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Measurement of the Heat Capacity of Molybdenum (Standard Reference Material) in the Range 1500–2800 K

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Measurement of the heat capacity of molybdenum (Standard Reference Material 781 of the National Bureau of Standards) in the temperature range 1500–2800 K by a subsecond-duration, pulse-heating technique is described. The results of the measurements on three specimens are in agreement within 0.6%. The heat capacity of molybdenum in the temperature range 1500–2800 K based on the present results is expressed by the following function (standard deviation = 0.5%):

$$C_p = -3.0429 + 4.7215 \times 10^{-2}T - 2.3139 \times 10^{-5}T^2 + 4.7090 \times 10^{-9}T^3$$

where T is in K and C_p is in $J \cdot mol^{-1} \cdot K^{-1}$. The inaccuracy of the reported results is estimated to be not more than 3%.

KEY WORDS: heat capacity; high temperature; molybdenum; rapid heating; reference material.

1. INTRODUCTION

Molybdenum is a standard reference material[2] for enthalpy and heat capacity in the temperature range 273–2800 K [1]. The measurements leading to the certified values have been performed using the following three different calorimeters at the National Bureau of Standards: (1) Bunsen ice calorimeter (273–1173 K), (2) adiabatic receiving calorimeter (1173–2100 K), and (3) pulse calorimeter (1500–2800 K). The objective of

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this paper is to report the details of the heat capacity measurements with the pulse calorimeter in the temperature range 1500–2800 K.[3]

2. METHOD

The method is based on rapid resistive self-heating of the specimen from room temperature to high temperatures (above 1500 K) in less than one second by the passage of an electrical current pulse through it; and on measuring, with millisecond resolution, current through the specimen, potential drop across the specimen, and the specimen temperature. The current through the specimen is determined from the measurement of the potential difference across a standard resistance placed in series with the specimen. The potential difference across the middle one-third of the specimen is measured between spring-loaded, knife-edge probes. The specimen temperature is measured at the rate of 1200 times per second with a high-speed photoelectric pyrometer [2]. The small hole in the wall at the middle of the tubular specimen provides an approximation to blackbody conditions for optical temperature measurements. The data are recorded with a digital data acquisition system every 0.4 ms with a full-scale signal resolution of about one part in 8000. Details regarding the construction and operation of the measurement system, the methods of measuring experimental quantities, and other pertinent information, are given in earlier publications [3, 4].

3. MEASUREMENTS

The measurements were performed on three tubular specimens which were fabricated from adjacent portions of the same molybdenum rod. Spark source mass spectrometry measurements on the rod have indicated a purity of at least 99.95 mass percent. The details regarding the nature and amount of impurities and other relevant specimen characterizations are documented by the Office of Standard Reference Materials at the National Bureau of Standards. The tubular specimens were fabricated from the rods by removing the center portion by an electroerosion technique. The nominal dimensions of the specimens were: length, 76 mm; outside diameter, 6.3 mm; and wall thickness, 0.5 mm. The outer surface of the specimens was polished to reduce heat loss due to thermal radiation when heated to high temperatures.

[3] Portions of this paper have been published earlier [1]. The results reported here for the range 1500–2800 K in no way supersede the certified values given earlier [1] for SRM 781 for the range 273–2800 K.

Table I. Summary of Experiments Performed on Three Molybdenum Specimens[a]

Range code	Temp. range (K)	Specimen 1			Specimen 2		Specimen 3
		S 1f[b]	S 1s[b]		S 2		S 3
I	1500–1650	1	6		15		27
II	1650–1800	2	7		16		28
III	1800–2000	3	8		17		29
IV	2000–2250	4	9		18	20–26	30
V	2250–2650	5	10	11, 12	19		31
VI	2300–2800			13, 14			

[a]The arabic numbers indicate the sequence of experiments in chronological order.
[b]Letters f and s designate "first heating" and "second heating," respectively.

