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U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

Standard Reference Materials:

ENTHALPY AND HEAT CAPACITY STANDARD REFERENCE MATERIAL: MOLYBDENUM SRM 781, FROM 273 TO 2800 K

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Standard Reference Materials:
ENTHALPY AND HEAT CAPACITY STANDARD REFERENCE MATERIAL: MOLYBDENUM SRM 781, FROM 273 TO 2800 K

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ENTHALPY AND HEAT CAPACITY STANDARD REFERENCE MATERIAL: MOLYBDENUM SRM 781, FROM 273 TO 2800 K

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Abstract

The relative enthalpy of NBS Standard Reference Material No. 781 (99.95 mass-percent pure, polycrystalline molybdenum: a metallic, high-temperature enthalpy and heat-capacity standard) has been measured with two differently designed, receiving-type calorimeters in the temperature ranges 273 to 1173 K and 1173 to 2100 K, respectively. The smoothed enthalpy data derived from these measurements are believed to have an inaccuracy not exceeding 0.6 percent at any temperature in these ranges. The heat capacity of Standard Reference Material No. 781 has also been measured in the temperature range 1500 to 2800 K using a millisecond-resolution pulse technique with resistive self-heating. This technique measured, in addition, hemispherical total emittance. In this highest temperature range, the smoothed heat-capacity data are believed to be in error by no more than 3 percent. A complete description of all the NBS experimental techniques and a detailed analysis of all suspected sources of errors are presented. Equations representing the smoothed NBS enthalpy and heat-capacity data for SRM-781 molybdenum in the range 273.15 to 2800 K are presented along with a table of these data calculated from the equations at selected temperatures. A bibliography of all known publications on the enthalpy and heat capacity of molybdenum has been compiled. The NBS-measured enthalpy and heat-capacity data for molybdenum have been compared with those of all the principal investigators and compilers reported in the literature.

Key Words: Drop calorimetry; emittance; enthalpy; heat capacity; high-speed measurements; high temperature; molybdenum; pulse calorimetry; standard reference material; thermodynamic functions.

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[a] Deceased.

1. Introduction

Calorimetric standard reference materials are employed to verify the continued, correct functioning of individual calorimeters and to provide a meaningful basis for intercomparing calorimeters of similar or different design. The principal criteria for choosing these standard reference materials ("SRM's") are that they be readily available in forms of high purity and stability, that the thermal property for which each was chosen be accurately known, and that they themselves contribute no extraneous heat effects which would significantly affect the inaccuracy or imprecision of measuring the thermal properties.

The National Bureau of Standards has played a leading role in developing and promoting such SRM's for applications in combustion calorimetry, solution calorimetry and differential thermal analysis [1][a]. Since 1970, the National Bureau of Standards has also offered pure synthetic sapphire (α-Al_2O_3) as an SRM for enthalpy and heat-capacity measurements over the temperature range 273 to 2250 K. This certification of α-Al_2O_3 was based upon relative-enthalpy measurements on this material carried out at NBS [2,16].

Due to significant advances in high-temperature materials and measuring technology in recent years, a need has arisen for enthalpy and heat-capacity SRM's usable at temperatures above 2250 K. In addition, many of the newer high-temperature techniques for measuring thermophysical properties are restricted to materials which are more amenable to physical shaping than α-Al_2O_3 and which exhibit metallic electrical conductivity. Molybdenum was chosen from among the candidate refractory materials for a high-temperature enthalpy and heat-capacity SRM since it possesses all the required qualities described above. Its high melting point (2894 K) [3] affords a considerable extension of the temperature range above that covered by α-Al_2O_3. Also of importance is the fact that there exists a considerable published body of thermophysical data for molybdenum (see section 7). The extensive documentation of its physical, chemical, and thermal properties in the literature lends confidence in the choice of it as an SRM.

The National Bureau of Standards Office of Standard Reference Materials ("OSRM") has obtained a quantity of annealed, polycrystalline molybdenum rod in diameters 3.18 and 6.35 mm. Specimens chosen at random from this material were used in relative-enthalpy measurements on molybdenum over the temperature ranges 273.15 to 1173 K and 1173 to 2100 K. Two different designs of receiving-type calorimeter were used in these measurements. Up to 1173 K, a Bunsen ice calorimeter was used and above this temperature (there being negligible overlap of these two temperature ranges), an adiabatic receiving-type calorimeter was used. In addition, the heat capacity of another specimen chosen from the same OSRM lot was measured over the temperature range 1500 to 2800 K. The

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[a] Figures in brackets refer to literature references in section 9 of this paper.

data up to 2800 K were obtained by using a millisecond-resolution pulse-calorimetric technique employing resistive self-heating of the specimen. This technique simultaneously measured the heat capacity and the hemispherical total emittance. In the following sections, all details of the thermal measurements with the three calorimeters are described. All the NBS enthalpy and heat-capacity data are critically examined to evaluate causes affecting their imprecision and overall inaccuracy. The NBS relative-enthalpy and heat-capacity results are compared with all significant original data on these properties reported in the literature for molybdenum.

2. Samples

The molybdenum for the enthalpy and heat-capacity measurements was chosen from the stock of 3.18-mm and 6.35-mm-diameter rods made available by the NBS Office of Standard Reference Materials as SRM-781. These had been obtained from the General Electric Company where they were made by sintering high-purity powder, swaging, grinding to final diameter and annealing at 1725 K in a high vacuum. Two specimens of 3.18-mm-diameter rod, denoted as specimens "A" and "C", were used in the measurements; also, two specimens of 6.35-mm-diameter rod, called specimens "B" and "D". In addition, a few enthalpy measurements above 1173 K were made on a specimen (designated "E"), machined from a rod of 3-pass electron-beam zone-refined polycrystalline molybdenum obtained from the Materials Research Corporation (MRC) of Orangeburg, NY. Specimen "E" was classified by MRC as being of "MARZ grade"[a] and having a purity of 99.992 mass percent.

2.1 Sample Characterization

2.1.a Qualitative Spectrochemical Analyses

Portions of three specimens - A and B (OSRM sample) and E (MRC sample) - were analyzed separately. The results are given in table 1. In the case of specimen E, special care was taken to remove all surface contamination, to consume the sample completely in the arc excitation and to use a high-purity reference sample of molybdenum. This analytical technique does not account for the important non-metals, but indicated a total metallic impurity level less than 0.02 percent for specimens A and B and a lesser metallic impurity level for specimen E, consistent with the supplier's claimed purity.

2.1.b Spark-Source Mass Spectrometry

A specimen from the OSRM lot from which specimens A and B were taken was first etched in nitric acid, then washed with distilled water and boiled in distilled water to clean the surface. This specimen was then presparked to identify and remove any remaining surface contamination.

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[a] Use of company or trade-names does not imply recommendation by the National Bureau of Standards.

Table 1

Qualitative spectrochemical analyses of the molybdenum samples, in mass percent

Element[a]	OSRM Sample (SRM-781)		MRC Sample
	Specimen A (3.18mm diam. rod)	Specimen B (6.35mm diam. rod)	Specimen E (triple-zone-refined)
	%	%	%
Al	0.001 - 0.01	0.001 - 0.01	?
Ca	< 0.001	< 0.001	< 0.0001
Cu	< 0.001	< 0.001	< 0.0001
Fe	0.001 - 0.01	0.001 - 0.01	< 0.0001
Mg	< 0.001	< 0.001	< 0.0001
Mo	> 10	> 10	> 10
Si	< 0.001	< 0.001	< 0.001

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[a] The following elements were also analyzed for, but not detected: Ag, As, Au, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Ga, Ge, Hf, Hg, In, Ir, La, Mn, Na, Nb, Ni, Os, P, Pb, Pd, Pt, Rh, Ru, Sb, Sc, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, and Zr. The estimated limit of detection of any alkali metal is 0.005 percent.

