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Thermodynamic Properties of Manganese and Molybdenum

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This work reviews and discusses the data on the various thermodynamic properties of manganese and molybdenum available through March 1985. These include heat capacity, enthalpy, enthalpy of transitions and melting, vapor pressure, and enthalpy of vaporization. The existing data have been critically evaluated and analyzed. The recommended values for the heat capacity, enthalpy, entropy, and Gibbs energy function from 0.5 to 2400 K for manganese and from 0.4 to 5000 K for molybdenum have been generated, as have heat capacity values for supercooled β -Mn and for γ -Mn below 298.15 K. The recommended values for vapor pressure cover the temperature range from 298.15 to 2400 K for manganese and from 298.15 to 5000 K for molybdenum. These values are referred to temperatures based on IPTS-1968. The uncertainties in the recommended values of the heat capacity range from $\pm 3\%$ to $\pm 5\%$ for manganese and from $\pm 1.5\%$ to $\pm 3\%$ for molybdenum.

Key words: critical evaluation; data analysis; enthalpy; enthalpy of fusion; enthalpy of vaporization; Gibbs energy function; heat capacity; manganese; molybdenum; recommended values; vapor pressure.

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1. Introduction

The principal objective of this work was to critically evaluate and analyze all the available data and information on the heat capacity, enthalpy, and vapor pressure of manganese and molybdenum, and to generate the recommended values of these and other thermodynamic properties from below 1 K to the melting point and above.

The discussion of the thermodynamic properties and the details of data analysis are reported in Sec. 2 for manganese and Sec. 3 for molybdenum. The recommended values cover the temperature range from below 1 to 2400 K for manganese and to 5000 K for molybdenum.

The details of the data analysis have been discussed elsewhere.¹ The value of the gas constant used in this paper is $R = 8.314\ 41\ \text{J mol}^{-1}\ \text{K}^{-1}$.

2. Thermodynamic Properties of Manganese

Manganese is a transition metal with atomic weight 54.938. Four crystalline allotropic forms exist (Table 1): α has a complex bcc (A12) prototype structure, β has a complex cubic (A13) prototype structure, γ has an fcc (A1) structure isotropic with Cu, and δ has a bcc (A2) structure isotropic with W. Transformation between the α and β phase is rather sluggish. β -Mn can be preserved at low temperature by quenching; γ -Mn can be preserved at low temperature upon quenching only by adding very small amounts of copper or nickel. In the absence of new measurements on various transition temperatures, the values listed in Table 1 selected by Hultgren *et al.*⁴¹ were adopted after converting them to IPTS-68.

2.2. Low-Temperature Heat Capacity

a. α -Manganese

There have been numerous measurements of the electronic specific heat coefficient γ . Some of them, from which

Table 1. Structures and transition temperatures of manganese

Type	Structure	T _{trans.,} (K)	Remarks
α -Mn	bcc (A12)	980 \pm 20	T _{α-β}
β -Mn	c (A13)	1360 \pm 10	T _{β-γ}
γ -Mn	fcc (A1)	1411 \pm 15	T _{γ-δ}
δ -Mn	bcc (A2)	1519 \pm 5	T _{fus}

the recommended values are derived, are listed in Table 2. The recommended heat capacity values below 5 K are based on the above measurements except that Gaumer's³ values tend to be gradually higher above 1 K to 17% higher at 3 K. A small nuclear contribution below 1 K proportional to T^{-2} is reported in Refs. 3-8. The recommended C_p° values above 5 K are based on the data of Kelley *et al.*⁹ C_p° values of Booth *et al.*¹⁰ and of Gunther¹¹ are, respectively, 10% and 6% lower while those of Braun *et al.*¹² are 3% lower than the recommended values. C_p° values of Elson *et al.*¹³ and of Armstrong and Grayson-Smith¹⁴ are as much as 20% higher than the recommended values; possibly their samples contained small amounts of β -Mn. A small anomaly leading to a maximum C_p° at 98 K was ascribed to an antiferromagnetic Néel transformation.

Integration of the recommended C_p° values yields $H^{\circ}(298.15\ \text{K}) - H^{\circ}(0\ \text{K}) = 4998 \pm 10\ \text{J mol}^{-1}$ and integration of C_p°/T values yields $S^{\circ}(298.15\ \text{K}) = 32.221 (\pm 0.10)\ \text{J mol}^{-1}\ \text{K}^{-1}$.

b. β -Manganese

The recommended C_p° values are based on the data of Shinkoda *et al.*¹⁵ and of Butera and Craig¹⁶ except that the data of Shinkoda *et al.*¹⁵ above 12 K are up to 20% lower. The data of Booth *et al.*¹⁰ are about 14% lower than the recommended values. Shinkoda *et al.*¹⁵ observed a gradual upturn of C_p/T versus T^2 at low temperature which they described as due to spin fluctuations. It is therefore impossible to derive electronic specific heat coefficient.

The recommended C_p° values yielded $H^{\circ}(298.15\ \text{K}) - H^{\circ}(0\ \text{K}) = 5194 \pm 10\ \text{J mol}^{-1}$ and $S^{\circ}(298.15\ \text{K}) = 34.905 \pm 0.20\ \text{J mol}^{-1}\ \text{K}^{-1}$.

Table 2. Electronic specific heat coefficient of manganese

Source	$\gamma, \text{nJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$
Franzosi et al. ²	13.72
Gaumer ³	12.10
Guthrie ⁴	12.55
Martin and Heer ⁵	14.13
Stetsenko ⁶	15.98
Guthrie et al. ⁷	12.80
Scurlock and Stevens ⁸	12.01
Recommended value	12.47 \pm 0.05

c. γ -Manganese

The recommended C_p° values are based on the data of Franzosini *et al.*,² Kelley *et al.*,⁹ Ho,¹⁷ and Ho and Phillips¹⁸ for electrolytically deposited copper-stabilized samples. The electronic specific heat coefficient of $9.2 \text{ mJ mol}^{-1} \text{ K}^{-2}$ is based on the data from Refs. 17 and 18, in which a small nuclear contribution below 0.5 K proportional to T^{-2} was also reported. The recommended C_p° values yielded $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 5188 \pm 10 \text{ J mol}^{-1}$ and $S^\circ(298.15 \text{ K}) = 33.140 \pm 0.25 \text{ J mol}^{-1} \text{ K}^{-1}$.

The recommended C_p° values for all three phases are reported in Table 3 and are shown in Fig. 1 along with a few experimental data sets.

2.3. High-Temperature Heat Capacity (Solid)

The recommended C_p° values are based on the fairly consistent data of Braun *et al.*,¹² Naylor,¹⁹ Wust *et al.*,²⁰ Armstrong and Grayson-Smith,²¹ Backhurst,²² Awbery *et al.*,²³ and Margrave.²⁴ The heats of transitions, $\Delta H_{\alpha-\beta} = 2225 \pm 200 \text{ J mol}^{-1}$, $\Delta H_{\beta-\gamma} = 2120 \pm 330 \text{ J mol}^{-1}$, and $\Delta H_{\gamma-\delta} = 1880 \pm 330 \text{ J mol}^{-1}$ selected by Hultgren *et al.*¹ have been adopted.

2.4. High-Temperature Heat Capacity (Liquid)

The recommended enthalpy of fusion is based on the recent measurements of Sato and Kleppa.²⁵ They reported a value of $11\,000 \pm 840 \text{ J mol}^{-1}$ for enthalpy of fusion which they calculated from their measured value of $12\,760 \pm 630 \text{ J mol}^{-1}$ for the enthalpy of fusion of γ -Mn and the known $\Delta H_{\alpha-s}$ and enthalpies of pure undercooled liquid manganese. This compares with a value of $12\,058 \text{ J mol}^{-1}$ reported by Hultgren *et al.*¹ and $14\,100 \text{ J mol}^{-1}$ reported by Braun *et al.*¹²

A constant value of $46.038 \pm 2.00 \text{ J mol}^{-1} \text{ K}^{-1}$ recommended for the heat capacity of molten manganese is based on the value selected by Hultgren *et al.*,⁴¹ which compares with $47.6 \text{ J mol}^{-1} \text{ K}^{-1}$ reported by Braun *et al.*¹²

Other thermodynamic quantities reported in Table 4 are calculated from the recommended C_p° values. The recommended C_p° values are shown in Fig. 2 along with a few experimental data sets. The estimated uncertainties in the heat capacity are about $\pm 5\%$ below 20 K, $\pm 3\%$ from 20 to 298.15 K, and about $\pm 5\%$ above 298.15 K. The estimated uncertainty of values for supercooled β -Mn and γ -Mn is about $\pm 5\%$ below 20 K and $\pm 3\%$ from 20 to 298.15 K.