Before the start of the experiments, the specimens were heat treated by subjecting them to 20 heating pulses up to 2500 K. The sequence (in chronological order) of the experiments (a total of 31) performed on the three specimens is summarized in Table I. The temperature interval (1500–2800 K) was divided into six ranges in order to optimize the operation of the pyrometer. All the experiments (with the exception of experiment 12) in the range 1500–2650 K were conducted with the specimen in a vacuum environment at approximately 1.3×10^{-3} $N \cdot m^{-2}$ ($\sim 10^{-5}$ torr). Because of the relatively high vapor pressure of molybdenum at high temperatures, the experiments in which the specimen was heated to temperatures above 2650 K were conducted with the specimen in an argon environment at about atmospheric pressure.

One of the experiments (experiment 12) in the temperature range V was performed with the specimen in an argon environment. A comparison of the results of experiments 11 and 12, one with the specimen in vacuum and the other in argon, respectively, does not show any significant difference in the measured property. Optical measurements performed on the chamber window before and after the pulse experiments did not show any change in its transmission. Also, weight measurements before and after the entire set of pulse experiments on a given specimen did not show any change in specimen weight.

To study the possible effects that may be attributable to the rate at which the specimen heats, seven experiments (experiments 20–26) in the temperature range IV were conducted on specimen 2 using different heating rates (1000–8000 $K \cdot s^{-1}$). The results are discussed in the section on "Estimate of Errors." These experiments were performed to demonstrate the effect of the heating rate on the measurements and were not used in the final computations of molybdenum heat capacity. To optimize the operation of the measurement system, the heating rate of the specimen was varied depending on the desired temperature range by adjusting the value of the resistance in series with the specimen.

Duration of current pulses in the experiments (excluding experiments 20–26) ranged from 400 to 560 ms; and the heating rate ranged from 5100 to 6800 $K \cdot s^{-1}$. Radiative heat loss from the specimen amounted to approximately 1% at 1500 K, 2% at 2000 K, 5% at 2500 K, and 8% at 2800 K. The magnitude of the current pulses ranged from 1800 to 2500 A. Before and after the pulse experiments, specimen resistance at room temperature was measured with a Kelvin bridge.

4. EXPERIMENTAL RESULTS

The details of the procedure for calculating heat capacity from experimental data have been described in an earlier publication [3]. Heat capacity was determined from the measurements of current, voltage, and temperature during the heating period. A correction for heat loss due to thermal radiation was made based on data obtained during the initial radiative cooling period. The data during the cooling period yielded values for the hemispherical total emittance (Fig. 1), which were fitted by a linear function in temperature using the least squares method. The function

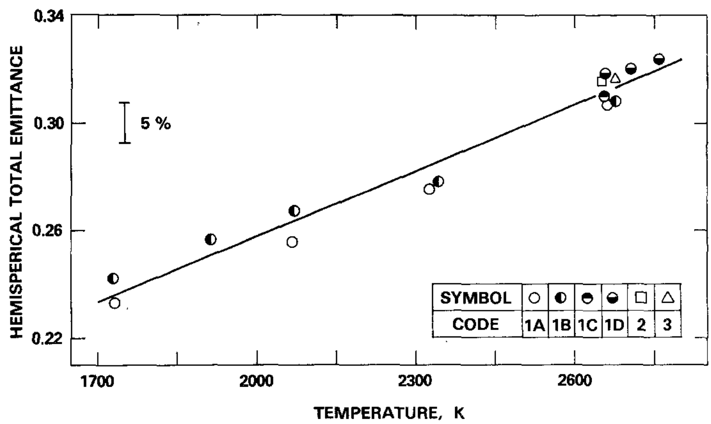

Fig. 1. Hemispherical total emittance of molybdenum. The designation of the code numbers and letters is as follows:

1A	Specimen 1, experiments 1, 3–5
1B	Specimen 1, experiments 6–10
1C	Specimen 1, experiment 11
1D	Specimen 1, experiments 12–14
2	Specimen 2, experiment 19
3	Specimen 3, experiment 31

Table II. Heat Capacity Difference, ΔC_p, for Various Specimens and Sets of Experiments[a]

j	i: S 3	S 2	S 1s
S 1f	0.48	− 0.07	0.18
	0.48	0.16	0.21
S 1s	0.31	− 0.24	
	0.35	0.24	
S 2	0.55		
	0.55		

[a] $\Delta C_p = 100(C_{p_i} - C_{p_j})/C_{p_j}$. Upper numbers represent algebraic difference in percent; lower numbers represent absolute difference in percent; symbol designations are those used in Table I.