Table 2

Mass - spectrometric analysis of a representative specimen from the SRM-781 molybdenum lot

Elements Measured[b]				Elements Showing Interference[b]			
Element	Impurity level[a]	Element	Impurity level[a]	Element	Impurity level[a]	Element	Impurity level[a]
Ag	1	Sb	0.5	Ar	<20	N	<10
Al	7	Si	40	Au	<10	Nb	<3
As	2	V	0.4	B	<0.1	Ni	<20
Ca	9	W	56	Ba	<1	O	<30
Cr	12	Zn	0.26	C	<3	Os	<6
Cu	15			Cd	<8	Pd	<6
Fe	40			Cl	<0.1	Pt	<4
Ga	0.1			Co	<7	Re	<1
K	20			Cs	<0.2	Rh	<0.2
Mn	2			In	<0.5	S	<1
Mo	(matrix)			Ir	<3	Sc	<0.3
P	0.6			Li	<0.3	Sn	<30
Rb	0.3			Mg	<31	Ta	<25

[a] Parts per million (ppm) by mass.

[b] H and He were not analyzed for and interference was complete for F, Ne, Na, and Ti. In addition to the elements listed, the following were reported as "not detected" and were estimated to be present - if at all - in amounts not exceeding 1 ppm (some estimated at substantially lower levels; e.g., Be <0.01 ppm.): Ac, Be, Bi, Br, Ce, Dy, Er, Eu, Ge, Gd, Hf, Hg, Ho, I, Kr, La, Lu, Nd, Pa, Pb, Pm, Po, Pr, Pu, Ra, Ru, Se, Sm, Sr, Tb, Tc, Te, Th, Tl, Tm, U, Xe, Y, Yb, and Zr. "Interference" refers to the obscuring of lines for a given element by Mo matrix lines and lines from other impurities.

The mass-spectrometric results are given in table 2. Note the near-completeness of the coverage of the elements, and particularly, the low levels of low-atomic-weight elements. The apparent enthalpy and heat capacity of molybdenum would be particularly affected by the presence of these elements; see section 6.1. This analytical technique indicated a total impurity of 0.02 percent by mass of the elements detected, and set a total upper limit of 0.02 percent by mass for the elements (except F, Ne, Na, and Ti) partially masked by major interference.

2.1.c Electronic Characterization (RRR ratio)

Measurement of the residual resistivity ratio (RRR: the ratio of the electrical resistivity of a metallic specimen at the ice point to its resistivity at the normal boiling point of helium) has been applied for estimating the concentration of metallic impurities and defects in a metallic specimen [4,5]. The RRR's of sixteen specimens of 6.35-mm-diameter molybdenum rod chosen from the OSRM lot were measured using an eddy-current decay method [83, 84, 85]. In this method, prior cleaning and annealing of the specimens was important. The specimens were chosen randomly from the 6.35-mm-diameter rods (no 3.18-mm-diameter rods were included) but bore no known relation to specimens B and D discussed above. They were cleaned with ethyl alcohol, then heavily electroetched to remove surface contamination. A pure molybdenum electrode in an electrolyte of sulfuric acid and methyl alcohol was used. Annealing for one hour at 1273 K in a high vacuum, followed by slow cooling, did not yield stable RRR's. The adopted conditions, a minimum of two annealing treatments of two hours duration each at 1473 K followed by slow cooling, did result in RRR values stable within the resolution of the RRR measurements, however. The results of these measurements are presented in table 3. Note that specimen Nos. 2, 4, 9, 11, 13, and 14 seem to form a fairly homogeneous group with a mean RRR of 70.4 and a standard deviation of a single observation of 0.7. Also, specimen Nos. 5, 6, 7, 10, 12, 15, 16, and 17 form a somewhat-less homogeneous group with a mean of 58.1 and a standard deviation of a single observation of 1.6. Two specimens, Nos. 3 and 8, have RRR's of higher value. There is no known reason for this segregation.

Since the observed RRR values did not agree well with prior observed RRR values for other metals with similar impurity levels typified by tables 1 and 2, a hypothetical calculation of the possible overall impurity level was carried out. In this calculation (see table A1), the maximum total metallic impurity level has been derived under the following assumptions: 1) Ca, Mg, and Si are assumed to be absent or at least to make no substantial contribution to the residual resistivity, 2) Despite the evidence of the qualitative spectrochemical analysis (table 1), various other transition-metal contaminants are present, namely Ni, Al, and Co at levels equal to those observed for Fe; and Nb, Ta, W, and Zr are present at some common, unspecified atomic concentration, 3) Nb, Ta, W, and Zr have equal specific effects on the residual resistivity at 4 K equal to 0.3 μΩ·*cm* per atomic percent of impurity [7]. See table A1.

Table 3

Residual resistivity ratios for OSRM SRM 781 6.35-mm O.D. molybdenum rods

Specimen No.[d]	RRR = $\frac{\rho_{273\ K}}{\rho_{4\ K}}$	Group I[a]	Group II[a]
2[b]	70.6	70.6	
3	80.9	——	——
4	69.4	69.4	
5	57.5		57.5
6	58.3		58.3
7	60.7		60.7
8	77.8	——	——
9	69.9	69.9	
10	57.4		57.4
11	71.1	71.1	
12	55.8		55.8
13	70.1	70.1	
14	71.2	71.2	
15	59.4		59.4
16	56.7		56.7
17	59.2		59.2
Mean	66.6	70.4	58.1
s[c]	8.4	0.7	1.6

[a] For an explanation of this grouping, see text, section 2.1.c.

[b] Specimen 1 was used as the electrode material in etching the other specimens.

[c] Computed standard deviation of a single observation.

[d] These specimen numbers are valid only within the context of the residual-resistivity-ratio measurements and bear no relation to specimen designations accompanying the heat-measurement data.

The atomic fraction of each of the elements Nb, Ta, W, and Zr calculated under these assumptions is 0.0307 atom percent (see table A1). Expressing these fractions as mass percentages and adding the levels of Fe, Ni, Co and Al, yields an estimated overall metallic impurity level of 0.216 mass percent. Thus, under these assumptions, the OSRM SRM-781 molybdenum samples may be considered at least 99.78-mass percent pure. Note that this calculation is based on the RRR of only specimen No. 12. Specimen No. 3 (RRR = 80.9) under the same assumptions, will have impurity levels about two thirds of those listed in table A1. This would correspond to a purity of 99.85 mass percent. The levels of impurity implied by the RRR characterization far exceed those found by the spectrochemical and mass-spectrometric analyses detailed in tables 1 and 2. The cause of the disagreement is not known. Because it was felt to be much more reliable, the mass-spectroscopically-measured purity has been accepted as the purity of SRM-781.

2.2 Sample Preparation and Assignment

The molybdenum specimens A, B, C, D, and E mentioned above were subjected to preliminary cleaning and additional annealing prior to the enthalpy and heat-capacity measurements. The following sections describe these preparatory procedures and the assignment of the specimens to the three measuring ranges and calorimeters used in this investigation.

