644.523	-312.801	8.170

GLASS <--> LIQUID
 TRANSITION
 -- CRYSTAL <--> LIQUID

$\Delta_f H^\circ(\text{MoO}_3, l, 298.15 \text{ K})$ is calculated from that of the crystal by adding the enthalpy of fusion, $\Delta_{\text{fus}} H^\circ$, and the difference in enthalpy, $H^\circ(1074 \text{ K}) - H^\circ(298.15 \text{ K})$, between the crystal and liquid.

Heat Capacity and Entropy
 The heat capacity is derived from the enthalpy data (1074–1392 K) measured by King *et al.*¹ The heat capacity is assumed constant above and below the measured range. At 750 K, a glass transition is assumed, below which the heat capacity is taken to be the same as that of the crystal. $S^\circ(\text{MoO}_3, l, 298.15 \text{ K})$ is calculated in a manner analogous to that used for the enthalpy of formation.

Cosgrove and Snyder² also measured enthalpy data for MoO₃(l) in the temperature range from 1068 to 1300 K. Their smooth values are 2.5 to 4.0 percent higher than our tabulated values.

Fusion Data
 Refer to the crystal table for details.

Vaporization Data
 Effusion³ and transpiration⁴ measurements indicate that MoO₃(g) is not the major species found in the vapor above MoO₃ condensed phases. Both sets of measurements indicate the presence of polymeric species (MoO₃)_x, where the predominant species near the normal boiling point are those for x = 3 and 4. At higher temperatures the equilibrium shifts toward lower x but MoO₃(l) will reach 1 atm at 1380 ± 30 K based primarily on the transpiration measurements of Ackermann *et al.*⁵ Feiser,⁶ using indirect methods, reported a normal boiling point of 1438 K. We adopt Brewer's estimate⁷ and emphasize that this represents vaporization to a mixture of gases, (MoO₃)_x.

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PREVIOUS: June 1967 CURRENT: September 1978

Molybdenum Oxide (MoO₃) Mo₂O₃(l)

Molybdenum Oxide (MoO₃)

CRYSTAL-LIQUID

0 to 1074 K crystal (oP16)
above 1074 K liquid

Refer to the individual tables for details.

M_r = 143.9382 Molybdenum Oxide (MoO₃)

Mo₂O₃(cr,l)

T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p ^o = 0.1 MPa		log K _r
		S ^o / J·K ⁻¹ ·mol ⁻¹	-(G ^o - H ^o (T _r))/T	H ^o - H ^o (T _r) / kJ·mol ⁻¹	ΔG ^o / kJ·mol ⁻¹	
0	0	0	INFINITE	-12.590	-740.150	INFINITE
100	31.648	19.553	132.814	-11.376	-743.735	375.563
200	59.279	50.977	84.136	-6.632	-745.249	181.125
298.15	74.881	71.760	71.760	0	-745.170	-668.079
300	75.107	78.224	77.761	0.139	-745.158	-667.601
400	83.094	101.065	80.821	8.098	-744.111	-641.890
500	87.751	120.130	86.830	16.650	-742.696	-616.494
600	91.776	136.487	93.775	25.627	-741.074	-591.403
700	95.814	150.936	100.927	35.006	-739.250	-566.599
800	100.031	164.003	108.007	44.796	-737.186	-542.072
900	104.441	176.037	114.906	55.018	-734.839	-517.821
1000	109.039	187.278	121.587	65.691	-732.172	-493.847
1074.000	112.562	195.186	126.387	73.889	---	---
1074.000	126.951	240.376	126.387	122.424	---	---
1100	126.951	243.413	129.118	125.724	-680.265	22.382
1200	126.951	254.459	139.109	138.420	-675.811	-471.337
1300	126.951	264.620	148.378	151.115	-671.472	-452.541
1400	126.951	274.028	157.022	163.810	-667.247	-434.112
1500	126.951	282.787	165.117	176.505	-663.139	-416.012
1600	126.951	290.980	172.730	189.200	-659.152	-398.212
1700	126.951	298.677	179.915	201.895	-655.290	-380.690
1800	126.951	305.933	186.716	214.590	-651.560	-363.395
1900	126.951	312.797	193.173	227.285	-647.968	-346.333
2000	126.951	319.309	199.319	239.980	-644.523	-329.475
						-312.801
						8.170

PREVIOUS.