(standard deviation = 2%) that represents the hemispherical total emittance results for molybdenum in the temperature range 1700–2700 K is

$$\epsilon = 9.40 \times 10^{-2} + 8.21 \times 10^{-5} T \quad (1)$$

where T is in K.

In order to compare the heat capacity results of different specimens, and also of different heatings for the same specimen, data in the range 1500–2650 K were fitted separately for each specimen and for each heating by third degree polynomial functions in temperature using the least squares method. The standard deviation of an individual point from the functions was in the range 0.3–0.5%. The differences in the heat capacity results are summarized in Table II. It may be seen that the differences are in the range 0.1–0.6%. Since these differences are comparable to the imprecision of the measurements, it may be concluded that no significant differences exist between the results obtained on different specimens and different heatings of the same specimen. The final results were obtained by fitting a third degree polynomial function in temperature to all the data. The function (standard deviation = 0.5%) that represents the heat capacity results for molybdenum in the temperature range 1500–2800 K is

$$C_p = -3.0429 + 4.7215 \times 10^{-2} T - 2.3139 \times 10^{-5} T^2 + 4.7090 \times 10^{-9} T^3 \quad (2)$$

where T is in K, and C_p is in $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$. The heat capacity of molybdenum computed using Eq. (2) is given in Table III. In the computations of heat capacity, the atomic weight of molybdenum was taken as 95.94 [5]. All the results reported in this paper are based on the International Practical Temperature Scale of 1968 [6]. Figure 2 shows the deviation

Table III. Heat Capacity of Molybdenum According to Eq. (2)

T (K)	C_p ($J \cdot mol^{-1} \cdot K^{-1}$)
1500	31.61
1600	32.55
1700	33.49
1800	34.44
1900	35.43
2000	36.50
2100	37.68
2200	38.98
2300	40.44
2400	42.09
2500	43.95
2600	46.06
2700	48.44
2800	51.12

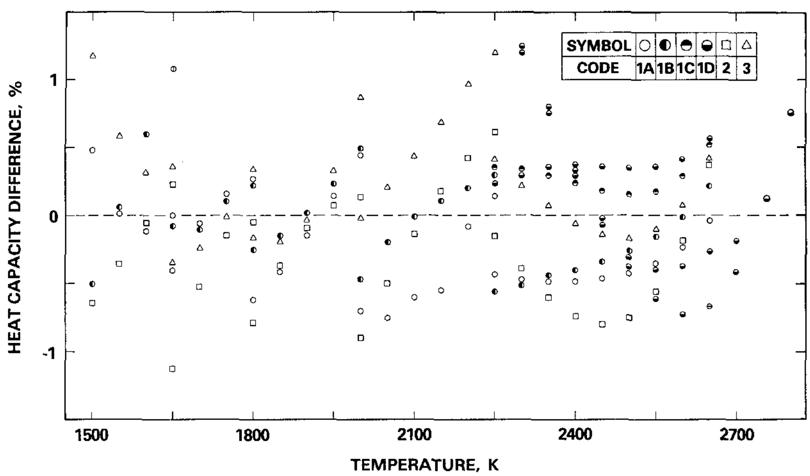

Fig. 2. Deviation of the measured heat capacity values for molybdenum from Eq. (2). The designation of the code numbers and letters is as follows:

1A	Specimen 1, experiments 1–5
1B	Specimen 1, experiments 6–10
1C	Specimen 1, experiment 11
1D	Specimen 1, experiments 12–14
2	Specimen 2, experiments 15–19
3	Specimen 3, experiments 27–31

of the measured heat capacity values for the different specimens and heatings from the values calculated using Eq. (2). The results on heat capacity obtained from individual experiments are given in Tables AI and AII of the Appendix.

5. ESTIMATE OF ERRORS

The details for estimating the errors in measured and computed quantities in high-speed experiments with the present measurement system are given in an earlier publication [3]. In the present work, the specific items in the error analysis were recomputed whenever the present conditions differed from those in the earlier publication. It may be seen from the results summarized in Table IV that the imprecision[4] of the heat capacity measurements is 0.5% and that the inaccuracy[5] in the results is estimated to be not more than 3%.