2.2.a Adiabatic-Receiving-Calorimeter Range (1173 to 2100 K)

Relative enthalpy measurements on each of the specimens A, B, and E were made in an adiabatic receiving calorimeter in the temperature range 1173 to 2100 K. Specimen A, which consisted of four sections of OSRM SRM-781 molybdenum rod, 3.18 mm in diameter and 25.4 mm in length, was first etched with HNO_3, then with HCl and subsequently cleaned in boiling distilled water. After this treatment, the surface apparently discolored when in contact with room air, but without detectable weight gain; Specimen A was excluded from extended contact with room air thereafter. It was then annealed for two hours at 1473 K and 1.3 kPa pressure of argon. Specimen B, a single section of OSRM SRM-781 molybdenum rod, 6.35 mm in diameter and 25.4 mm in length was cleaned in the same manner but was not specially annealed. Note, however, that the first enthalpy measurement on it was made only after it had been held at about 1700 K for about 40 minutes and this circumstance may have affected its annealing. At least, a repetition of this heating did not change its enthalpy significantly (see table 6). Specimen E, the high-purity MRC molybdenum, was cleaned with solvents and boiling distilled water but was neither etched nor annealed prior to the heat measurements on it. After heat measurements in the temperature range 1173 to 2100 K were completed, specimen A was combined with specimen C, described below, and the combination treated as one composite specimen in all subsequent heat measurements.

2.2.b Bunsen-Ice-Calorimeter Range
(273 to 1173 K)

Relative enthalpy measurements in this temperature range were carried out on a composite specimen consisting of specimens A and C together. Specimen C comprised four sections of the 3.18-mm-diameter OSRM SRM-781 molybdenum rod, each 50.8 mm long. These were chemically etched and cleaned in the same fashion as specimen A, and subjected to the same annealing treatment described for specimen A, above.

2.2.c High-Speed, Pulse-Calorimeter Range
(1500 to 2800 K)

Heat-capacity measurements over the temperature range 1500 to 2800 K were performed on three separate segments of specimen D. For this purpose, specimen D, a segment of 6.35-mm-diameter OSRM SRM-781 molybdenum rod, was divided into three equal segments of length 76 mm each. These segments are designated as specimens D1, D2, and D3. Each of these had a central cylindrical portion (including the entire segment axis) removed by an electro-erosion technique. This resulted in three tubes of wall thickness 0.5 mm. The outer surface of each of these three tubular specimens was then highly polished to reduce heat loss due to thermal radiation during the high-temperature experiments. Before the start of these experiments, the three specimens were heat-treated by subjecting each of them to 20 heating pulses during each of which a maximum temperature of about 2500 K was attained.

3. Calorimetric Apparatus and Procedure

The enthalpy and heat-capacity measurements of the present investigation were carried out over three temperature ranges in three calorimeters of different design and operating principle. The sections which follow describe these apparatuses briefly under headings appropriate to each apparatus and provide further literature references to more detailed descriptions. Also covered are special operational features of value in evaluating the molybdenum data of this study and further details on the physical preparation and handling of the specimens during the measurements. See section 2.1 for details concerning the elemental characterization of the various molybdenum specimens.

3.1 Bunsen Ice Calorimeter
(Temperature Range: 273.15 to 1173 K)

3.1.a Apparatus

The enthalpy, relative to the enthalpy at 273.15 K, of molybdenum specimens A and C, combined, was measured over the temperature range 273.15 to 1173 K with a Bunsen ice calorimeter. This is a highly precise type of phase-change, receiving calorimeter in which an amount of energy to be measured causes the melting of ice in a spatially confined ice-water system. The amount of ice melted (or some quantity proportional to this) is then taken as the measure of this energy. This method and the apparatus employed at NBS have been described previously in considerable detail [2, 8, 9, 10].

Briefly, a sample whose relative enthalpy is to be measured is first suspended in the isothermal zone of a controlled-temperature furnace until it reaches a steady temperature. It is then dropped in almost free fall into a re-entrant well of the calorimeter. The heat transferred to the calorimeter as the sample cools to the calorimeter temperature (very nearly 273.15 K) melts a portion of the calorimeter ice. The resulting change in volume of the calorimeter's confined ice-water system is measured with a sensitive mercury dilatometer. Calibration [9, 10, 11] of the calorimeter (i.e., measuring the proportionality between the energy transferred to the calorimeter and the ensuing volume change of the ice-water system referred to above) is carried out with accurately measured quantities of electrical energy converted to heat in a specially-designed electrical heater which fits within the calorimeter well. In this measurement technique, samples are usually encapsulated in order to guarantee their integrity and to prevent their reaction with the furnace atmosphere. Separate enthalpy measurements on an empty container are made over the same furnace temperature range as obtained in the measurements on the container-plus-sample in order that the reproducible but unknown heat lost during the fall may be accounted for. It is not necessary to know this heat loss during the fall explicitly if one can assume that it is the same for a full as for an empty container. It then cancels when the empty-container measured heat is subtracted from that for the container-plus-sample.

3.1.b Procedure

Specimens A and C, comprising a total mass of 20.8297 grams of molybdenum (approximately 0.2 moles), were hermetically sealed in a 0.3 mm-wall, (90 Pt-10 Rh) container together with helium at several hectopascals[a] pressure at room temperature. Since it was not practical to measure separately the relative enthalpy of the container actually used to hold the molybdenum, the required empty-container enthalpies (see section 3.1.a) were derived from existing enthalpy measurements (table A2)

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[a] 1.3 h*Pa* = 1 mm Hg.

made on two entirely comparable containers of very nearly the same mass during a prior enthalpy study (α-Al_2O_3, SRM 720 [2].) A total of fourteen enthalpy measurements at ten temperatures uniformly covering the temperature range of the ice calorimetric measurements were made on the encapsulated specimens. The emtpy-container measurements consisted of a total of twenty measurements on two empty containers in the same temperature range. Container masses were routinely checked before and after each measurement to preclude the possiblity of unsuspected leaks or losses of container material.

The furnace temperature was measured up to 773 K by a platinum resistance thermometer, and above 773 K by two homogeneous Pt/(90 Pt-10 Rh) thermocouples. The thermometer and both thermocouples were calibrated by the Temperature Section of NBS on the scale IPTS-48 but all readings were corrected [12] to the basis of IPTS-68 [13]. Both thermocouples were compared up to 773 K with the thermometer in place in the calorimeter furnace, and a slight adjustment in their calibrations (0.1 K at and above 773 K) was made to avoid a temperature discontinuity at 773 K.

3.2 Adiabatic Receiving Calorimeter
(Temperature Range: 1173 to 2100 K)

3.2.a Apparatus

The enthalpy, relative to the enthalpy at 298.15 K, of molybdenum specimens A, B, and E (taken separately) was measured in the temperature range 1173 to 2100 K with an adiabatic receiving calorimeter. This apparatus, depicted and partially described in one prior publication [14], has been used in several other high-temperature enthalpy studies, notably of tungsten (to 2600 K) [15], aluminum oxide (SRM-720) [16], and beryllium aluminate ($BeO \cdot Al_2O_3$) [17]. Since considerable operating experience has been gained with this calorimeter and some modifications to it have been made since the prior description [14], somewhat more detail will be given here for this apparatus than for either of the two other calorimeters used in the present study.