CURRENT: September 1978

Molybdenum Oxide (MoO₃)

Mo₂O₃(cr,l)

Molybdenum Oxide (MoO₃)

Molybdenum Oxide (MoO₃)

IDEAL GAS

Molybdenum Oxide (MoO₃)

$\Delta_f H^\circ(0\text{ K}) = 1740.126 \pm 21.3\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(298.15\text{ K}) = [283.897 \pm 12.6]\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(0\text{ K}) = -342.22 \pm 20.9\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(298.15\text{ K}) = -346.44 \pm 20.9\text{ kJ}\cdot\text{mol}^{-1}$
 $M_r = 143.9382$
 $\Delta_f H^\circ(0\text{ K}) = -342.22 \pm 20.9\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(298.15\text{ K}) = -346.44 \pm 20.9\text{ kJ}\cdot\text{mol}^{-1}$
 $\sigma = 3$
 $I_a/I_b/I_c = [3.0307222 \times 10^{-11}] \text{ g}^3\cdot\text{cm}^6$

Vibrational Frequencies and Degeneneracies
 ν, cm^{-1}
 978 (1)
 [340](1)
 924 (2)
 [310](2)

Ground State Quantum Weight: (1)
 Point Group: C_{3v}
 Bond Distance Mo-O = [1.731] Å
 Bond Angle O-Mo-O = 99°
 Product of the Moments of Inertia: $I_a/I_b/I_c = [3.0307222 \times 10^{-11}] \text{ g}^3\cdot\text{cm}^6$

Enthalpy of Formation
 Burns *et al.*¹ determined the partial pressures of gaseous oxides MoO₂, MoO₃, (MoO₃)₂, in equilibrium with powdered MoO₃ by mass spectrometry. Blackburn *et al.*² and Chizhikov *et al.*³ also investigated the vapor pressures above molybdenum dioxide by the Knudsen effusion method. These studies¹⁻⁴ involve the disproportionation of MoO₃(cr) to Mo(cr) and MoO₃(g). DeMaria *et al.*⁵ reported the partial pressures of MoO(g), MoO₂(g), and O(g) in the Mo-Al₂O₃ system from mass spectrometry.

Source	Reaction	T/K	Data Points	$\Delta_f H^\circ(298.15\text{ K})$, kcal·mol ⁻¹	Drift	$\Delta_f H^\circ(298.15\text{ K})$, kcal·mol ⁻¹
1	1.5 MoO ₂ (cr) → MoO ₃ (g) + 0.5 Mo(cr)	1481-1777	34	131.7 ± 1.5	128.0 ± 0.8	-2.2 ± 0.9
2	1.5 MoO ₂ (cr) → MoO ₃ (g) + 0.5 Mo(cr)	1592-1918	119	133.5 ± 1.4	124.0 ± 1.3	-6.3 ± 0.8
3	1.5 MoO ₂ (cr) → MoO ₃ (g) + 0.5 Mo(cr)	1818-2028	7	108.8 ± 6.4	121.2 ± 1.6	6.3 ± 3.4
4	1.5 MoO ₂ (cr) → MoO ₃ (g) + 0.5 Mo(cr)	1500-1730	Eqn	137.9	133.1 ± 0.5	-3.0
5	Mo(cr) + 3 O(g) → MoO ₃ (g)	2281-2416	6	-210.5 ± 28.0	-253.7 ± 4.0	-18.6 ± 11.8