The effect of the specimen heating rate on the heat capacity measurements was investigated by performing seven experiments (experiments 20–26) on specimen 2 using different heating rates ranging from about 1000 to 8000 $K \cdot s^{-1}$. The results at 2000 K obtained from these experiments (Fig. 3) show that the measurements corresponding to heating rates lower than about 4000 $K \cdot s^{-1}$ were dependent on heating rate, while those higher than about 4000 $K \cdot s^{-1}$ were relatively insensitive to the changes in heating rate. The maximum difference in the heat capacity results, corresponding to the range 4000–8000 $K \cdot s^{-1}$, was less than 0.2%. Since the experiments

[4] Imprecision refers to the standard deviation of an individual point as computed from the difference between the measured value and that from the smooth function obtained by the least squares method.

[5] Inaccuracy refers to the estimated total error (random and systematic). Sometimes it is also referred to as "uncertainty."

Table IV. Summary of the Error Analysis

Quantity	Imprecision[a]	Inaccuracy[a]
Temperature (at 2000 K)	0.3 K	5 K
Current	0.03%	0.1%
Voltage	0.04%	0.1%
Hemispherical total emittance	2 %	5 %
Heat capacity	0.5 %	3 %

[a] Definition of the terms is given in the text.

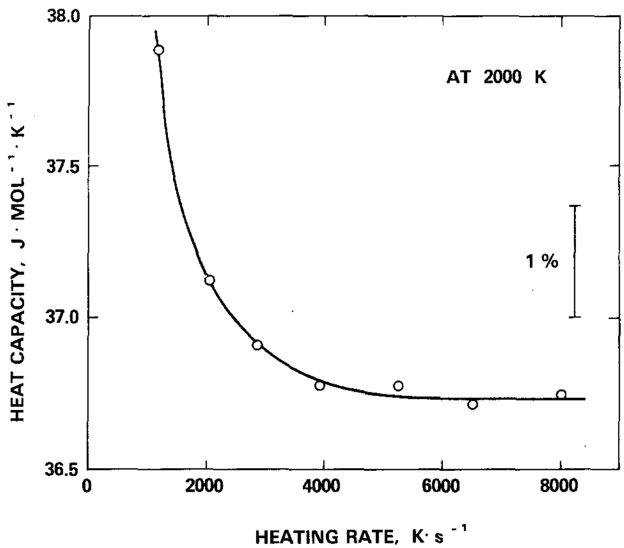

Fig. 3. Dependence of measured heat capacity (at 2000 K) of molybdenum on specimen heating rate.

(outside of the above seven) conducted in the present work correspond to heating rates in the range 5500–6700 K · s^{-1} (at 2000 K), the reported final results are not dependent on the specimen heating rate.

When a specimen heats at a low rate, temperature gradients are established in the axial direction due to heat conduction from the specimen to the clamps. The error in heat capacity due to temperature gradients in the specimen is manifested in two ways:

1. By lowering the effective temperature of the specimen with respect to its midpoint value, a low value for the effective heat capacity results.
2. By lowering the effective temperature in the specimen with respect to its midpoint value, a low value for the average specimen temperature results. Since in measurements by pulse heating techniques, heat capacity is inversely proportional to dT/dt (rate of change of temperature with time), lowering of the effective temperature yields a high value for heat capacity.

It may be seen that the cases in items (1) and (2) above have opposite effects. However, because of its more sensitive nature (derivative), the case in item (2) dominates over that in item (1). Thus, the effect of low specimen heating rates is high values for measured heat capacity, as seen in Fig. 3.

6. DISCUSSION

Heat capacity results obtained in the present work for the three molybdenum specimens under different experimental conditions were reproducible and internally consistent. The close agreement (within 0.1%) of electrical resistance measurements at room temperature before and after the entire set of pulse experiments on a given specimen indicates that no