Table 3. Recommended low-temperature heat capacity of manganese

T K	$C_p^\circ, \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$			T K	$C_p^\circ, \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$		
	α -Mn	β -Mn	γ -Mn		α -Mn	β -Mn	γ -Mn
0.5	0.00825		0.00566	120	17.190	18.128	17.848
0.7	0.00931		0.00700	125	17.738	18.680	18.443
1	0.0125	0.0650	0.00952	130	18.252	19.184	18.980
2	0.0253	0.120	0.0189	140	19.148	20.050	19.964
3	0.0387	0.175	0.0291	150	19.941	20.808	20.872
4	0.0529	0.229	0.0403	160	20.664	21.501	21.638
5	0.0675	0.284	0.0523	170	21.316	22.148	22.319
6	0.0826	0.341	0.0666	175	21.622	22.448	22.630
7	0.0988	0.399	0.0833	180	21.920	22.734	22.921
8	0.1118	0.457	0.102	190	22.467	23.247	23.463
9	0.1229	0.517	0.124	200	22.961	23.700	23.960
10	0.163	0.576	0.149	210	23.409	24.130	24.421
15	0.316	0.882	0.329	220	23.831	24.533	24.861
20	0.541	1.242	0.595	225	24.029	24.722	25.071
25	0.890	1.734	0.980	230	24.226	24.900	25.278
30	1.407	2.368	1.532	240	24.592	25.235	25.685
40	3.004	4.000	3.119	250	24.928	25.547	26.090
50	5.078	5.876	5.063	260	25.239	25.833	26.488
60	7.253	7.858	7.214	270	25.531	26.101	26.873
70	9.503	9.955	9.445	273.15	25.618	26.183	26.992
75	10.601	10.997	10.475	280	25.800	26.353	27.250
80	11.710	12.008	11.483	290	26.043	26.590	27.629
90	14.001	13.881	13.334	298.15	26.225	26.779	27.938
95	15.142	14.721	14.208				
98	15.822 ^a	15.189	14.718				
99	15.260	15.340	14.884				
100	14.888	15.492	15.041				
105	15.467	16.207	15.794				
110	16.044	16.878	16.494				
115	16.623	17.527	17.193				

^aAntiferromagnetic Neel temperature.

α -Mn	β -Mn	γ -Mn	Mn(g)
$\gamma, \text{ mJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$	12.47 ± 0.05	9.2	
$H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})$ $\text{J} \cdot \text{mol}^{-1}$	4998 \pm 10	5194 \pm 10	5188 \pm 15
$S^\circ(298.15 \text{ K})$ $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	32.221 \pm 0.10	34.905 \pm 0.20	33.140 \pm 0.25
			173.606 \pm 0.001

2.5. Ideal Gas Properties

$C_p^\circ(g)$ values reported in Table 4 are taken from Chase.²⁶ Other thermodynamic quantities for Mn(g) are calculated from $C_p^\circ(g)$ values using $R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$ and $S^\circ(298.15 \text{ K}) = 173.606 \pm 0.001 \text{ J mol}^{-1} \text{ K}^{-1}$ as reported by Chase.²⁶

2.6. Vapor Pressure Data

Application of the Third Law test to the vapor pressure measurements gave the enthalpy of sublimation at 298.15 K as shown in Table 5. The values for ΔG° , p , and ΔH° of Table 6 are calculated using $\Delta_{\text{sub}}H^\circ(298.15 \text{ K})$ and the Gibbs and the enthalpy values for Mn(s, l) and Mn(g) from Table 4.

Most of the measurements for the thermodynamic properties have been carried out at temperatures based on IPTS-48 or IPTS-58. It is worth noting that the effect of converting these properties to IPTS-68 is well within the uncertainties of these values.

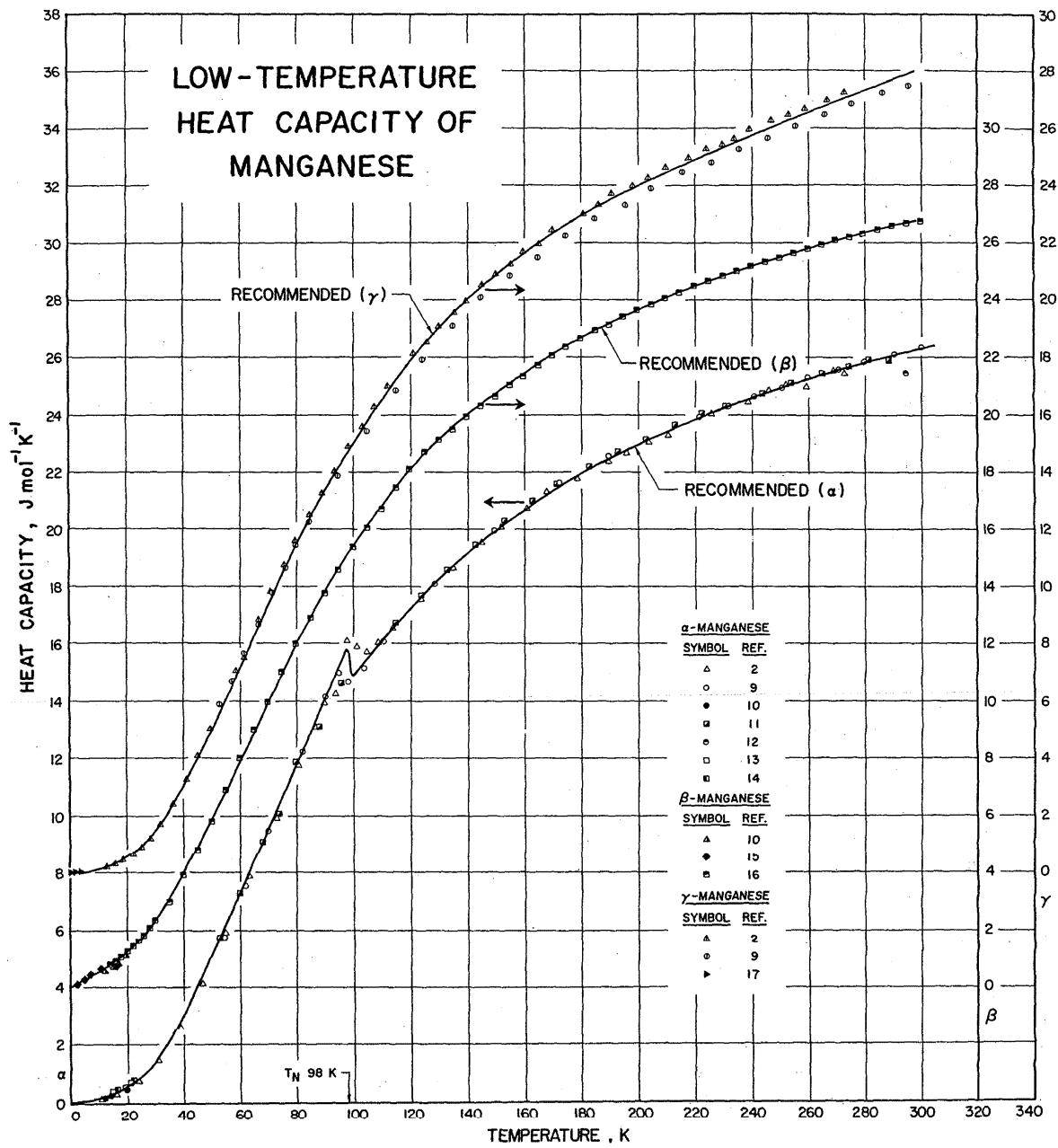


FIG. 1. Low-temperature heat capacity of manganese.