The apparatus (see figure 1 of reference [14]) consists of an adiabatic calorimeter positioned above a controlled-temperature, induction-heated furnace and optically separated from it by a shutter. An encapsulated specimen of the substance under investigation is suspended by a tungsten wire in the furnace until it reaches a steady temperature. This temperature is measured with an automatic optical pyrometer. The shutter is momentarily opened and the capsule is then rapidly lifted a distance of 0.8 m into the adiabatic calorimeter. The shutter is manually opened and closed on the same timed sequence during all experiments. The energy transferred to the calorimeter from the specimen and container while within the calorimeter causes the temperature of the central measuring portion of this calorimeter to rise to a new steady level while a surrounding shield is simultaneously heated to maintain the temperature differences between this central portion and the shield at a minimum (adiabatic principle). The measured specimen energy is calculated as the product of the observed temperature rise of the calorimeter and its total heat capacity (a small correction is made for calorimeter heat leak). Calibration of the calorimeter (i.e., measurement of its total heat capacity under adiabatic conditions) is carried out in separate experiments using accurately measured quantities of energy converted to heat in an electric heater situated within the calorimeter. Separate measurements on the heat content of the empty specimen containers are made at each specimen-measuring temperature. Subtraction of the empty-container heat-content values from the corresponding heat-content data for the specimen-plus-container yields the heat content of the specimen alone. This assumes that the heat loss to the surroundings during the lift into the receiving portion of the calorimeter is a function of container temperature and surface emissivity only and that all lifts take place in time intervals of equal length. The container is exposed to a room-temperature zone outside of the calorimeter for about 0.1 second during its transfer from the furnace to the calorimeter.

The central measuring portion of the adiabatic calorimeter consists of two concentric cylinders, the inner one of nickel and the outer one of copper. These are thermally coupled to each other through a common circumferential ring of 8 mm thickness and located between the cylinders at mid-height. This feature delays the temperature response of the outer (copper) surface of this central measuring portion by several minutes and reduces the temperature control problems, at moderate or high rates of heating, associated with the surrounding adiabatic shield. A guard jacket surrounds the adiabatic shield and is controlled at a temperature slightly below that of the shield. The calorimeter heat leak is thus kept small and almost constant throughout its temperature range.

The rise in the calorimeter temperature during an experiment is measured with a copper resistance thermometer wound around and cemented onto the copper cylinder. This has been compared with a platinum resistance thermometer calibrated by the Temperature Section of the NBS.

Control of the shield and guard is achieved using the information provided by copper resistance thermometers wound on and cemented to these bodies. The adiabatic calorimeter has a total heat capacity of about 2900 joules per kelvin and operates in the range 298 to 338 K. The electrical energy supplied to the calorimeter during calibration is calculated from the observed voltage, current, and active time interval of a heater element situated within the calorimeter. This energy is also corrected for the observed calorimeter heat leak. The calorimeter has been electrically calibrated eight times to date and the standard deviation of the accumulated calibration data points from a smooth representation is estimated to be ± 0.004 percent.

The induction-heated furnace consists of a central hollow graphite core (to couple with the induction coil) with surrounding concentric layers of carbon black (25 nanometer particle size) and fine silicon carbide powder, the entirety contained within a heavy-wall quartz tube. The carbon black and silicon carbide are used for thermal insulation inside the quartz tube since they do not appreciably couple with the working coil below 2300 K. After thoroughly degassing the furnace parts by heating to 2800 K under high vacuum, the calorimeter and furnace are operated in a 1 cm^3s^{-1} flow of argon at 13.3 kilopascals pressure. Around the quartz tube is a water-cooled copper working coil shaped as a solenoid with closer turn spacing near the ends to decrease the temperature gradient near the furnace core, where the capsule hangs.

One-half centimeter below the lower limit of the normal capsule position at the center of the furnace is a diaphragm with a 3.18 mm hole. An automatic optical pyrometer is focused up through this hole onto the bottom of the capsule for temperature measurement and control of the furnace. The pyrometer has been periodically calibrated by the Optical Radiation Section of the NBS. The uncertainty of this instrument is now estimated (95-percent confidence limits) to be ±0.9 K at 1200 K, ±0.8 K at 1350 K, ±0.8 K at 1500 K, ±1.3 K at 1675 K, and ±3.0 K at 2475 K. Since the furnace temperature measurement is the most critical measurement, extra effort and frequent checks have been exercised to see that the conditions of the environment during the use of the pyrometer simulate those during its calibration and that the system optics are clean.

An exploratory graphite probe the size of the specimen container was used to measure the temperature gradient along the furnace axis. This test showed that the temperature along this axis is uniform to ±2.5 K for 20 centimeters upwards from the lower limit of the normal container position at 2300 K after two hours furnace warm-up time.

The capsule lifting device, a small servo motor, is driven by an operational amplifier signal, so chosen as to provide an upwards acceleration of constant magnitude for the first half of the lift of the hot capsule from the furnace to the calorimeter. The tension in the lifting wire is constant during the first half of the lift and is essentially zero during the second half of the lift. The total time of the lift is monitored by an interval timer gated by the amplifier signal. It does not vary by more than ±2 ms out of 600 ms.

3.2.b Procedure

The relative enthalpy measurements on specimens A, B, and E in the adiabatic receiving calorimeter were completed prior to the measurements in the Bunsen ice calorimeter described above. The specimen masses were: A, 8.20415 grams; B, 8.18014 grams; E, 13.95978 grams. During these experiments, each specimen was contained within a molybdenum capsule with a closely fitting (but not hermetically sealed) lid in the argon atmosphere of the furnace and calorimeter. Both the capsule and the lid were machined from a molybdenum rod claimed to be of 99.95-percent purity. Specimen and capsule masses were measured before and after each enthalpy measurement. The mass of specimen A did not vary by more than 0.06 milligrams below 2000 K. At 2000 K, a total mass increase of 0.30 milligrams (0.004 percent) was observed for this specimen and at 2100 K, the total specimen mass had increased by 0.40 milligrams (0.005 percent) above its initial value. The assumption was made that this mass increase was due to carbon from the furnace atmosphere. It was considered too small to warrant a correction. Specimens B and E, which were not subjected to these high temperatures, showed no mass increase.

Twelve furnace temperatures nearly uniformly covering the range from 1170 to 2100 K were chosen. A table of random numbers selected by a computer was used to arrange these furnace temperatures in a chronological sequence. This method of determining the temperature sequence of the experiments was followed so as to avoid the possible introduction of a bias into the measurements arising from gradual changes in the condition of the furnace insulation or in the automatic optical pyrometer. A total of twenty-seven relative-enthalpy measurements were made, most of them (twenty) on specimen A; four measurements were made on specimen B and three on specimen E.

Since the final calorimeter temperature is in general not equal to the reference temperature (298.15 K), a small correction is necessary in order to refer the measured enthalpies to this reference temperature. The maximum value of this correction occurred in an experiment at 2100 K and amounted to 2 percent of the net measured heat at this furnace temperature. In this instance, the final temperature of the adiabatic calorimeter was 315.65 K. These corrections were applied using the molybdenum heat-capacity evaluations of references [18] and [19] and are believed to be in error by no more than 5 percent, thus contributing an error to the corrected specimen enthalpy not exceeding 0.1 percent.