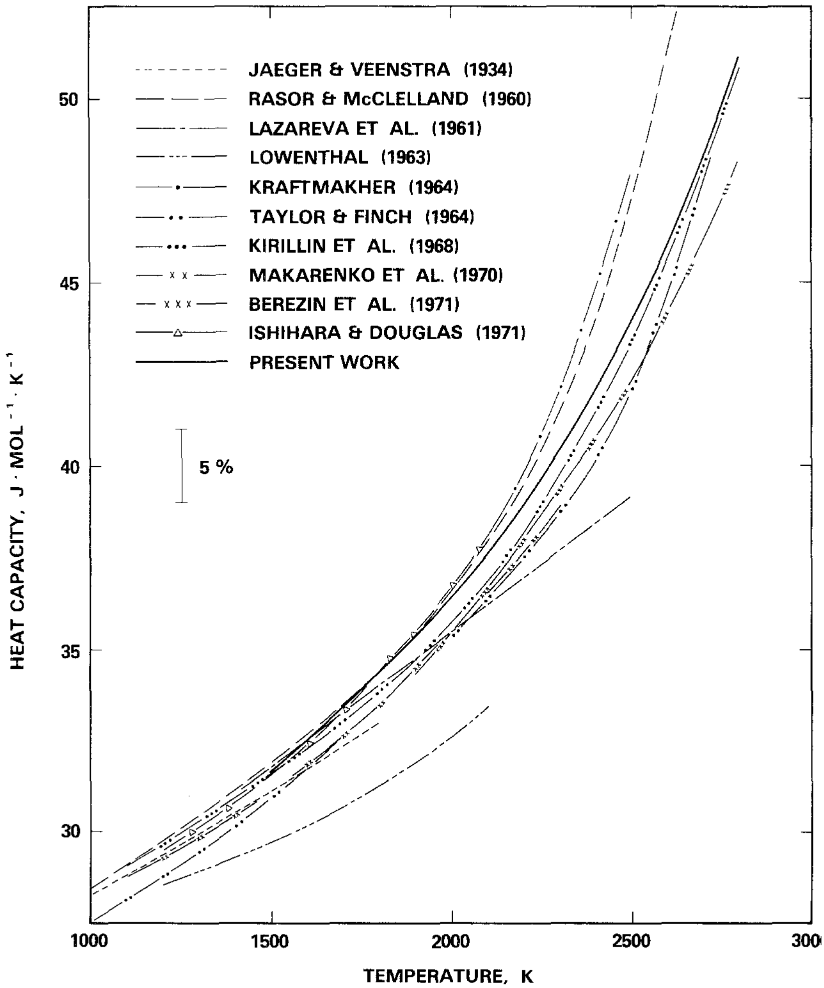

Fig. 4. Heat capacity of molybdenum reported in the literature.

Table V. Heat Capacity Difference: Literature Values Minus Present Work Values, in Percent

				Temperature (K)						
Investigators	Ref.	Year	Method	1600	1800	2000	2200	2400	2600	2800
Jaeger and Veenstra	7	1934	Drop	−2.5	−4.2					
Rasor and McClelland	8	1960	Pulse	0.4	0	0.4	1.4	4.8	11.1	
Lazareva et al.	9	1961	Drop	0	−1.2	−2.8	−5.2	−8.7		
Lowenthal	10	1963	Modul.	−7.4	−9.2	−10.7				
Kraftmakher	11	1964	Modul.	0	−0.8	−1.1	1.8	6.6		
Taylor and Finch	12	1964	Pulse	−2.5	−2.9	−3.2	−3.7	−4.6	−3.0	−0.4
Kirillin et al.[a]	13	1968	Drop	−0.7	−1.7	−2.2	−2.0	−1.5	−0.9	−0.3
Makarenko et al.	14	1970	Modul.	−2.1	−2.7	−2.8	−3.4	−5.6		
Berezin et al.	15	1971	Drop[b]			−2.2	−2.5	−3.1	−4.1	−5.6
Ishihara and Douglas	16	1971	Drop	−0.2	−0.1	0.7				

[a] The results of this paper are also published in the paper by Chekhovskoi and Petrov [18].
[b] Specimen was held at high temperatures by electromagnetic levitation.