Table 4. Recommended high-temperature thermodynamic properties of manganese^a

T K	Condensed Phase				Gas Phase Mn(g)			
	C_p^0 $J \cdot mol^{-1} \cdot K^{-1}$	$H^0 - H^0(Tr)$ $J \cdot mol^{-1}$	S^0 $J \cdot mol^{-1} \cdot K^{-1}$	$-[G^0 - H^0(Tr)]/T$ $J \cdot mol^{-1} \cdot K^{-1}$	C_p^0 $J \cdot mol^{-1} \cdot K^{-1}$	$H^0 - H^0(Tr)$ $J \cdot mol^{-1}$	S^0 $J \cdot mol^{-1} \cdot K^{-1}$	$-[G^0 - H^0(Tr)]/T$ $J \cdot mol^{-1} \cdot K^{-1}$
298.15	26.225	0	0.000	32.221	20.786	0	0.000	173.606
300	26.267	49	0.162	32.222	20.786	38	0.129	173.606
400	28.395	2784	8.018	33.278	20.786	2117	6.109	174.422
500	30.287	5721	14.563	35.342	20.786	4196	10.747	175.962
600	31.929	8834	20.234	37.732	20.786	6274	14.537	177.686
700	33.433	12103	25.270	40.202	20.786	8353	17.741	179.414
800	34.788	15515	29.824	42.652	20.786	10431	20.517	181.083
900	36.039	19057	33.994	45.042	20.786	12510	22.965	182.671
980(a)	37.031	21979	37.103	46.896	20.786	14173	24.735	183.879
980(b)	37.578	24204	39.373	46.896	20.786	14173	24.735	183.879
1000	37.661	24956	40.133	47.398	20.786	14589	25.155	184.172
1100	38.097	28744	43.743	49.833	20.786	16667	27.136	185.590
1200	38.530	32576	47.076	52.151	20.786	18746	28.945	186.929
1300	38.965	36450	50.178	54.360	20.786	20824	30.608	188.196
1360(b)	39.226	38796	51.941	55.636	20.786	22071	31.546	188.923
1360(y)	42.577	40916	53.500	55.636	20.786	22071	31.546	188.923
1400	43.399	42636	54.746	56.513	20.786	22903	32.149	189.395
1411(y)	43.621	43114	55.087	56.752	20.786	23132	32.312	189.524
1411(b)	45.324	44994	56.419	56.752	20.786	23132	32.312	189.524
1500	45.961	49056	59.211	58.728	20.787	24982	33.583	190.534
1519(b)	46.093	49931	59.790	59.140	20.787	25377	33.845	190.744
1519(l)	46.038	60931	67.032	59.140	20.787	25377	33.845	190.744
1600	46.038	64660	69.424	61.232	20.788	27060	34.924	191.618
1700	46.038	69264	72.215	63.692	20.791	29139	36.185	192.650
1800	46.038	73868	74.846	66.030	20.797	31219	37.373	193.636
1900	46.038	78471	77.335	68.256	20.806	33299	38.498	194.578
2000	46.038	83075	79.697	70.380	20.822	35380	39.566	195.482
2100	46.038	87679	81.943	72.412	20.845	37464	40.582	196.348
2200	46.038	92283	84.085	74.359	20.880	39550	41.553	197.181
2300	46.038	96887	86.131	76.228	20.930	41640	42.482	197.983
2324	46.038	97992	86.609	76.665	20.946	42143	42.699	198.172
2400	46.038	101490	88.091	78.024	20.997	43736	43.374	198.756

$$\begin{aligned}
 T_{\alpha-\beta} &= 980 \pm 20 \text{ K} & \Delta H_{\alpha-\beta} &= 2225 \pm 200 \text{ J} \cdot \text{mol}^{-1} & \Delta S_{\alpha-\beta} &= 2.270 \pm 0.20 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\
 T_{\beta-\gamma} &= 1360 \pm 10 \text{ K} & \Delta H_{\beta-\gamma} &= 2120 \pm 330 \text{ J} \cdot \text{mol}^{-1} & \Delta S_{\beta-\gamma} &= 1.559 \pm 0.24 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\
 T_{\gamma-\delta} &= 1411 \pm 15 \text{ K} & \Delta H_{\gamma-\delta} &= 1880 \pm 330 \text{ J} \cdot \text{mol}^{-1} & \Delta S_{\gamma-\delta} &= 1.332 \pm 0.23 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\
 T_{fus} &= 1519 \pm 5 \text{ K} & \Delta_{fus} H^0 &= 11000 \pm 840 \text{ J} \cdot \text{mol}^{-1} & \Delta_{fus} S^0 &= 7.242 \pm 0.55 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}
 \end{aligned}$$

^aEnthalpy reference temperature = Tr = 298.15 K.

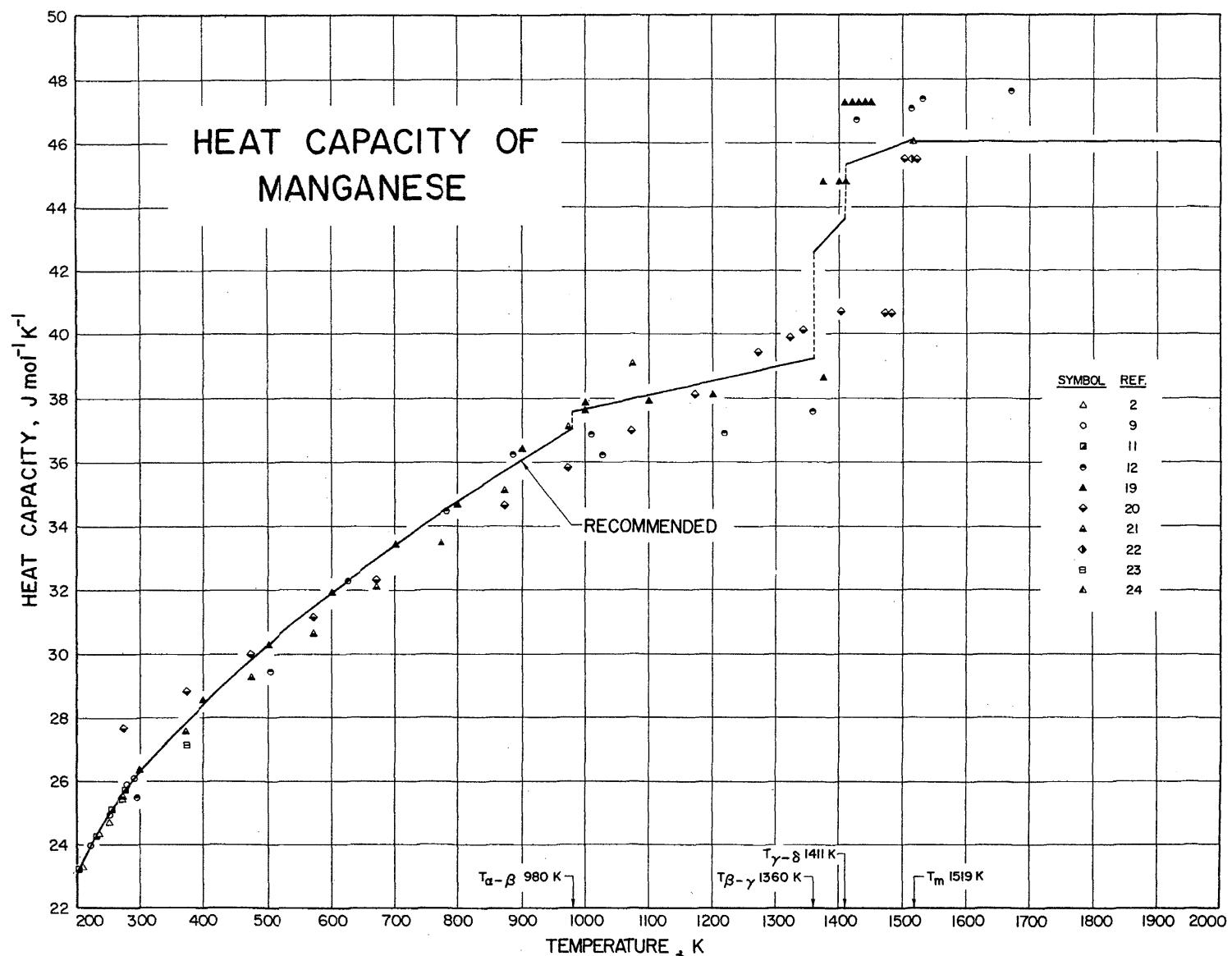


FIG. 2. Heat capacity of manganese.