The selected enthalpy of formation is -82.8 kcal·mol⁻¹, based on the 3rd law value of $\Delta_f H^\circ(298.15\text{ K})$ of Burns *et al.*¹ The choice is made because there is serious doubt about the data of Blackburn³ as discussed by Burns *et al.*¹ In addition, the assumption made by Plane² that they only vapor species of any importance is MoO₃ may be erroneous. The mass spectrometric work of Burns *et al.*¹ is thus preferred. Our adopted value differs slightly from the value of -82.57 kcal·mol⁻¹ adopted by Brewer,⁶ which is also based on Burns *et al.*¹ The difference is a result of slight differences in Gibbs energy functions in the respective auxiliary data for Mo(cr).⁶⁷

The heat of atomization calculated from the JANAF tables⁶ is $\Delta_a H^\circ(0\text{ K}) = 415.9 \pm 5.1\text{ kcal}\cdot\text{mol}^{-1}$.

Heat Capacity and Entropy
 In a recent IR matrix isolation study, Hewett *et al.*⁸ observed peaks at 976 and 922 cm⁻¹ which they assigned to stretching modes of MoO₃(g). We add 2 cm⁻¹ to these frequencies to correct for the matrix effect. The observation of two stretching modes in the infrared spectrum suggests a pyramidal C_{3v} structure for MoO₃(g). Hewett *et al.*⁸ performed a normal coordinate analysis using a bond distance of 1.8 Å and an estimated bending force constant (f_b) of 0.296 mdyn/Å. Variations of 20% in f_b changed the calculated stretching frequencies by only a few cm⁻¹. The calculated stretching frequencies were more sensitive to the estimated pyramidal angle (β) which was adjusted to obtain the best fit to the observed stretching frequencies of oxide molecules containing ¹⁶O, and mixed ¹⁶O-¹⁸O. The final results yielded $\beta = 61.5 \pm 2^\circ$ and values of 261, 275 and 275 cm⁻¹ for the bending frequencies of Mo¹⁶O₃. Due to the insensitivity of the normal coordinate analysis to f_b , these bending frequencies are useful only for comparing changes due to isotopic substitution. In contrast, we adopt bending frequencies of 310, 310 and 340 cm⁻¹ and a bond distance of 1.73 Å as selected by Brewer⁶ for consistency with other metal oxides. The pyramidal angle of 61.5° is adopted, the possible effect of using a shorter bond distance during the normal coordinate analysis is unknown. The pyramidal angle of 61.5° corresponds to an O-Mo-O bond angle of 99°. Based on the adopted structure, the principal moments of inertia are $I_a = I_b = [12.8372 \times 10^{-37}] \text{ g}\cdot\text{cm}^2$ and $I_c = [18.3909 \times 10^{-37}] \text{ g}\cdot\text{cm}^2$. The thermochemical functions are consistent with those of Brewer.⁶

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⁶JANAF Thermochemical Tables: Mo(cr) and Mo(g), 3-31-78; MoO₂(cr), 9-30-78; O(g), 3-31-77; WO₃(g), 9-30-66.
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⁸W. D. Hewett, J. H. Newton and W. Weltner, Jr., *J. Phys. Chem.* **79**, 2640 (1975).

Molybdenum Oxide (MoO₃)

Molybdenum Oxide (MoO₃)

IDEAL GAS

Molybdenum Oxide (MoO₃)

Mo₂S₂(cr)Molybdenum Sulfide (MoS₂)

CRYSTAL

Molybdenum Sulfide (MoS₂)M_r = 160.06

Pearson Notation: hP6
 $S^{\circ}(298.15\text{ K}) = 62.572 \pm 0.08\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fm}} = 2023 \pm 50\text{ K}$ [p = 1 atm S₂(g)]