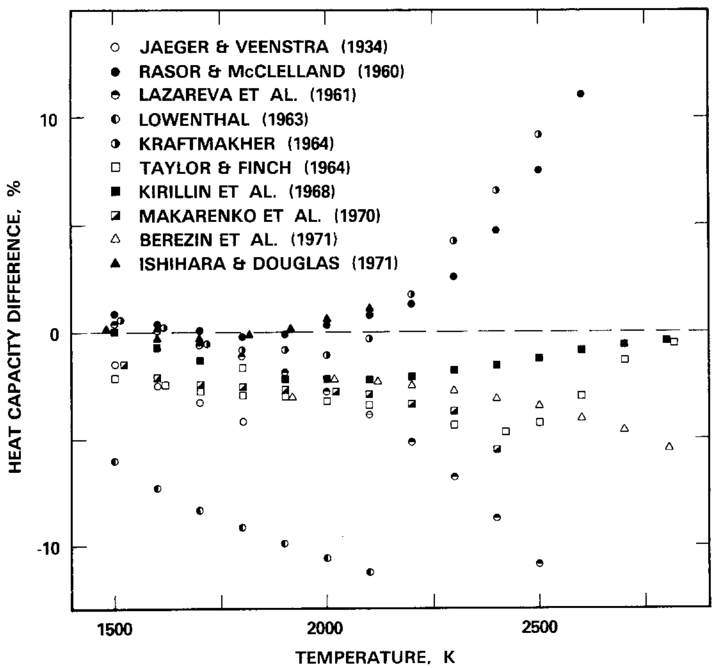

Fig. 5. Difference of heat capacity results reported in the literature with those of the present work. The "zero" line represents the present work results according to Eq. (2).

significant irreversible structural or chemical changes had taken place in the specimens as the result of their heating to high temperatures.

The experimental results on heat capacity of molybdenum at high temperatures reported in the literature are presented in Fig. 4. Only the most recent results originated from the same laboratory are considered. Thus, the earlier results of Kirillin et al. [17] and Cezairliyan et al. [3] are replaced by the more recent results of Kirillin et al. [13] and of the present work, respectively. For internal consistency, all the literature results were converted to correspond to the International Practical Temperature Scale of 1968. It may be seen that up to about 2000 K the heat capacity results (with the exception of those by Lowenthal [10]) fall within a 5% bandwidth. However, at temperatures above 2000 K the results diverge considerably, yielding differences as much as 20% at 2500 K.

A comparison of the literature results with those of the present work is given in Table V and graphically in Fig. 5. The literature results represent data obtained using different techniques which may be classified under the following categories: "drop," "modulation," and "pulse." There is no evidence of any significant bias in the results with respect to a particular measurement technique. Estimates of errors in papers cited lead to an estimate of inaccuracy in previously reported heat capacity of approximately 4–7% in the temperature range considered. The agreement is within the combined estimated errors in most cases.

Comparison of the present work results with those of Kirillin et al. [13] and Ishihara and Douglas [16], which are likely to be the most reliable results reported in the literature, shows an agreement, on the average, of about 1.3% with those of Kirillin et al. and about 0.4% with those of Ishihara and Douglas. The results of the measurements of the electrical resistivity of the specimens used in the present work were reported in an earlier publication [19].

APPENDIX

Table AI. Experimental Results on Heat Capacity of Molybdenum (Specimens 1, 2, and 3) in the Temperature Range 1500–2650 K[a]