3.3 High-Speed Pulse Calorimeter
(Temperature Range: 1500 to 2800 K)

3.3.a Apparatus

The heat capacity and hemispherical total emittance of molybdenum specimen D were measured in the temperature range 1500 to 2800 K using a millisecond-resolution pulse technique which employed resistive self-heating of the specimen. The apparatus used in this technique and the method of calculating the heat capacity from the observed quantities have already been described in considerable detail [20,21]. Briefly, the tubular specimen is heated in a vacuum or inert-gas atmosphere from room temperature to high temperatures (above 1500 K) in less than one second by passing an electric current pulse through it. Simultaneously, measurements are made (with millisecond resolution) of the potential difference across a standard resistor placed in series with the specimen, the axial potential drop along the specimen and the specimen temperature. The specimen current is determined from the measured potential difference across the calibrated standard resistor. The axial potential drop across the middle one third of the specimen is measured between spring-loaded, knife-edge probes. A rectangular (0.5 x 1.0 mm) hole in the wall at the middle of the tubular specimen provides an approximation to blackbody conditions for optical temperature measurement. The specimen temperature is measured at the rate of 1200 times per second with a high-speed photoelectric pyrometer [22] focused on this hole along a diametral axis normal to the tube axis. The digital data acquisition system used to record all the measurements is capable of recording a set of signals corresponding to temperature, potential drop and current approximately every 0.4 millisecond with a full-scale signal resolution of about one part in 8000.

3.3.b Procedure

The heat-capacity measurements were performed on three tubular specimens which had been fabricated from adjacent segments of specimen D. These were designated specimens D1, D2 and D3. Specimen geometries and other details are given in section 2.2.c.

In order to optimize the operation of the pyrometer, the entire temperature interval in which these heat-capacity measurements were carried out (1500 to 2800 K) was divided into six smaller intervals (or "ranges") as follows:

Range I:	1500 to 1650 K	Range IV:	2000 to 2250 K
Range II:	1650 to 1800 K	Range V:	2250 to 2650 K
Range III:	1800 to 2000 K	Range VI:	2300 to 2800 K

In each of these smaller intervals a different absorbing filter was used in the high-speed, photoelectric pyrometer. At least four pulse experiments were performed in each temperature interval, save interval VI in which only two were performed. A single pulse experiment normally provides sufficient data to permit calculation of the heat capacity and hemispherical total emittance throughout the entire interval. All specimens were measured at least once in each temperature interval except that only specimen D1 was measured in the sixth interval.

The chronological sequence of the 31 experiments which were performed on specimens D1, D2 and D3 is summarized in table 4 to show the total number of experiments performed on each specimen. All the experiments (except number 12) in the range 1500 to 2650 K were conducted with the specimen in a vacuum environment at approximately 1.3×10^{-5} hectopascals ($\sim 10^{-5}$ torr) total pressure. Because of the relatively high vapor pressure of molybdenum at high temperature, the experiments (numbers 13 and 14) in which the specimen was heated to temperatures above 2650 K (Range VI) were conducted with the specimen in an argon environment at about atmospheric pressure. Also, one of the experiments (number 12) in Range V was performed 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 difference in the measured property. Optical measurements performed on the sample chamber window before and after the pulse experiments did not show any change in its transmission. Also, mass measurements before and after the complete set of pulse experiments for each specimen failed to detect any change in specimen mass. The electrical resistance of each specimen was measured at room temperature both before and after the pulse experiments, using a Kelvin bridge. Current and potential-drop measurements on each specimen during the pulse experiments provided the data for determination of the electrical resistivity of SRM-781 molybdenum at 1500, 2000, and 2500 K.

To study the effects which may be attributable to the specimen heating rate, seven experiments (numbers 20 to 26) in the temperature Range IV were conducted on specimen D2 using different heating rates from 1200 to 8000 $K \cdot s^{-1}$. The results are discussed in section 6.4. These experiments were performed to demonstrate the effect of heating rate on the measurements and the data were not used in the final smoothing of the molybdenum heat-capacity data.

The duration of the current pulses in the experiments (excluding experiments 20 to 26) ranged from 400 to 560 ms and the heating rates ranged from 5100 to 6800 $K \cdot s^{-1}$. Radiative heat loss from the specimen amounted to approximately 1 percent of the total energy input at 1500 K, 2 percent at 2000 K, 5 percent at 2500 K, and 8 percent at 2800 K. The magnitude of the current pulses ranged from 1800 to 2500 A.

4. Enthalpy and Heat-Capacity Measurements

4.1 Bunsen Ice Calorimeter: $(H_T - H_{273.15\ K})$

In any accurate drop calorimetry, including the present work, the relative enthalpy of the empty sample container is measured separately. This permits accounting for both heat lost in subsequent enthalpy measurements on the container-plus-sample and for the heat content of the container itself. Since it was not practical in the present case to separately measure the relative enthalpy of the container actually used to hold the molybdenum, the required empty-container enthalpies were derived from enthalpy measurements on two entirely comparable empty containers used in a previous study [2]. These data are repeated for

Table 4

Chronological order[a] of experiments performed on SRM-781 molybdenum specimens D1, D2, and D3

Range Code	Temp. Range K	Specimen D1			Specimen D2		Specimen D3
		First Series	Second Series	Third Series	First Series	Second Series	
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)[c]	30
V	2250-2650	5	10	11,12[b]	19	—	31
VI	2300-2800	—	—	13[b],14[b]	—	—	—

[a] The numbers 1 to 31 indicate the sequence of experiments in the chronological order performed.

[b] These experiments only carried out in argon gas at atmospheric pressure. All other experiments carried out in vacuum ($1.3 \cdot 10^{-5}$hPa).

[c] Heating-rate tests. These experiments excluded in smoothing the heat-capacity data. See table 12.

convenience in table A2. In order to reduce the effect of random errors in these enthalpy data on the empty container, they were smoothed by fitting an equation to them by the method of least squares (equation (1) of reference [2]). This equation is:

$$H_T - H_{273.15} = (4.529744)(10^{-8})(T-273.15)^3 + (8.068654)(10^{-5})(T-273.15)^2 + (1.901653)(T-273.15) - (34.94647)(T-273.15)/T, \qquad (1)$$

in which H is given in J and temperature, T, in K (IPTS-68).

The individual measurements on the container-plus-sample are listed in column 2 of table 5 in the order in which they were measured. These represent the total mercury mass, $m_{\text{tot.}}$, forced into the calorimeter during an experiment. These data correspond to temperatures slightly different than those of column 1 (average difference = 0.4 K and no difference exceeded 1 K). Therefore, the corrections, $\delta m_{\text{tot.}}$, given in column 3 must be added to the data of column 2 in order that the gross observed heats (Q_{gross}, column 4) derived from column 2 correspond to the temperatures of column 1. These corrections were calculated using tabulated heat-capacity data on the container materials and the molybdenum sample [23,24], along with the real observed sample temperatures and a calorimeter calibration constant of 270.49 joules per gram of mercury [11]. The gross observed heats, Q_{gross}, of column 4 were derived by multiplying the mass of mercury (column 2 plus column 3) by this same calibration constant. The container heat values ($Q_{\text{cont.}}$, column 5) were calculated from equation (1) using the temperatures of column 1. The net measured sample heats ($H_T - H_{273.15}$, column 6) were calculated by subtracting column 5 from column 4 and converting to a molar basis (atomic weight = 95.94 [25]). Columns 7 and 8 give the deviations, $\delta(H_T - H_{273.15})$, of the net enthalpy data from smooth values (δ = net - smooth) calculated from equation (8). The predominance of negative values for the deviations arises from the fact that equation (8) was fit simultaneously to three sets of heat data, of which table 5 comprises but one set. See section 5 for details of smoothing the data.