Table 5. Values for enthalpy of sublimation of manganese at 298.15 K

Source	$\Delta_{\text{sub}}H^{\circ}(298.15 \text{ K}), \text{ kJ} \cdot \text{mol}^{-1}$
Bogatyrev and Golubtsov ²⁷ , 1043-1158 K Knudsen method	286.20 \pm 1.25
Pratt and Spencer ²⁸ , 1248-1620 K Torsion-effusion method	284.87 \pm 0.10
Wiedemeier ²⁹ , 1269-1448 K Torsion-effusion method	289.64 \pm 0.29
Butler et al. ³⁰ , 1075-1335 K Knudsen method	281.12 \pm 0.60
Woolf et al. ³¹ , 1518-1811 K Transport method	279.40 \pm 0.33
McCabe and Hudson ³² , 1075-1235 K Knudsen method	280.44 \pm 1.04
Baur and Brunner ³³ , 1587-1987 K Boiling point method	285.30 \pm 2.00
Lindscheid and Lange ³⁴ , 1278-1647 K Knudsen-torsion method	284.07 \pm 4.98
Ehlert ³⁵ , 800-1200 K Mass spec-Knudsen method	277.76 \pm 0.83
Krenzer and Pool ³⁶ , 973-1273 K Knudsen method	281.31 \pm 0.39
Snoes et al. ³⁷ , 1169-1269 K Mass spec-Knudsen method	283.19 \pm 0.13
Tanaka ³⁸ , 1623-1673 K Transportation method	282.05 \pm 0.06
Nemets and Nikolaev ³⁹ , 1094-1485 K Absorption method	283.71 \pm 2.10
Gee and Rosengqvist ⁴⁰ , 1517-1818 K Transportation method	281.04 \pm 0.15
Recommended value	282.40 \pm 2.00

Table 6. Recommended vapor pressure of manganese^{a,b}

T K	p atm	ΔG° $\text{J} \cdot \text{mol}^{-1}$	ΔH° $\text{J} \cdot \text{mol}^{-1}$	p atm	T K
298.15	8.13×10^{-43}	240246	282400	10^{-10}	858
300	1.64×10^{-42}	239985	282389	10^{-9}	911
400	3.13×10^{-30}	225942	281733	10^{-8}	973
500	6.97×10^{-23}	213090	280075	10^{-7}	1045
600	5.31×10^{-18}	198428	279840	10^{-6}	1128
				10^{-5}	1227
700	1.58×10^{-14}	184952	278650	10^{-4}	1345
800	6.20×10^{-12}	171655	277316	10^{-3}	1492
900	6.29×10^{-10}	158534	275853	10^{-2}	1687
980(a)	1.27×10^{-8}	148157	274594	10^{-1}	1949
980(b)	1.27×10^{-8}	148157	272369	1	2224
1000	2.47×10^{-8}	145626	272033	$\Delta_{\text{vap}}H^{\circ}(2324 \text{ K}) = 97.483 \pm (0.86)$	
1100	4.80×10^{-7}	133067	270323	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	
1200	5.59×10^{-6}	120666	268370		
1300	4.40×10^{-5}	108413	266774	$\Delta_{\text{sub}}H^{\circ}(0 \text{ K}) = 281.201 \pm (2.00)$	
1360(b)	1.31×10^{-4}	101190	265675	$\text{J} \cdot \text{mol}^{-1}$	
1360(r)	1.31×10^{-4}	101130	263555		
1400	2.54×10^{-4}	96365	262667		
1411(r)	3.03×10^{-4}	95059	262418		
1411(b)	3.03×10^{-4}	95059	260538		
1500	1.12×10^{-3}	84691	258326		
1519(b)	1.46×10^{-3}	82494	257846		
1519(r)	1.46×10^{-3}	82494	246846		
1600	3.90×10^{-3}	73782	244800		
1700	1.15×10^{-2}	63171	242275		
1800	2.95×10^{-2}	52709	239751		
1900	6.83×10^{-2}	42388	237228		
2000	0.144	32196	234705		
2100	0.281	22134	232185		
2200	0.513	12192	229667		
2300	0.884	2364	227153		
2324	1.000	0	226551		
2400	1.446	-7357	224646		

^a1 atm = 101325 Pa^b ΔG° refers to $\Delta_{\text{sub}}H^{\circ}$ when $T < T_{\text{fus}}$ and $\Delta_{\text{vap}}H^{\circ}$ when $T > T_{\text{fus}}$ (and similarly for ΔH°).

2.7. References

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3. Thermodynamic Properties of Molybdenum

3.1. Phases and Structures

Molybdenum has a bcc (A2) structure isotropic with W. The melting point is based on the selection of Bedford *et al.*¹ which compares with the following determinations (IPTS-1968) listed in Table 7. Roberts¹² reports a value of 0.912 K for the superconducting transition temperature.

3.2. Low-Temperature Heat Capacity

There have been numerous measurements of the electronic specific heat coefficient γ and the Debye temperature θ_D for normal (in magnetic field) molybdenum. Some of them from which the recommended values are derived are listed in Table 8. Considerable weight was given to the measurements of Rorer,¹⁸ Rorer *et al.*,¹⁹ and of Claus²² because of the extremely high purity (99.999%) specimens which they used.

The recommended heat capacity values for normal molybdenum below 4 K were derived from the recommended γ and θ_D values and $R = 8.314\ 41\ J\ mol^{-1}\ K^{-1}$ using the following relation:

$$C_p^\circ = \gamma T + (1943.75/\theta_D^3)T^3.$$

The recommended C_p° values from 4 to 298.15 K agree well with the C_p° measurements of Horowitz and Daunt,¹³ Wolcott,¹⁶ Morin and Maita,¹⁷ Taylor and Finch,²⁴ Clusius and Franzosini,²⁵ Simon and Zeidler,²⁶ Cooper and Langstroth,²⁷ Khriplovich and Paukov,²⁸ Bronson *et al.*,²⁹ Dittmars *et al.*,³⁰ and of Savchenko and Moiseeva.⁴⁰ The data of Cape³¹ are slightly higher than the recommended values. The recommended value of $C_p^\circ = 23.900 \pm 0.04$

Table 7. Melting point of molybdenum

Source	T _{fus} , K
Rudy and Progulski ²	2897 \pm 9
Riley ³	2896 \pm 10
Knapton <i>et al.</i> ⁴	2886 \pm 10
Edwards and Johnstone ⁵	2898
Chiotti ⁶	2894
Worthing ⁷	2889 \pm 10
Chekhovskoi and Kats ⁸	2898 \pm 9
Kenisarin <i>et al.</i> ⁹	2899
Latta and Fryxell ¹⁰	2896 \pm 15
Kenisarin <i>et al.</i> ¹¹	2899 \pm 9
Cezairliyan <i>et al.</i> ⁶⁷	2894 \pm 10
Recommended value	2897 \pm 5

Table 8. Electronic specific heat coefficient and Debye temperature of molybdenum

Source	$\gamma, mJ \cdot mol^{-1} \cdot K^{-2}$	θ_D, K
Horowitz and Daunt ¹³	2.134	445
Bryant and Keesom ¹⁴	1.93 1.91	427 \pm 26 458 \pm 15
Rayne ¹⁵	2.197	
Wolcott ¹⁶	2.113	470
Morin and Maita ¹⁷	2.008	470
Rorer ¹⁸	1.75 1.83	375 \pm 10 423 \pm 15
Rorer <i>et al.</i> ¹⁹	1.81 1.89 1.87	382 \pm 10 461 \pm 10 456 \pm 10
Viswanathan ²⁰	1.75 1.75 1.75	458 449 440
Viswanathan <i>et al.</i> ²¹	1.75 1.75 1.75 1.75 1.75 1.75 1.75	527 458 506 440 516 449 467
Claus ²²	1.867	
Veal <i>et al.</i> ²³	2.200	470
Recommended value	1.85 \pm 0.02	430 \pm 20

Table 9. Recommended low-temperature heat capacity of molybdenum

T K	C_p°		T K	C_p°	
	$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$		$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$
0.4	0.00544 ^a	0.00741 ^b	90	11.910	
0.5	0.00109 ^a	0.000928 ^b	100	13.498	
0.6	0.00169 ^a	0.00112 ^b	110	14.875	
0.8	0.00305 ^a	0.00149 ^b	120	16.101	
0.912	0.00395 ^a	0.00171 ^b	125	16.658	
1	0.00187		130	17.178	
2	0.00390		140	18.090	
3	0.00621		150	18.889	
4	0.00896		160	19.571	
5	0.0121		170	20.154	
6	0.0156		175	20.420	
7	0.0194		180	20.662	
8	0.0237		190	21.113	
9	0.0284		200	21.521	
10	0.0341		210	21.890	
15	0.0834		220	22.228	
20	0.213		225	22.388	
25	0.428		230	22.540	
30	0.770		240	22.821	
35	1.265		250	23.064	
40	1.909		260	23.275	
50	3.698		270	23.461	
60	5.912		273.15	23.515	
70	8.079		280	23.626	
75	9.112		290	23.777	
80	10.094		298.15	23.900	

^a Superconductor

^b Nonsuperconductor in magnetic field

$$C_{(electronic)} = \gamma T \quad \gamma = 1.85 \pm 0.02 \text{ } mJ \cdot mol^{-1} \cdot K^{-2}$$