T/K	Enthalpy Reference Temperature = T _r = 298.15 K			Standard State Pressure = p ^o = 0.1 MPa		
	C _p ^o	S ^o - [G ^o - H ^o (T)]/T	H ^o - H ^o (T)	ΔH ^o	ΔG ^o	log K _r
0	0	INFINITE	0	-273.314	-273.314	INFINITE
100	24.050	12.991	110.098	-274.317	-272.409	142.292
200	51.840	39.359	68.080	-275.476	-269.998	70.516
298.15	63.555	62.572	62.572	-276.144	-267.156	46.805
300	63.680	62.965	62.573	-276.155	-267.100	46.506
400	68.910	67.099	65.146	-281.141	-263.922	34.452
500	71.756	67.805	70.155	-284.502	-259.125	27.071
600	73.597	111.057	75.897	-287.017	-253.800	22.095
700	75.019	122.511	81.756	-288.951	-248.105	18.514
800	76.232	132.610	87.494	-290.530	-242.159	15.811
900	77.278	141.650	93.018	-293.134	-233.867	13.573
1000	78.241	149.842	98.297	-296.882	-215.682	11.266
1100	79.119	157.341	103.329	-305.620	-197.623	9.384
1200	79.998	164.263	108.127	-304.356	-179.680	7.821
1300	80.835	170.699	112.691	-303.101	-161.841	6.503
1400	81.672	176.721	117.052	-301.851	-144.098	5.376
1500	82.467	182.383	121.220	-300.646	-126.444	4.403
1600	83.262	187.730	125.211	-300.030	-108.869	3.554
1700	84.057	192.802	129.039	-300.596	-91.367	2.807
1800	84.810	197.628	132.717	-301.839	-73.931	2.145
1900	85.605	202.235	136.255	-303.617	-56.555	1.555
2000	86.358	206.645	139.665	-305.959	-39.233	1.025
2100	87.111	210.876	142.956	-308.826	-21.958	0.546
2200	87.906	214.947	146.137	-313.210	-4.726	0.112
2300	88.659	218.871	149.214	-318.211	12.469	-0.283
2400	89.412	222.660	152.196	-323.861	29.633	-0.645

Enthalpy of Formation

The adopted enthalpy of formation is from Brewer¹ and is a weighted average of calorimetric² and equilibrium³ values. O'Hare *et al.*² obtained $\Delta_f H^{\circ}(298.15\text{ K}) = 65.8 \pm 1.2\text{ kcal}\cdot\text{mol}^{-1}$ using a fluorine bomb calorimeter. Larson and Elliott³ studied the equilibrium $\text{MoO}_2(\text{cr}) + 2\text{ SO}_2(\text{g}) = \text{MoS}_2(\text{cr}) + 3\text{ O}_2(\text{g})$ via emf technique (1051–1372 K); using auxiliary data^{1,4} Brewer calculated $\Delta_f H^{\circ}(\text{MoS}_2, 298.15\text{ K}) = -66.64 \pm 0.6\text{ kcal}\cdot\text{mol}^{-1}$ from their results. Thermodynamic analysis of other calorimetric and equilibrium measurements^{5–7} are summarized by O'Hare *et al.*² and Mills.⁸

Heat Capacity and Entropy

The adopted values of C_p^o are from Brewer¹ and are based on experimental C_p^o data (6–346 K) of McBride and Westrum⁹ and high temperature enthalpy data (523–1204 K) of Fredrickson and Chasanov.¹⁰ C_p^o values above 1200 K are extrapolated. The recent enthalpy data (500–1700 K) of Volovik *et al.*¹¹ agrees with enthalpies in this table to within ±2% to 2000 K. Older C_p^o data of Smith *et al.*¹² and Anderson¹³ contain considerable scatter and are given no weight.

S^o(298.15 K) is obtained from the appropriate integration of the adopted C_p^o data based on S^o(10 K) = 0.012 cal·K⁻¹·mol⁻¹.

Fusion Data

The crystal structure of MoS₂ is (hP6). Mering and Levaldi¹⁴ have shown that nonstoichiometric sulfur-rich modifications (which have essentially the hP6 structure with expansion and distortion of the lattice) can be prepared as metastable compositions up to MoS_{2.56}; amorphous metastable phases are obtained with higher sulfur contents. For information on other metastable phases, refer to¹⁵ and¹⁶ According to Brewer's¹ phase diagram the compositional range of stability decreases as the temperature increases.