4.2 Adiabatic Receiving Calorimeter: $(H_T - H_{298.15\ \text{K}})$

The results of the enthalpy measurements on molybdenum in the range 1170 to 2100 K are tabulated in table 6. The temperatures of column 1 are the actual furnace temperatures to which the heat data of column 4 correspond. Column 2 gives the (random) chronological order in which the heat data were obtained on the specimens of column 3. This random order of the measurements was determined with the aid of a table of random numbers in order to eliminate bias in the measurements due to possible changes in the quality of the furnace insulation or a possible gradual change in the automatic optical pyrometer. Columns 4 and 5 give, respectively, the results of the heat measurements on the container-plus-sample (Q_{gross}) and the empty container ($Q_{\text{cont.}}$). A single day's experiments usually consisted of four heat measurements at a single temperature; two on the container-plus-sample and two on the empty container.

Table 5

Enthalpy data (referred to 273.15 K) on the SRM 781 molybdenum sample

$\frac{T^{a}}{\mathrm{K}}$	$\frac{m_{\mathrm{tot.}}}{\mathrm{mg}}$	$\frac{\delta m_{\mathrm{tot.}}}{\mathrm{mg}}^{b}$	$\frac{Q_{\mathrm{gross}}}{\mathrm{J}}^{c}$	$\frac{Q_{\mathrm{cont.}}}{\mathrm{J}}^{d}$	$\frac{H_T-H_{273.15}}{\mathrm{J\cdot mol^{-1}}}^{e}$	$\delta(H_T-H_{273.15})^{f}$	
						$\delta/\mathrm{J\cdot mol^{-1}}$	% of $(H_T-H_{273.15})_{\mathrm{sm.}}$
323.15	1281.00	+ 4.75	347.78	89.88	1187.9	- 8.0	-0.67
	1290.94	+ 1.52	349.60	89.88	1196.2	+ 0.3	+0.02
373.15	2589.95	+16.50	705.02	181.65	2410.6	-12.8	-0.53
	2599.90	+14.81	707.25	181.65	2420.9	- 2.5	-0.10
473.15	5346.62	- 9.37	1443.67	369.15	4949.2	- 1.3	-0.03
573.15	8143.89	-18.84	2197.75	560.69	7540.2	-10.0	-0.13
673.15	10980.89	- 8.27	2967.98	755.70	10189.6	-19.0	-0.19
773.15	13901.71	- 4.52	3759.05	954.06	12919.6	+ 2.4	+0.02
	13887.58	+ 2.29	3757.07	954.06	12910.4	- 6.7	-0.05
873.15	16843.89	+ 0.57	4556.26	1155.81	15662.2	- 9.6	-0.06
973.15	19869.33	-11.77	5371.27	1361.09	18470.6	- 1.2	-0.01
1073.15	22930.14	-17.37	6197.68	1570.10	21314.3	- 6.2	-0.03
1173.15	26070.25	-30.87	7043.39	1783.06	24228.7	+ 5.3	+0.02
	26053.34	-31.48	7038.65	1783.06	24206.8	-16.5	-0.07

[a] IPTS-68 [13].

[b] Based on enthalpy data of references [23] and [24].

[c] Calculated assuming real calorimeter calibration constant of 270.49 joules per gram of mercury [11].

[d] Smoothed values for container from equation (1).

[e] Atomic weight = 95.94 [25]; mass of sample = 20.8297 g.

[f] $\delta(H_T-H_{273.15}) = (H_T-H_{273.15})$, column 6, $-(H_T-H_{273.15})$, smoothed, equation (8).

Table 6

Enthalpy data (referred to 298.15 K) on the SRM-781 molybdenum sample

$\frac{T^{a}}{K}$	Sequence of measurement ("run No.")	Specimen	$\frac{Q_{gross}}{J}$	$\frac{Q_{cont.}}{J}$ ^{b}	$\frac{H_T-H_{298.15}}{J \cdot mol^{-1}}$ ^{c}	$\delta(H_T-H_{273.15})^{d,e}$	
						$\delta/J \cdot mol^{-1}$	% of $(H_T-H_{273.15})_{sm.}$
1170.4	13	A	4428.46	2407.31	23635	+85.8	+0.36
	14	B	5841.48	2409.74	23585	+35.8	+0.15
1198.6	19	A	4588.66	2498.04	24447	+68.9	+0.28
	20	A	4587.69	2498.39	24432	+52.9	+0.21
1299.1	17	A	5146.85	2800.39	27439	+65.7	+0.23
	18	A	5148.06	2800.27	27454	+80.7	+0.29
	26	B	5143.51	2801.32	27470	+96.7	+0.34
	27	A	5150.57	2802.52	27457	+83.7	+0.30
1399.6	5	A	5704.73	3094.72	30522	+84.0	+0.27
	6	A	5705.41	3095.91	30516	+78.0	+0.25
1499.0	11	A	6286.80	3411.95	33617	+73.2	+0.21
	12	A	6288.54	3412.27	33634	+90.2	+0.26
	25	B	6285.99	3421.58	33595	+48.2	+0.14
1601.6	3	A	6879.15	3727.95	36850	+15.7	+0.04
	4	A	6878.91	3729.27	36832	- 2.3	-0.01
1699.1	1	A	7462.60	4040.31	40021	-26.6	-0.06
	2	B	9868.17	4044.93	40021	-26.6	-0.06
1699.2	23	B	7503.71	4076.06	40201	+150.0	+0.37
	24	B	7505.01	4080.20	40168	+117.0	+0.29
1800.7	15	A	8137.48	4405.26	43643	+150.0	+0.34
	16	A	8139.31	4406.55	43650	+156.0	+0.35

Table 6 (continued)

Enthalpy data (referred to 298.15 K) on the SRM 781 molybdenum sample

$\frac{T^a}{\mathrm{K}}$	Sequence of measurement ("run No.")	Specimen	$\frac{Q_{\mathrm{gross}}}{J}$	$\frac{Q_{\mathrm{cont.}}}{J}$ [b]	$\frac{H_T-H_{298.15}}{\mathrm{J \cdot mol^{-1}}}$ [c]	$\delta(H_T-H_{273.15})$[d,e]	
						$\delta/\mathrm{J \cdot mol^{-1}}$	%of $(H_T-H_{273.15})_{\mathrm{sm.}}$
1899.6	9	A	8776.34	4756.18	47010	+60.6	+0.13
	10	E	11585.03	4756.18	46932	+38.6	+0.08
2001.2	7	A	9439.63	5105.33	50684	+70.2	+0.14
	8	A	9442.77	5105.33	50721	+107.2	+0.21
2102.4	21	A	10186.17	5528.69	54463	+75.7	+0.14
	22	A	10186.17	5528.50	54465	+77.7	+0.14

[a] IPTS-68 [13].

[b] See section 4.2 for procedure by which container heat data were corrected.