Crystal, Mo(s)	Gas, Mo(s)
H ⁰ (298.15 K) - H ⁰ (0 K) 4585 \pm 10 J · mol ⁻¹	6197.3 \pm 0.2 J · mol ⁻¹
S ⁰ (298.15 K) 28.592 \pm 0.08 J · mol ⁻¹ · K ⁻¹	181.841 \pm 0.002 J · mol ⁻¹ · K ⁻¹

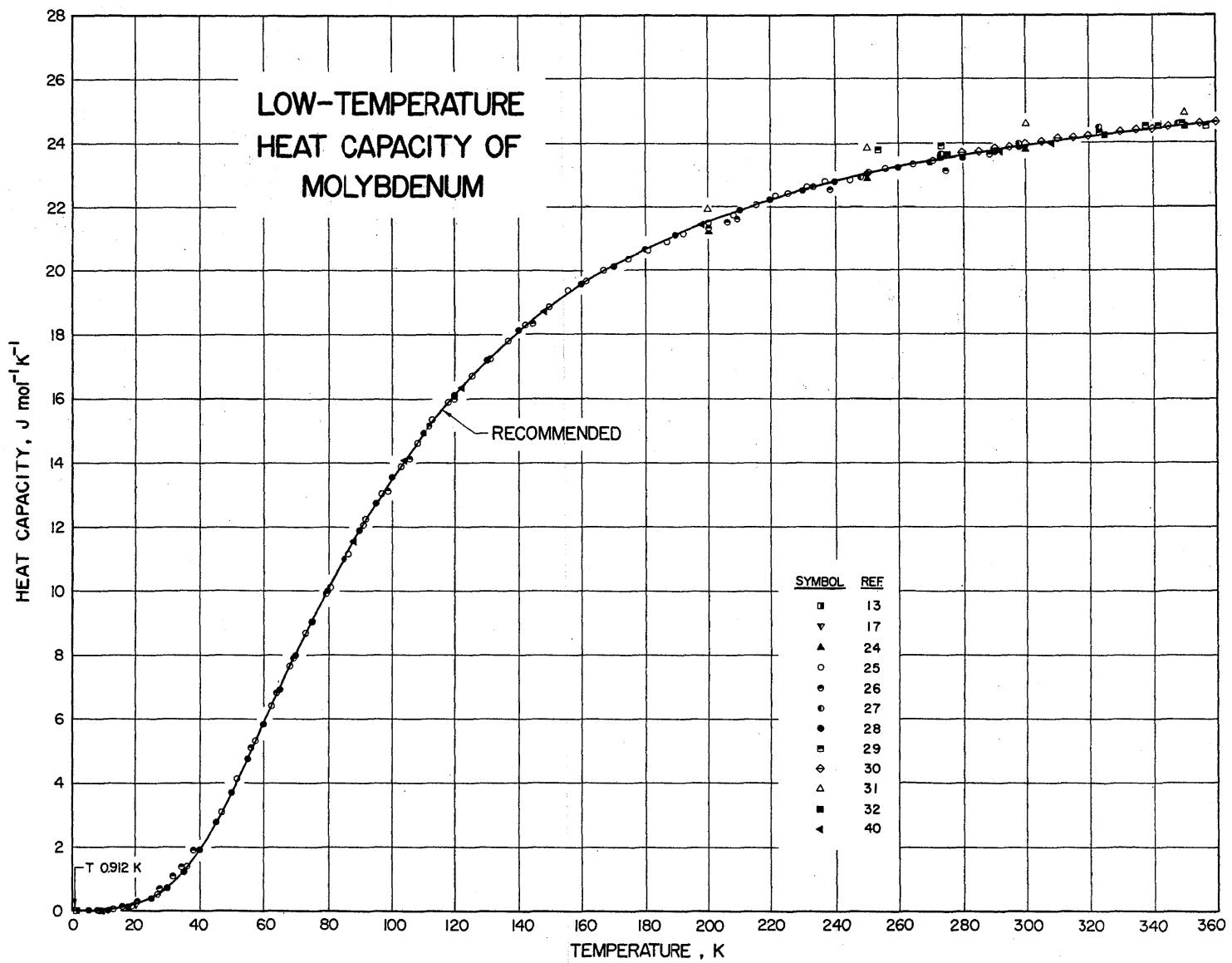


FIG. 3. Low-temperature heat capacity of molybdenum.

$J \text{ mol}^{-1} \text{ K}^{-1}$ at 298.15 K is slightly lower than the previously selected value by Hultgren *et al.*³³ The adoption of a lower C_p° value at 298.15 K was a result of the most recent careful studies of Khriplovich and Paukov²⁸ on a very pure molybdenum sample. These values are tabulated in Table 9 and shown in Fig. 3 along with the experimental data. Integration of the recommended C_p° and C_p°/T values yielded $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})$ and $S^\circ(298.15 \text{ K})$ values listed in Table 10 along with the values from other sources. The recommended C_p° values for superconducting molybdenum agree well with the C_p° measurements of Rorer¹⁸ and Rorer *et al.*¹⁹

3.3. High-Temperature Heat Capacity (Solid)

There has been a considerable amount of recent work developing techniques for measurements at high temperatures. Among the new techniques, Trevorton and Margrave,³⁷ Chekhovskoi and Berezin,⁴⁷ and more recently Betz and Frohberg³⁹ used levitation drop calorimetry. C_p° measurements using an electric pulse are actively being improved.

Due to the large amount of data available on the enthalpy measurements, the data were converted to a simple

$$y = [H^\circ(T) - H^\circ(298.15 \text{ K})]/(T - 298.15)$$

function and thermodynamic functions were derived. Agreement between y values calculated from enthalpy data and the recommended values for most compositions is shown in Table 11.

Heat capacity values obtained from y values were compared with directly measured C_p° data. In order to obtain

TABLE 10. Thermodynamic constants of molybdenum at 298.15 K

Source	$C_p^\circ(298.15 \text{ K})$ $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})$ $\text{J} \cdot \text{mol}^{-1}$	$S^\circ(298.15 \text{ K})$ $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Khriplovich and Paukov ²⁸	23.86	4589	28.56
Ditmars <i>et al.</i> ³⁰	23.92		
Douglas and Ditmars ³²	23.924		
Hultgren <i>et al.</i> ³³	24.038	4594	28.660
Chase <i>et al.</i> ³⁴	23.932	4586	28.602
Glushko <i>et al.</i> ³⁵	23.932	4580	28.57
Brewer and Lamoreaux ³⁶	23.937	4586	28.602
Savchenko and Moiseeva ⁴⁰	23.816		
Present value	23.900 ± 0.04	4585 ± 10	28.592 ± 0.08

Table 11. Percentage deviation in heat capacity of molybdenum

Source	Deviation, %
Douglas and Ditmars ³²	-0.1
Piefer ⁴¹	± 0.3
Ishihara and Douglas ⁴²	0.5
Jaeger and Veenstra ⁴³	-0.6
Kirillin <i>et al.</i> ⁴⁴	± 1
Betz and Frohberg ³⁹	-1
Kirillin <i>et al.</i> ⁴⁵	up to -1.5
Chekhovskoi and Petrov ⁴⁶	-1.5
Chekhovskoi and Berezin ⁴⁷	-2
Ronson <i>et al.</i> ²⁹	up to 2
Kothen ⁴⁹	up to -2
Lazareva <i>et al.</i> ⁵⁰	-2
Krivorotenko <i>et al.</i> ⁵¹	up to -2.4
Conway <i>et al.</i> ⁵¹	up to -3
Fieldhouse <i>et al.</i> ⁵²	± 3.5
Lucks and Deem ⁵³	± 6
Redfield and Hill ⁵⁴	± 10
Cooper and Longstroth ⁵⁵	up to 13

better agreement with reliable C_p° data, it was necessary to adjust y values slightly. Thus C_p° values obtained in this manner agree with the literature data as given in Table 12. The C_p° values adopted by Chase *et al.*,³⁴ who essentially followed the selections of Brewer and Lamoreaux,³⁶ agree well to $\pm 0.5\%$ with the recommended values. However, the C_p° values reported by Choudhary and Brooks⁴⁸ are up to 8% lower than the recommended values. A systematic plot of percent deviation in y values from various measurements is shown in Fig. 4 and the percent deviation in C_p° values is shown in Fig. 5.

3.4. High-Temperature Heat Capacity (Liquid)

The recommended value for the enthalpy of melting, $\Delta_{\text{fus}} H^\circ = 39100 \pm 1500 \text{ J mol}^{-1}$, was obtained by extrapolating solid and liquid enthalpies to the melting point $T_{\text{fus}} = 2897 \text{ K}$. The values given in Table 13 are reported in the literature.