Based on Cannon's evidence¹⁶ of a melting point in excess of 2073 K, Brewer¹ adopted a congruent melting point of 2173 K. However, congruent melting is observed only at high sulfur pressures; the melting point of 2173 K corresponds to a S₂(g) pressure of ~4 atm. Incongruent melting points up to 350 K lower may be obtained depending upon the pressure of S₂(g). The adopted melting point is that selected by Brewer¹ for an S₂(g) pressure of 1 atm. Mills⁸ adopted a 1 atm value of 1458 K which appears much too low.

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PREVIOUS:

CURRENT: June 1978

Molybdenum Sulfide (MoS₂)Mo₂S₂(cr)

Mo₂S₃(cr)

Molybdenum Sulfide (Mo₂S₃)

CRYSTAL

Molybdenum Sulfide (Mo₂S₃)

Pearson notation: mP10
 $S^\circ(298.15\text{ K}) = 114.976 \pm 8.4\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fus}} = 2080 \pm 20\text{ K}$
 $\Delta_f H^\circ(0\text{ K}) = \text{Unknown}$
 $\Delta_f H^\circ(298.15\text{ K}) = -407.103 \pm 8.4\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{sub}} H^\circ = -129\,704 \pm 41.8\text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation is taken from the critical review by Brewer.¹ His linear regression analysis of equilibrium data, which is based on Cubicciotti's sigma-plot method,² yields both $\Delta_f H^\circ(298.15\text{ K})$ and $S^\circ(298.15\text{ K})$. The data used in Brewer's analysis are outlined below. Auxiliary data are taken from the JANAF tables.³

Source	Reaction	T/K
McCabe ⁴	A	1303 - 1425
Isakova ⁵	B	1523 - 1738
Hager and Elliott ⁶	C	1366 - 1612
Stubbles and Richardson ⁷	C	1119 - 1467
Pouillard and Perrot ⁸	C	1030 - 1280
Stubbles and Richardson ⁷	D	1270 - 1470
Pouillard and Perrot ⁸	D	1030 - 1280

Reactions: (A) $2\text{ Mo}(\text{cr}) + 3/2\text{ S}_2(\text{g}) = \text{Mo}_2\text{S}_3(\text{cr})$
 (B) $2\text{ MoS}_2(\text{cr}) = \text{Mo}_2\text{S}_3(\text{cr}) + 1/2\text{ S}_2(\text{g})$
 (C) $2\text{ Mo}(\text{cr}) + 3\text{ H}_2\text{S}(\text{g}) = \text{Mo}_2\text{S}_3(\text{cr}) + 3\text{ H}_2(\text{g})$
 (D) $2\text{ MoS}_2(\text{cr}) + \text{H}_2(\text{g}) = \text{Mo}_2\text{S}_3(\text{cr}) + \text{H}_2\text{S}(\text{g})$

Heat Capacity and Entropy

There are no experimental high temperature heat capacity or enthalpy studies. The adopted heat capacity, which is assumed to represent the high temperature crystal form, is based on the estimate of Gronvold and Westrum,⁹ $C_p^\circ = 26.36 + 7.88 \times 10^{-3}T = 2.30 \times 10^7/T^2$. The value of $S^\circ(298.15\text{ K})$ is taken from Brewer, refer above.

Rastogi and Ray¹⁰ measured the low temperature $C_p^\circ(350\text{ K})$ but report only $C_p^\circ(298.15\text{ K}) = 33.2\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. This value apparently refers to the low temperature superstructure crystal form but is not expected to differ significantly from the high temperature form. The reason for the 7 cal·K⁻¹·mol⁻¹ discrepancy between the Rastogi-Ray value of $C_p^\circ(298.15\text{ K})$ and that adopted here is not known but it should be mentioned that the Rastogi-Ray value is well above the classical limit of 15R. Insufficient information on sample preparation and calorimetric technique is available to assess the validity of the Rastogi-Ray data.