[c] Atomic weight = 95.94 [25]. Specimen masses as follows:

m_A = 8.20415 g (runs 1-6); 8.20445 g (runs 7-27). See section 4.2.

m_B = 8.18014 g

m_E = 13.95978 g

[d] Data of these two columns computed using $H_T-H_{298.15}$ data of column 6, augmented by 593.6 $\mathrm{J \cdot mol^{-1}}$. See section 4.2.

[e] $\delta(H_T-H_{273.15}) = (H_T-H_{298.15} + 593.6)$, column 6, $- (H_T-H_{273.15})$, smoothed, equation (8).

The last measurement of a day was always made on the same system as the first measurement of that day. Prior investigation had indicated that one probable cause of difference between these first and last measurements of a day was a gradual change in the temperature distribution along the furnace core (even though the apparent container temperature was unchanged). This difference, for the present measurements, averaged 0.05 percent and did not exceed 0.10 percent of the empty-container heat. In order to reduce the contribution of this suspected gradual change in temperature distribution to the overall measurement imprecision, the measured empty-container heats appear in column 5 corrected to their expected values at the actual time of the corresponding container-plus-sample heat measurements.

The net measured sample heat ($H_T - H_{298.15}$, column 6) was calculated by subtracting column 5 from column 4 and converting to a molar basis (atomic weight = 95.94 [25]). Specimen A had an initial mass of 8.20415 g. After the measurement at 2000 K (seventh in the series) its mass was observed to have increased by 0.3 mg to 8.20445 g and thereafter, to have stayed essentially constant. It was assumed that this apparent mass increase was due to pickup of carbon from the susceptor. It was calculated that the error incurred by neglecting the carbon nature of this addition would introduce an error into the molar enthalpy, $H_T - H_{298.15}$, no greater than 0.016%. This was considered negligible and was not corrected for. Specimens B and E, which were not subjected to the highest temperature, did not change in mass.

The derivation of the smoothed enthalpy values from the data of column 6 is described in section 5. Prior to smoothing and calculating the deviations, $\delta(H_T - H_{273.15}) = (H_T - H_{273.15})_{\text{meas.}} - (H_T - H_{273.15})_{\text{smooth}}$, appearing in columns 7 and 8, the data of column 6 were all augmented by an amount, $H_{298.15} - H_{273.15\ \text{K}} = 593.6\ \text{J·mol}^{-1}$ to convert them to the base temperature 273.15 K. This enthalpy increment was derived from a provisional smoothing of relative enthalpy data on the same sample taken in the range 273.15 to 1173.15 K (see section 4.1 and table 5). It agrees very well with the value 594 J·mol^{-1} derived by Reilly and Furukawa [18] from their analysis of the low-temperature heat-capacity data for molybdenum. The predominance of positive values for the deviations of columns 7 and 8 arises from the fact that equation (8) was derived from a simultaneous fit to three sets of data, of which table 6 comprises but one set.

4.3 High-Speed Pulse Calorimeter: C_p, 1500 to 2800 K

The experimental results on the heat capacity of SRM-781 molybdenum in the temperature range 1500 to 2800 K are given in tables 7 and 8, while the results on the hemispherical total emittance are given in table A3. In table 7, columns 2, 4, 6, and 8 give values of C_p while columns 3, 5, 7, and 9 give the deviation of these values from the corresponding smooth values of C_p calculated from equation (7); $\delta C_p = (C_p) - (C_p)_{\text{smooth}}$. Two series of heat-capacity measurements, designated "first" (F) and "second" (S), were carried out on specimen D1.

Note that all heating rates for the experiments of tables 7 and 8 exceeded 5000 $K \cdot s^{-1}$. Two series of measurements were also carried out on specimen D2. The second series, the data for which are tabulated separately as table 12, was performed to investigate the effect of heating rate on the heat-capacity data (see section 6.4). The data of table 12 were not included in any final smoothing of the heat-capacity data for SRM-781. Complete details of the procedure for calculating heat capacity and hemispherical total emittance from the measured current, potential drop, and temperature during the pulse-heating and radiative-cooling periods have been given in reference [21]. In the calculation of C_p, using equation (2) of reference [21], values of potential drop (e) and current (i) are first calculated from smooth functions at the temperature at which C_p is desired. These functions are polynomial smoothing functions of temperature which are fitted to the e and i data recorded at 0.4 ms intervals (see section 3.3.a). A correction is included in each heat-capacity datum for heat loss by thermal radiation. This correction was based on temperature data recorded during the cooling period. See section 3.3.b for details on the radiative heat losses. Cooling-period data were not adequate to permit evaluation of hemispherical total emittance for experiments 2, 15 through 18 and 20 through 30. The measurements on the three specimens yielded the following average values for the electrical resistivity of SRM-781 molybdenum (units, $\mu\Omega \cdot cm$): 5.45 at 293 K, 38.1 at 1500 K, 53.3 at 2000 K, and 69.0 at 2500 K.

5. Smoothing the NBS Data

As a first step in obtaining one unified representation of the enthalpy and heat-capacity data presented in Section 4., the relative-enthalpy data obtained with the Bunsen ice calorimeter (table 5, column 6) and with the adiabatic receiving calorimeter (table 6, column 6) were individually smoothed. To accomplish this, each of these sets of enthalpy data was fitted by the method of least squares with several different functions, having up to five disposable constants. The functions chosen to represent these enthalpy data were the ones yielding a minimum standard deviation of residues of those tried and are as follows:

$$H_T - H_{273.15} = -2333.9 + (25.79244)T + (1.73410 \times 10^{-3})T^2 - 862.870\ \ell nT \qquad (2)$$

The unit of H is $J \cdot mol^{-1}$; the range of applicability of equation (2) is 1173.15 K > T > 273.15 K.

Standard deviation of percent residues = 0.28%, and

$$H_T - H_{298.15} = -(6.18063 \times 10^3) + (21.6641)T + (3.24129 \times 10^{-3})T^2 + (1.590 \times 10^6)\exp(-16000/T) \qquad (3)$$

The unit of H is $J \cdot mol^{-1}$/ the range of applicability of equation (3) is 2100 K > T > 1170 K

Standard deviation of percent residues = 0.13%.

Table 7

Heat-capacity results on the SRM-781 molybdenum sample in the temperature range 1500 to 2650 K