Table 12. Percentage deviation in enthalpy for molybdenum

Source	Deviation, %
Cezairliyan ⁵⁶	+0.15
Ditmars et al. ³⁰	+0.15 (<1900 K) up to 0.58 (>1900 K)
Getting and West ³⁸	+0.5
Righini and Rosso ⁵⁷	+0.7
Hassett ⁵⁸	1
Boggs and Weibelt ⁵⁹	+2
Fedorov ⁶⁰	up to 2
Kraftmakher ⁶¹	+1 (<2100 K) up to 9 (>2100 K)
Makarenko et al. ⁶²	3 (<1900 K) up to -5 (>1900 K)
Taylor and Finch ⁶³	-3 (<1600 K) up to 8 (>1600 K)
Cezairliyan et al. ⁶⁴	-4
Cezairliyan ⁶⁵	up to 4
Butler and Inn ⁶⁶	up to -4
Makarenko et al. ⁶²	+4
Mebed et al. ⁶⁸	up to -4
Boggs and Weibelt ⁵⁹	up to 4.5
Filippov and Yurchak ⁶⁹	up to -5.5
Cezairliyan et al. ⁷⁰	up to -6.8
Boggs and Weibelt ⁵⁹	up to 8
Rudkin et al. ⁷¹	up to 9
Lowenthal ⁷²	up to -12
Lehman ⁷³	up to -13
Balakin et al. ⁷⁴	up to -14
Dikhter and Lebedev ⁷⁵	up to -20 (<2750 K) up to 28 (>2750 K)

The enthalpy values of Table 14 agree (± 1500 J mol $^{-1}$) with the levitation drop calorimetric values of Betz and Frohberg.³⁹ Similar measurements of Trevorton and Margrave³⁷ yielded values 8–11 kJ mol $^{-1}$ lower and those of Chekhovskoi and Berezin⁴⁷ yielded values about 5 kJ mol $^{-1}$ lower than the recommended values. Measurements of Betz and Frohberg³⁹ were over a sufficient range of temperature to establish $C_{p(\ell)}^{\circ} = 40.350 \pm 2.00$ J mol $^{-1}$ K $^{-1}$, which is slightly higher than the values reported by Brewer and Lamoreaux³⁶ (37.782 ± 2.09 J mol $^{-1}$ K $^{-1}$) and Chase et al.³⁴ (35.982 ± 5.44 J mol $^{-1}$ K $^{-1}$).

The recommended C_p° values, along with the experimental data, are listed in Table 14 and shown in Fig. 6. Other quantities in Table 14 were calculated by integrating C_p° values. The estimated uncertainties in the heat capacity are $\pm 3\%$ below 10 K, $\pm 1.5\%$ from 10 to 298.15 K, $\pm 2\%$ above 298.15 K, and $\pm 3\%$ in the liquid region.

3.5. Ideal Gas Properties

Thermodynamic properties reported in Table 14 are calculated from $C_{p(g)}^{\circ}$ and $S^{\circ}(298.15 \text{ K}) = 181.841$ J mol $^{-1}$ K $^{-1}$ reported by Chase⁸³ and $R = 8.314\ 41$ J mol $^{-1}$ K $^{-2}$.

3.6. Vapor Pressure Data

Various Langmuir vapor pressure measurements were tested with the aid of the Third Law. These numerical calculations yielded the following $\Delta_{\text{sub}} H^{\circ}$ (298.15 K) values listed in Table 15. The values for ΔG° , p , and ΔH° reported in Table 16 are calculated using $\Delta_{\text{sub}} H^{\circ}$ (298.15 K) and Gibbs values for Mo(s, ℓ) and Mo(g) from Table 14.

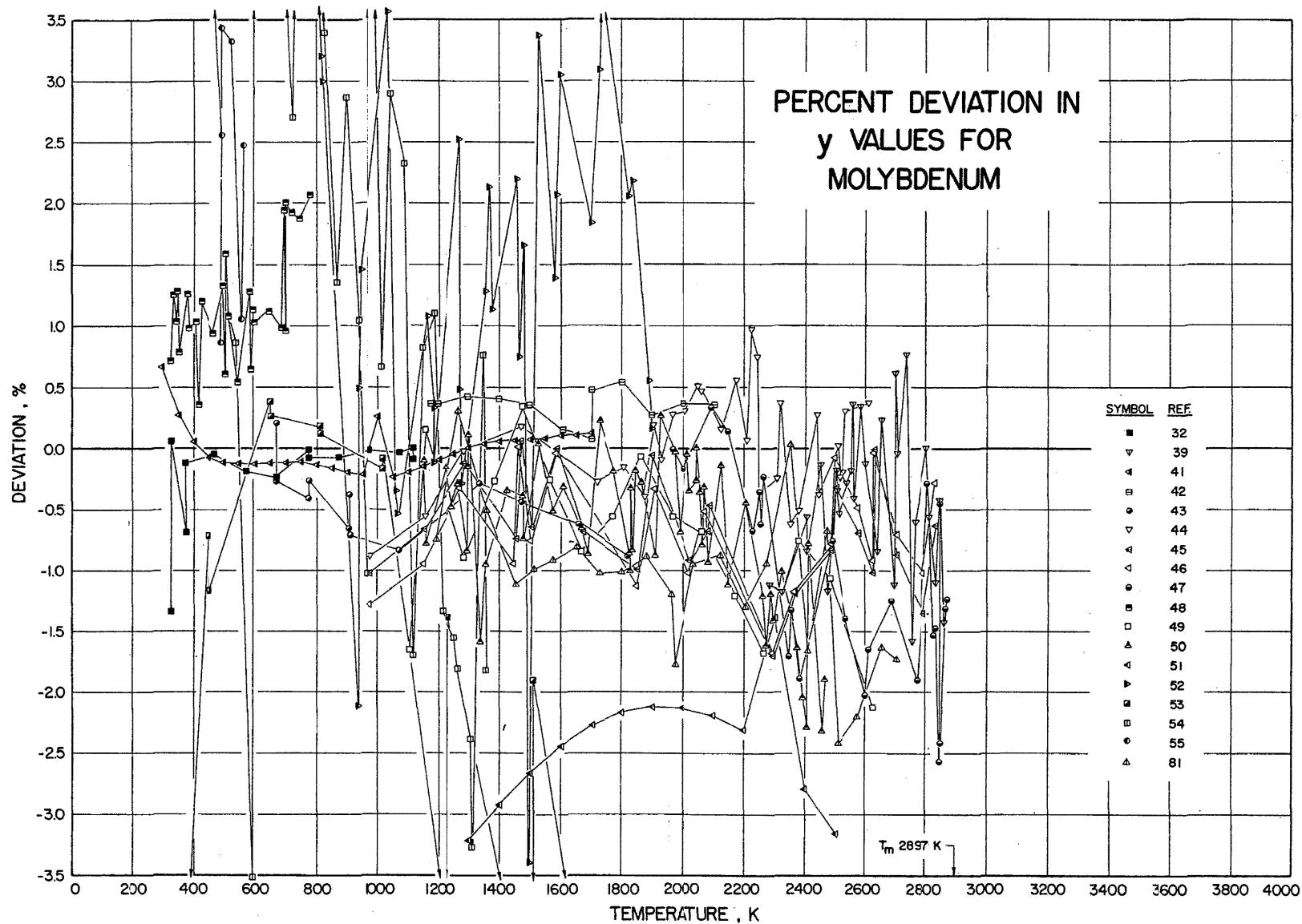


FIG. 4. Percent deviation in γ values for molybdenum.