Phase Data

The crystal structure of Mo₂S₃ is monoclinic and belongs to space group P2₁/m above 310 K.¹¹ Below 310 K all axes are doubled and a superstructure is formed. The heat of transition is reported to be 5 cal·K⁻¹·mol⁻¹.¹⁰ The stability region for Mo₂S₃ is from 900 ± 40 K¹ to the melting point. Below 900 K the material is metastable with respect to disproportionation to MoS₂ and MoS₃(cr). However equilibrium is established very slowly below 1100 K^{11,12} and, once prepared, Mo₂S₃ may be quenched and stored indefinitely at room temperature. The enthalpy of decomposition at 900 K ($\Delta_{\text{decomp}} H^\circ$) for the reaction Mo₂S₃(cr) → 1/2 Mo₂(cr) + 3/2 MoS₂(cr) is calculated from the JANAF tables.³

Fusion Data

We adopt the congruent melting point from Brewer.¹ The enthalpy of fusion is estimated assuming an entropy of fusion of ~3 cal·K⁻¹·g-atom⁻¹ as suggested by Kubaschewski *et al.*¹³ This gives an enthalpy of fusion of 31 kcal·mol⁻¹ and the uncertainty is estimated to be 10 kcal·mol⁻¹.

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T/K	C _p ^o	S ^o	-(G ^o -H ^o (T))/T	H ^o -H ^o (T)	Δ _f H ^o	Δ _f G ^o	log K _f
0							
100							
200							
298.15	109.294	114.976	114.976	0.	-407.103	-395.654	69.317
300	109.489	115.653	114.978	0.202	-407.116	-395.583	68.877
400	117.464	148.339	119.381	11.583	-414.437	-391.374	51.108
500	122.926	175.164	127.934	23.615	-419.287	-385.077	40.229
600	127.399	197.981	137.764	36.136	-422.753	-377.985	32.898
700	131.405	217.925	147.812	46.079	-425.196	-370.904	27.625
800	135.162	235.719	157.797	52.469	-426.942	-362.372	24.651
900	138.775	251.848	167.283	56.107	-428.146	-352.811	20.361
1000	142.297	266.652	176.491	60.161	-428.687	-324.638	16.938
1100	145.762	280.378	185.319	104.564	-428.623	-298.802	14.189
1200	149.186	293.208	193.781	119.312	-428.373	-273.233	11.894
1300	152.582	305.283	201.898	134.401	-427.954	-247.942	9.962
1400	155.957	316.714	209.695	149.828	-427.381	-222.970	8.317
1500	159.317	327.589	217.195	165.591	-426.668	-198.159	6.901
1600	162.666	337.978	224.421	181.691	-425.828	-173.650	5.669
1700	166.006	347.940	231.396	198.124	-424.873	-149.384	4.590
1800	169.339	357.523	238.138	214.892	-423.817	-125.354	3.638
1900	172.666	366.768	244.667	231.992	-422.674	-101.552	2.792
2000	175.989	375.709	250.996	249.425	-421.458	-77.970	2.036
2080.000	178.645	382.663	255.927	263.610	---	CRYSTAL ← -> LIQUID	---
2100	179.309	384.376	257.142	267.190	-543.184	-54.601	1.358
2200	182.625	392.794	263.118	285.286	-538.867	-31.436	0.746
2300	185.939	400.985	268.935	303.715	-534.523	-8.468	0.192
2400	189.251	408.968	274.604	322.474	-530.172	14.311	-0.311

PREVIOUS:

CURRENT: June 1978

Mo₂S₃(cr)

Molybdenum Sulfide (Mo₂S₃)

Molybdenum Sulfide (Mo₂S₃)

$S^\circ(298.15\text{ K}) = [181.170\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}]$
 $T_{\text{fus}} = 2080 \pm 20\text{ K}$

Enthalpy of Formation

$\Delta_f H^\circ(\text{Mo}_2\text{S}_3, \text{l}, 298.15\text{ K})$ is calculated from that of the crystal by adding the enthalpy fusion, of $\Delta_{\text{fus}} H^\circ$, and the difference in enthalpy, $H^\circ(2080\text{ K}) - H^\circ(298.15\text{ K})$, between the crystal and liquid.