Temp.	Specimen 1				Specimen 2[d]		Specimen 3[e]	
	First heating[b]		Second heating[c]					
(K)	C_p	ΔC_p	C_p	ΔC_p	C_p	ΔC_p	C_p	ΔC_p
1500	31.764	+ 0.48	31.452	− 0.50	31.409	− 0.64	31.992	+ 1.19
1550	32.091	+ 0.02	32.095	+ 0.03	31.972	− 0.35	32.275	+ 0.59
1600	32.517	− 0.11	32.752	+ 0.60	32.538	− 0.05	32.658	+ 0.32
1650	33.021	0.00	33.381	+ 1.08	33.097	+ 0.23	33.140	+ 0.36
1650	32.889	− 0.40	32.997	− 0.07	32.644	− 1.15	32.902	− 0.36
1700	33.467	− 0.06	33.457	− 0.09	33.313	− 0.52	33.406	− 0.24
1750	34.013	+ 0.16	33.962	+ 0.01	33.908	− 0.15	33.957	− 0.01
1800	34.532	+ 0.27	34.514	+ 0.22	34.421	− 0.05	34.553	+ 0.34
1800	34.223	− 0.63	34.350	− 0.25	34.166	− 0.79	34.381	− 0.16
1850	34.784	− 0.41	34.877	− 0.15	34.793	− 0.39	34.863	− 0.19
1900	35.381	− 0.15	35.438	+ 0.01	35.400	− 0.10	35.425	− 0.03
1950	36.008	+ 0.14	36.038	+ 0.22	35.987	+ 0.08	36.076	+ 0.33
2000	36.664	+ 0.44	36.682	+ 0.48	36.554	+ 0.14	36.829	+ 0.88
2000	36.250	− 0.70	36.331	− 0.47	36.175	− 0.91	36.501	− 0.01
2050	36.800	− 0.75	37.004	− 0.19	26.892	− 0.50	37.152	+ 0.21
2100	37.450	− 0.60	37.673	− 0.01	37.625	− 0.14	37.842	+ 0.44
2150	38.099	− 0.55	38.353	+ 0.11	38.376	+ 0.17	38.576	+ 0.69
2200	38.947	− 0.08	39.059	+ 0.20	39.145	+ 0.42	39.361	+ 0.97
2250	39.746	+ 0.15	39.808	+ 0.30	39.934	+ 0.62	40.205	+ 1.28
2250	39.515	− 0.44	39.467	− 0.56	39.631	− 0.15	39.844	+ 0.39
2300	40.254	− 0.47	40.237	− 0.51	40.281	− 0.40	40.531	+ 0.22
2350	41.043	− 0.48	41.054	− 0.46	40.994	− 0.60	41.269	+ 0.07
2400	41.889	− 0.48	41.922	− 0.40	41.781	− 0.74	42.066	− 0.06
2450	42.795	− 0.47	42.847	− 0.34	42.653	− 0.80	42.932	− 0.14
2500	43.769	− 0.42	43.839	− 0.26	43.626	− 0.75	43.882	− 0.17
2550	44.819	− 0.35	44.905	− 0.16	44.722	− 0.57	44.931	− 0.10
2600	45.958	− 0.23	46.059	− 0.01	45.965	− 0.21	46.100	+ 0.08
2650	47.198	− 0.04	47.315	+ 0.21	47.392	+ 0.37	47.416	+ 0.42

[a] Heat capacity (C_p) is in $J \cdot mol^{-1} \cdot K^{-1}$. The quantity ΔC_p is the percentage deviation of the individual results from the smooth function represented by Eq. (2) in the text.
[b] Corresponds to experiments 1–5.
[c] Corresponds to experiments 6–10.
[d] Corresponds to experiments 15–19.
[e] Corresponds to experiments 27–31.

Table AII. Experimental Results on Heat Capacity of Molybdenum (Specimen 1) in the Temperature Range 2250–2800 K[a]

Temp.	Experiment 11		Experiment 12		Experiment 13		Experiment 14	
(K)	C_p	ΔC_p	C_p	ΔC_p	C_p	ΔC_p	C_p	ΔC_p
2250	39.830	+ 0.35	39.786	+ 0.24				
2300	40.579	+ 0.34	40.573	+ 0.32	40.957	+ 1.26	40.962	+ 1.27
2350	41.363	+ 0.30	41.391	+ 0.36	41.563	+ 0.77	41.569	+ 0.79
2400	42.191	+ 0.24	42.246	+ 0.37	42.235	+ 0.34	42.235	+ 0.34
2450	43.074	+ 0.19	43.149	+ 0.36	42.983	− 0.02	42.970	− 0.05
2500	44.024	+ 0.16	44.109	+ 0.35	43.823	− 0.30	43.787	− 0.38
2550	45.059	+ 0.18	45.139	+ 0.36	44.771	− 0.46	44.701	− 0.62
2600	46.198	+ 0.29	46.255	+ 0.42	45.850	− 0.46	45.730	− 0.73
2650	47.467	+ 0.53	47.476	+ 0.55	47.092	− 0.27	46.900	− 0.68
2700					48.536	+ 0.19	48.243	− 0.41
2750							49.805	+ 0.12
2800							51.530	+ 0.79

[a] Heat capacity (C_p) is in $J \cdot mol^{-1} \cdot K^{-1}$. The quantity ΔC_p is the percentage deviation of the individual results from the smooth function represented by Eq. (2) in the text.

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