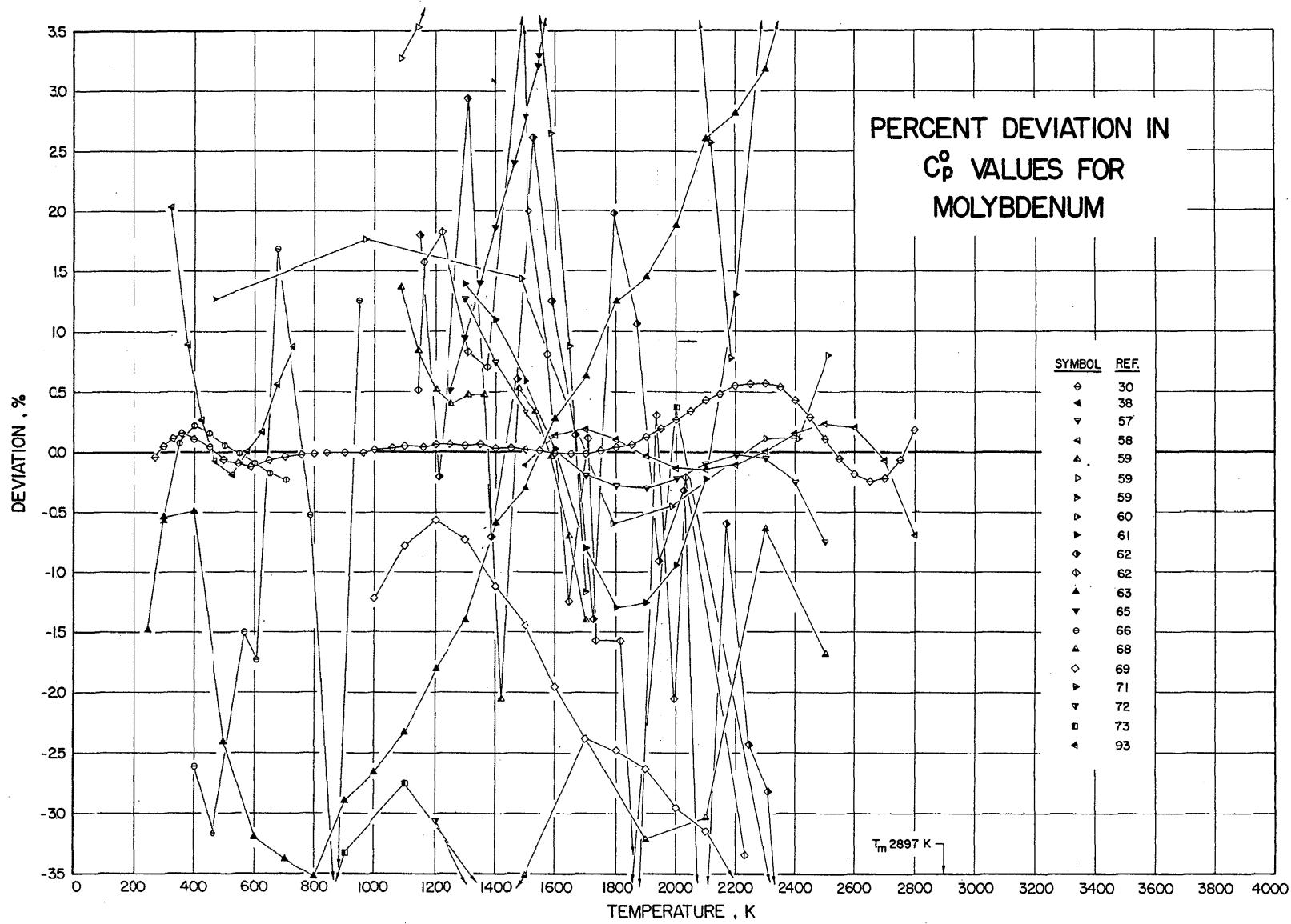
FIG. 5. Percent deviation in C_p° values for molybdenum.

Table 13. Values for enthalpy of fusion of molybdenum

Source	$\Delta_{\text{fus}} H^{\circ}, \text{J} \cdot \text{mol}^{-1}$
Chekhovskoi and Kats ⁸	36460 ± 1060
Treverton and Margrave ³⁷	34810
Betz and Frohberg ³⁹	39100
Chekhovskoi and Berezin ⁴⁷	36650 ± 860
Lebedev et al. ⁷⁶	41250
Seydel and Fischer ⁷⁷	48500 ± 2300
Shaner et al. ⁷⁸	35500
Martynyuk et al. ⁷⁹	38000
Gerasimov et al. ⁸⁰	37240
Seydel et al. ⁸²	48450
Recommended value	39100 ± 1500

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Table 14. Recommended high-temperature thermodynamic properties of molybdenum^a

T K	Condensed Phase				Gas Phase Mo(g)			
	C _p J·mol ⁻¹ ·K ⁻¹	H ⁰ -H ⁰ (Tr) J·mol ⁻¹	S ⁰ J·mol ⁻¹ ·K ⁻¹	-[G ⁰ -H ⁰ (Tr)]/T J·mol ⁻¹ ·K ⁻¹	C _p J·mol ⁻¹ ·K ⁻¹	H ⁰ -H ⁰ (Tr) J·mol ⁻¹	S ⁰ J·mol ⁻¹ ·K ⁻¹	-[G ⁰ -H ⁰ (Tr)]/T J·mol ⁻¹ ·K ⁻¹
298.15	23.900	0	0.000	28.592	20.786	0	0.000	181.841
300	23.918	44	0.148	28.592	20.786	38	0.129	181.841
350	24.555	1257	3.884	28.886	20.786	1078	3.332	182.093
400	25.078	2498	7.198	29.546	20.786	2117	6.109	182.657
450	25.507	3763	10.177	30.408	20.786	3156	8.556	183.383
500	25.874	5047	12.884	31.382	20.786	4196	10.747	184.197
550	26.192	6349	15.366	32.414	20.786	5235	12.727	185.050
600	26.470	7666	17.657	33.472	20.786	6274	14.537	185.921
650	26.721	8996	19.785	34.538	20.786	7314	16.199	186.789
700	26.960	10338	21.775	35.598	20.786	8353	17.741	189.649
750	27.197	11692	23.643	36.646	20.786	9392	19.174	188.492
800	27.432	13057	25.405	37.676	20.786	10431	20.517	189.318
850	27.671	14435	27.076	38.685	20.786	11471	21.775	190.121
900	27.905	15824	28.664	39.673	20.786	12510	22.965	190.906
950	28.139	17226	30.179	40.639	20.786	13549	24.087	191.666
1000	28.380	18638	31.628	41.582	20.787	14589	25.155	192.407
1100	28.900	21502	34.357	43.402	20.788	16667	27.136	193.825
1200	29.481	24420	36.896	45.138	20.793	18747	28.945	195.164
1300	30.129	27400	39.281	46.796	20.803	20826	30.610	196.431
1400	30.849	30449	41.540	48.383	20.823	22907	32.152	197.631
1500	31.647	33573	43.695	49.905	20.856	24991	33.590	198.770
1600	32.500	36780	45.764	51.369	20.910	27079	34.938	199.854
1700	33.398	40074	47.761	52.780	20.989	29174	36.207	200.887
1800	34.367	43462	49.697	54.144	21.100	31278	37.410	201.874
1900	35.145	46951	51.583	55.464	21.250	33395	38.555	202.819
2000	36.540	50548	53.428	56.746	21.443	35530	39.649	203.726
2100	37.748	54261	55.240	57.993	21.687	37686	40.701	204.597
2200	39.074	58102	57.026	59.208	21.985	39869	41.717	205.436
2300	40.503	62079	58.794	60.395	22.342	42085	42.702	206.245
2400	42.058	66206	60.550	61.556	22.761	44339	43.661	207.028
2500	43.830	70499	62.302	62.695	23.248	46639	44.600	207.785
2600	45.900	74982	64.060	63.813	23.802	48991	45.522	208.521
2700	48.390	79692	65.838	64.914	24.428	51402	46.432	209.235
2800	51.485	84681	67.651	66.000	25.127	53892	47.333	209.931
2897(±)	55.058	89844	69.462	67.042	25.870	56430	48.228	210.610
2897(±)	40.350	128944	82.959	67.042	25.870	56430	48.228	210.610
3000	40.350	133100	84.369	68.594	26.742	59061	49.120	211.274
3200	40.350	141170	86.973	71.449	28.647	64595	50.905	212.560
3400	40.350	149240	89.419	74.117	30.827	70538	52.706	313.800
3600	40.350	157310	91.725	76.620	33.256	76943	54.536	215.004
3800	40.350	165380	93.907	78.978	35.900	83855	56.404	216.178
4000	40.350	173450	95.977	81.206	38.713	91314	58.316	217.328
4200	40.350	181520	97.945	83.318	41.649	99349	60.275	218.462
4400	40.350	189590	99.822	85.326	44.658	107978	62.282	219.583
4600	40.350	197660	101.616	87.238	47.696	117214	64.334	220.694
4800	40.350	205730	103.333	89.065	50.725	127055	66.428	221.799
4983	40.350	213114	104.843	90.667	53.461	136589	68.376	222.806
5000	40.350	213800	104.981	90.812	53.713	137500	68.558	222.899

$$T_{\text{fus}} = 2897 (\pm 5) \text{ K} \quad \Delta_{\text{fus}} H^0 = 39100 \pm 1500 \text{ J} \cdot \text{mol}^{-1} \quad \Delta_{\text{fus}} S^0 = 13.497 \pm 0.52 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

^aEnthalpy reference temperature = Tr = 298.15 K.