Heat Capacity and Entropy

A constant liquid C_p° of $7.5\text{ cal}\cdot\text{K}^{-1}\cdot\text{g}\cdot\text{atom}^{-1}$ is assumed which yields a C_p° value of $37.5\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. This value is adopted above an assumed glass transition at 1450 K . The heat capacity of the crystal¹ is assumed below the glass transition.

$S^\circ(\text{Mo}_2\text{S}_3, \text{l}, 298.15\text{ K})$ is calculated by a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.¹

Decomposition Data

According to Brewer's phase diagram,² Mo₂S₃ has a very short liquid range at 1 atm S₂(g). We adopt a decomposition temperature of $2140 \pm 30\text{ K}$ based on the phase diagram.² Above this temperature Mo₂S₃(l) decomposes to S₂(g) plus a liquid poorer in sulfur than Mo₂S₃. At higher sulfur pressures, the liquid range is much more extensive.

References

- ¹JANAF Thermochemical Tables: Mo₂S₃(cr) 6-30-78.
²L. Brewer, Materials Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication of preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria; (September 29, 1978).

LIQUID

Molybdenum Sulfide (Mo₂S₃)Mo₂S₃(l)

T/K	C _p ^o	S ^o	-(G ^o -H ^o (T))/T	H ^o -H ^o (T)	Δ _f H ^o	log K _f
Enthalpy Reference Temperature = T _r = 298.15 K						
J·K ⁻¹ ·mol ⁻¹						
kJ·mol ⁻¹						
Standard State Pressure = p ^o = 0.1 MPa						
0						
100						
200						
298.15	109.294	181.170	181.170	0.	-270.304	48.808
	109.489	181.847	181.172	0.202	-270.316	48.516
	117.464	214.553	185.573	11.383	-277.637	28.052
	128.926	241.358	194.129	23.615	-282.487	29.395
	127.399	264.175	203.948	36.136	-285.953	24.446
	131.405	284.119	214.006	49.079	-288.396	20.874
	135.162	301.913	223.901	62.409	-290.142	18.176
	138.775	318.042	233.479	76.107	-292.488	15.878
	142.297	332.846	242.685	90.161	-294.887	13.270
	145.762	346.572	251.513	104.564	-297.316	11.150
	149.186	359.402	259.975	119.312	-299.744	9.306
	152.582	371.477	268.092	134.401	-302.155	7.923
	155.957	382.908	275.889	149.828	-304.548	6.671
1450.000	157.639	388.410	279.674	157.668	-306.917	5.594
1450.000	156.900	388.410	279.674	157.668	-306.917	5.594
1500	156.900	393.730	283.388	165.513	-309.947	4.660
1600	156.900	403.856	290.604	181.203	-313.516	3.842
1700	156.900	413.368	297.548	196.893	-317.044	3.120
1800	156.900	422.336	304.234	212.583	-320.527	2.479
1900	156.900	430.819	310.676	228.273	-324.000	1.905
2000	156.900	438.867	316.886	243.963	-327.469	1.389
2080.000	156.900	445.021	321.696	256.515	-330.922	0.972
2100	156.900	446.522	322.878	259.653	-331.841	0.498
2200	156.900	453.821	328.665	275.343	-335.124	0.110
2300	156.900	460.796	334.260	291.033	-338.341	-0.246
2400	156.900	467.473	339.672	306.723	-341.503	-0.574
2500	156.900	473.878	344.913	322.413	-344.618	-0.877
2600	156.900	480.032	349.992	338.103	-347.686	-1.159
2700	156.900	485.953	354.919	353.793	-350.714	-1.423
2800	156.900	491.659	359.701	369.483	-353.706	-1.671
2900	156.900	497.165	364.347	385.173	-356.663	-1.911
3000	156.900	502.484	368.863	400.863	-359.586	-2.142
3100	156.900	507.629	373.257	416.553	-362.474	-2.365
3200	156.900	512.610	377.535	432.243	-365.327	-2.581
3300	156.900	517.439	381.701	447.933	-368.144	-2.783
3400	156.900	522.122	385.763	463.623	-370.923	-2.972
3500	156.900	526.671	389.724	479.313	-373.663	-3.151

PREVIOUS:

CURRENT: June 1978

Molybdenum Sulfide (Mo₂S₃)Mo₂S₃(l)

Mo₂S₃(cr,l)

M_r = 288.06 Molybdenum Sulfide (Mo₂S₃)

CRYSTAL-LIQUID

Molybdenum Sulfide (Mo₂S₃)

298 to 2080* K crystal
above 2080 K liquid

Refer to the individual tables for details.

*This material is reported to be metastable with respect to disproportionation to Mo(cr) and MoS₂(cr) below 900 K. However, disproportionation is very slow and the material may be quenched and stored at room temperature indefinitely.

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa	
	C _p ^o	S° - [G° - H°(T _r)]/T	H° - H°(T _r)	ΔG°
	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	kJ·mol ⁻¹	kJ·mol ⁻¹
0				
100				
200				
298.15	109.294	114.976	0.	-395.654
300	109.489	114.978	0.202	-395.583
400	117.464	119.381	1.583	-391.374
500	122.926	127.934	23.615	-383.077
600	127.399	137.754	36.136	-377.885
700	131.405	147.812	49.079	-370.204
800	135.162	157.707	62.409	-362.222
900	138.775	167.285	76.107	-350.811
1000	142.297	176.491	90.161	-324.658
1100	145.762	185.319	104.564	-298.802
1200	149.186	193.781	119.312	-273.233
1300	152.582	201.898	134.401	-247.942
1400	155.957	209.695	149.828	-222.920
1500	159.317	217.195	165.591	-198.159
1600	162.666	224.421	181.691	-173.650
1700	166.006	231.396	198.124	-149.384
1800	169.339	238.138	214.892	-125.354
1900	172.666	244.667	231.992	-101.552
2000	175.989	250.996	249.425	-77.970
2080.000	178.645	255.927	263.610	-54.458
2080.000	156.900	445.021	393.314	CRYSTAL → LIQUID
2100	156.900	446.522	396.452	-413.922
2200	156.900	453.821	412.142	-38.841
2300	156.900	460.796	427.832	-21.915
2400	156.900	467.473	443.522	-5.033
2500	156.900	473.878	459.212	11.763
2600	156.900	480.032	474.902	28.548
2700	156.900	485.953	490.592	45.321
2800	156.900	491.659	506.282	62.101
2900	156.900	497.165	521.972	79.010
3000	156.900	502.484	537.662	96.290
3100	156.900	507.629	553.352	117.506
3200	156.900	512.618	569.042	136.666
3300	156.900	517.358	584.732	155.256
3400	156.900	521.822	600.422	174.194
3500	156.900	526.671	616.112	193.778

PREVIOUS.

CURRENT: June 1978

Molybdenum Sulfide (Mo₂S₃)

Mo₂S₃(cr,l)

Continuation of discussions of selected Mo species

of 6. In addition, we expect from the electronic levels of $\text{Mo}^{4+}(\text{g})^{11}$ that other electronic states will also be found and these are arbitrarily estimated in the level at 25000 cm^{-1} . The principal moments of inertia are: $I_A = 3.3489 \times 10^{-39}$, $I_B = 11.4373 \times 10^{-39}$, and $I_C = 14.7862 \times 10^{-39} \text{ g cm}^2$.

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The electronic levels and quantum weights are estimated from the data reported by Weltner and McLeod¹⁰ on WO_2 . The ground state is assumed to be 3A_1 , and the first excited level is assumed to lie close to the observed transitions at 7890 Å and 7806 Å in WO_2 . Since both these states are presumed to be triplet, we have assigned a total degeneracy