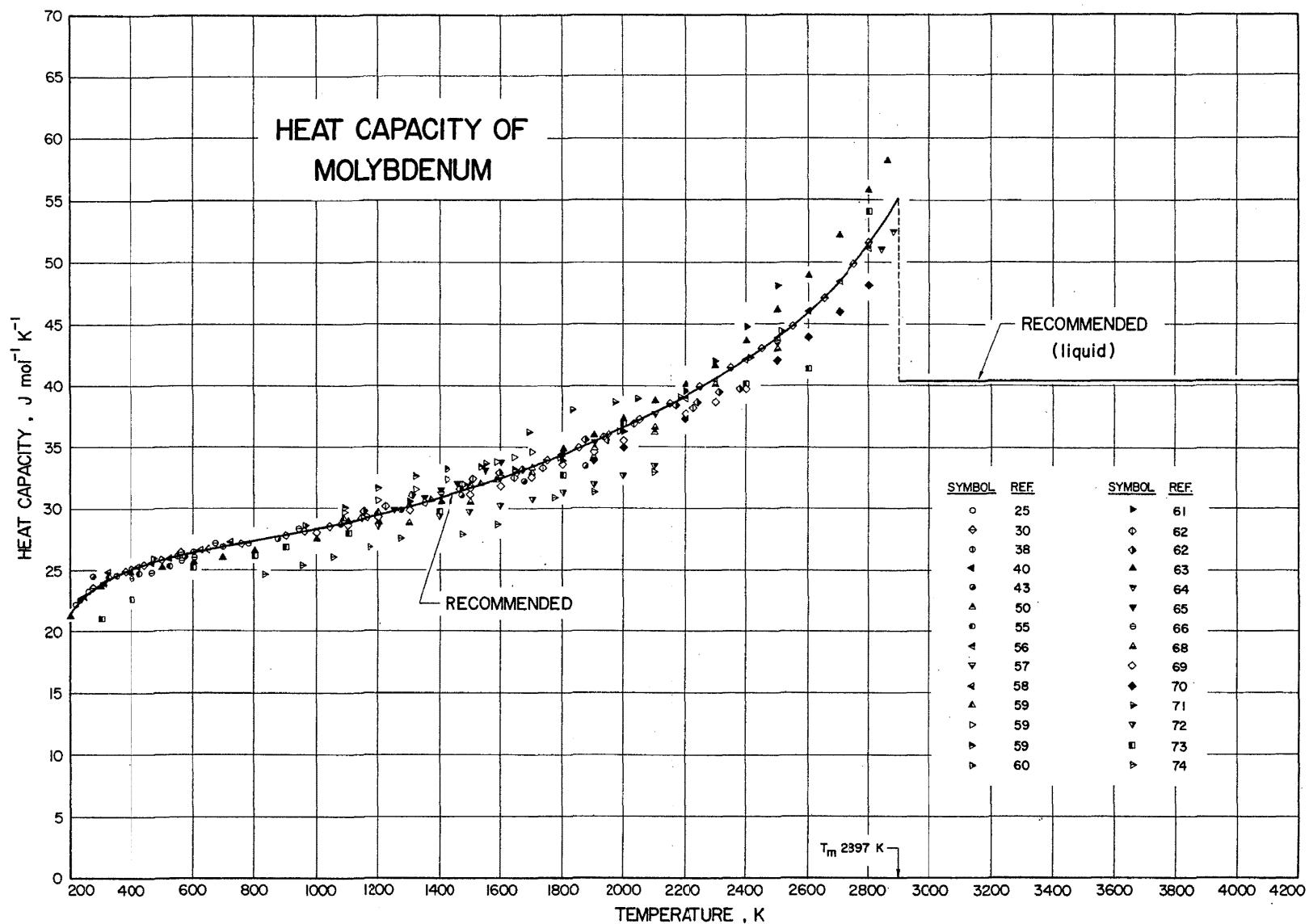


FIG. 6. Heat capacity of molybdenum.

Table 15. Values for enthalpy of sublimation of molybdenum at 298.15 K

Source	$\Delta_{\text{sub}} H^{\circ}(298.15 \text{ K})$, $\text{kJ} \cdot \text{mol}^{-1}$
Koch and Anable ⁸⁴ , 2890-2990 K	658.61 \pm 3.53
Kovtun and Kruglykh ⁸⁵ , 2243-2653 K	650.98 \pm 5.67
Fries ⁸⁶ , 2086-2326 K	655.68 \pm 1.52
Vozzella et al. ⁸⁷ , 2140-2523 K	659.54 \pm 1.95
Edwards et al. ⁸⁸ , 2151-2462 K	661.75 \pm 2.43
Zwikker ⁸⁹ , 1200-2500 K	663.87 \pm 1.25
Jones et al. ⁹⁰ , 2070-2504 K	655.29 \pm 4.22
Dekhtyar et al. ⁹¹ , 2293-2673 K	661.61 \pm 2.87
Recommended Value	658.50 (\pm 2.00)

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Table 16. Recommended vapor pressure of molybdenum^{a,b}

$$\text{Mo}(s, \lambda) = \text{Mo}(g)$$

<u>T</u> K	<u>p</u> atm	<u>ΔG°</u>		<u>ΔH°</u>	<u>p</u> atm	<u>T</u> K
		<u>J·mol⁻¹</u>	<u>$\text{J}^\circ\text{mol}^{-1}$</u>			
298.15	4.35×10^{-108}	612809	658500		10^{-10}	1945
300	2.24×10^{-107}	612525	658494		10^{-9}	2064
400	1.01×10^{-78}	597256	658119		10^{-8}	2200
500	1.55×10^{-61}	582093	657649		10^{-7}	2355
600	4.32×10^{-50}	567031	657108		10^{-6}	2534
					10^{-5}	2745
700	6.37×10^{-42}	552064	656515		10^{-4}	3004
800	8.42×10^{-36}	537186	655874		10^{-3}	3333
900	4.80×10^{-31}	522390	655186		10^{-2}	3746
1000	3.03×10^{-27}	507675	654451		10^{-1}	4278
1100	3.87×10^{-24}	493035	653665		1	4983
1200	1.49×10^{-21}	478469	652827	$\Delta_{\text{vap}}^{\text{S}^\circ}(4983 \text{ K}) = 116.792 \pm (0.69)$		
1300	2.28×10^{-19}	463975	651926	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$		
1400	1.69×10^{-17}	449553	650958			
1500	7.00×10^{-16}	435203	649918	$\Delta_{\text{sub}}^{\text{H}^\circ}(0 \text{ K}) = 656.888 \pm (2.00)$		
1600	1.81×10^{-14}	420924	648799	$\text{kJ} \cdot \text{mol}^{-1}$		
1700	3.18×10^{-13}	406718	647600			
1800	4.05×10^{-12}	392586	646316			
1900	3.92×10^{-11}	378526	644944			
2000	3.01×10^{-10}	364540	643482			
2100	1.90×10^{-9}	350632	641925			
2200	1.01×10^{-8}	336798	640267			
2300	4.61×10^{-8}	323045	638506			
2400	1.85×10^{-7}	309367	636633			
2500	6.61×10^{-7}	295775	634640			
2600	2.13×10^{-6}	282259	632509			
2700	6.30×10^{-6}	268833	630210			
2800	1.71×10^{-5}	255493	627711			
2897(s)	4.22×10^{-5}	242644	625086			
2897(?)	4.22×10^{-5}	242644	585986			
3000	9.71×10^{-5}	230460	584461			
3200	4.19×10^{-4}	206945	581925			
3400	1.51×10^{-3}	183578	579798			
3600	4.72×10^{-3}	160318	578133			
3800	1.30×10^{-2}	137140	576975			
4000	3.24×10^{-2}	114012	576364			
4200	7.41×10^{-2}	90895	576329			
4400	0.157	67769	576888			
4600	0.312	44602	578054			
4800	0.585	21377	579825			
4983	1.000	0	581975			
5000	1.048	-1935	582200			

^a1 atm = 101325 Pa^b ΔG° refers to $\Delta_{\text{sub}}^{\text{G}^\circ}$ when $T < T_{\text{fus}}$ and $\Delta_{\text{vap}}^{\text{G}^\circ}$ when $T > T_{\text{fus}}$
(and similarly for ΔH°).