$\frac{T^a}{K}$	Specimen D1						Specimen D2			Specimen D3		
	D1-F Series			D1-S Series			D2-F Series					
	$\frac{C_p^c}{J \cdot mol^{-1} \cdot K^{-1}}$		$\frac{\delta C_p/(C_p)_{sm.}{}^d}{\%}$	$\frac{C_p}{J \cdot mol^{-1} \cdot K^{-1}}$		$\frac{\delta C_p/(C_p)_{sm.}}{\%}$	$\frac{C_p}{J \cdot mol^{-1} \cdot K^{-1}}$		$\frac{\delta C_p/(C_p)_{sm.}}{\%}$	$\frac{C_p}{J \cdot mol^{-1} \cdot K^{-1}}$		$\frac{\delta C_p/(C_p)_{sm.}}{\%}$
1500	31.764	1[b]	+0.36	31.452	6	-0.62	31.409	15[e]	-0.76	31.992	27[f]	+1.08
1550	32.091		+0.08	32.095		+0.09	31.972		-0.29	32.275		+0.65
1600	32.517		+0.05	32.752		+0.78	32.538		+0.18	32.658		+0.49
1650	33.021		+0.21	33.381		+1.30	33.097		+0.44	33.140		+0.57
1650	32.889	2	-0.19	32.997	7	+0.14	32.644	16	-0.93	32.902	28	-0.15
1700	33.467		+0.14	33.457		+0.11	33.313		-0.32	33.406		-0.04
1750	34.013		+0.31	33.962		+0.16	33.908		-0.02	33.957		+0.14
1800	34.532		+0.34	34.514		+0.28	34.421		+0.01	34.553		+0.40
1800	34.223	3	-0.56	34.350	8	-0.19	34.166	17	-0.73	34.381	29	-0.10
1850	34.784		-0.46	34.877		-0.19	34.793		-0.43	34.863		-0.23
1900	35.381		-0.31	35.438		-0.15	35.400		-0.26	35.425		-0.18
1950	36.008		-0.14	36.038		-0.06	35.987		-0.20	36.076		+0.05
2000	36.664		+0.04	36.682		+0.12	36.554		-0.26	36.829		+0.49
2000	36.250	4	-1.09	36.331	9	-0.87	36.175	18	-1.29	36.501	30	-0.40
2050	36.800		-1.24	37.004		-0.69	36.892		-0.99	37.152		-0.29
2100	37.450		-1.18	37.673		-0.59	37.625		-0.72	37.842		-0.14
2150	38.099		-1.18	38.353		-0.52	38.376		-0.46	38.576		+0.06
2200	38.947		-0.74	39.059		-0.45	39.145		-0.23	39.361		+0.32
2250	39.746		-0.49	39.808		-0.34	39.934		-0.02	40.205		+0.66

Table 7 (continued)

Heat-capacity results on the SRM-781 molybdenum sample in the temperature range 1500 to 2650 K

T^a / K	Specimen D1						Specimen D2			Specimen D3		
	D1-F Series			D1-S Series			D2-F Series					
	C_p^{c} / $J \cdot mol^{-1} \cdot K^{-1}$		$\delta C_p/(C_p)_{sm.}^{d}$ / %	C_p / $J \cdot mol^{-1} \cdot K^{-1}$		$\delta C_p/(C_p)_{sm.}$ / %	C_p / $J \cdot mol^{-1} \cdot K^{-1}$		$\delta C_p/(C_p)_{sm.}$ / %	C_p / $J \cdot mol^{-1} \cdot K^{-1}$		$\delta C_p/(C_p)_{sm.}$ / %
2250	39.515	5	-1.07	39.467	10	-1.19	39.631	19	-0.78	39.844	31	-0.25
2300	40.254		-1.03	40.237		-1.08	40.281		-0.97	40.531		-0.35
2350	41.043		-0.94	41.054		-0.91	40.994		-1.06	41.269		-0.39
2400	41.889		-0.77	41.922		-0.69	41.781		-1.03	42.066		-0.35
2450	42.795		-0.54	42.847		-0.42	42.653		-0.87	42.932		-0.22
2500	43.769		-0.29	43.839		-0.13	43.626		-0.61	43.882		-0.03
2550	44.819		-0.04	44.905		+0.15	44.722		-0.26	44.931		+0.21
2600	45.958		+0.17	46.059		+0.39	45.965		+0.18	46.100		+0.48
2650	47.198		+0.31	47.315		+0.56	47.392		+0.72	47.416		+0.78

[a] IPTS-68 [13].

[b] Numbers outside brackets indicate chronological order of experiment.

[c] Atomic weight = 95.94 [25].

[d] $\delta C_p = C_p - (C_p)$, smooth, equation (7).

[e] See table 8 for experiments 11-14.

[f] See table 12 for experiments 20-26.

Table 8

Heat-capacity results on the SRM-781 molybdenum specimen D1 in the temperature range 2250 to 2800 K, series D1-T

T^{a}/K	Experiment 11[b]		Experiment 12		Experiment 13		Experiment 14	
	C_p^{c} / $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$\delta C_p/(C_p)_{sm.}$[d] / %	C_p / $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$\delta C_p/(C_p)_{sm.}$ / %	C_p / $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$\delta C_p/(C_p)_{sm.}$ / %	C_p / $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$\delta C_p/(C_p)_{sm.}$ / %
2250	39.830	-0.28	39.786	-0.39				
2300	40.579	-0.23	40.573	-0.25	40.957	+0.69	40.962	+0.71
2350	41.363	-0.16	41.391	-0.10	41.563	+0.32	41.569	+0.33
2400	42.191	-0.06	42.246	+0.07	42.235	+0.05	42.235	+0.05
2450	43.074	+0.10	43.149	+0.28	42.983	-0.11	42.970	-0.14
2500	44.024	+0.29	44.109	+0.49	43.823	-0.16	43.787	-0.24
2550	45.059	+0.50	45.139	+0.67	44.771	-0.15	44.701	-0.30
2600	46.198	+0.69	46.255	+0.82	45.850	-0.07	45.730	-0.33
2650	47.467	+0.88	47.476	+0.90	47.092	+0.09	46.900	-0.32
2700					48.536	+0.34	48.243	-0.27
2750							49.805	-0.13
2800							51.530	-0.08
	in vacuum		in argon					

[a] IPTS-68 [13].

[b] Experiment numbers belong to the same chronological sequence used in tables 4 and 7.

[c] Atomic weight = 95.94 [25].

[d] $\delta C_p = C_p - (C_p)$, smooth, equation (7).

The heat-capacity data obtained with the pulse calorimeter (tables 7 and 8) were fitted by the method of least squares with the third-degree polynomial function of temperature, given below:

$$C_p = -\ 3.0429 + (4.7215 \times 10^{-2})T - (2.3139 \times 10^{-5})T^2 + (4.7090 \times 10^{-9})T^3 \qquad (4)$$

The unit of C_p is $J \cdot mol^{-1} \cdot K^{-1}$; the range of applicability of equation (4) is 2800 K > T > 1500 K.

Standard deviation of percent residues = 0.5%.

Note that equation (4) was not used further in deriving the unified data representation. Equations (2) and (3) were differentiated to derive the corresponding best representations of heat capacity for the individual enthalpy data sets. Smooth heat capacities were then calculated from these derived heat-capacity functions at 50 K intervals from 250 to 2100 K. The heat-capacity data measured directly with the pulse calorimeter (tables 7 and 8) were next combined by arithmetically averaging them at each temperature in 50 K intervals from 1500 to 2800 K.

The smooth heat capacities derived from the enthalpy data and the average measured heat capacities of the pulse calorimeter measurements were then assigned weights based on a preliminary estimate of the overall inaccuracy of the heat-capacity values. Each smooth heat-capacity value derived from the ice-calorimeter data was assigned unit weight. The smooth heat-capacity values derived from the adiabatic-receiving-calorimeter data were all assigned the weight 0.500, and the averaged, measured heat-capacity data obtained from the pulse-calorimeter data were all assigned the weight 0.167. Note that the data of the adiabatic receiving calorimeter and that of the pulse calorimeter overlapped from 1500 to 2100 K. All these weighted heat-capacity data were then fitted, using the method of least squares, with a cubic spline function having four knots and of the form,

$$C_p = \sum_{\nu=0}^{3} a_\nu T^\nu + \sum_{\nu=1}^{4} b_\nu (T-\Theta_\nu)_+^3 \ , \qquad (5)$$

in which $(T-\Theta_\nu)_+ \equiv 0$ for $T \leq \Theta_\nu$. The knot temperatures, Θ_ν, were chosen near suspected inflection points in the heat-capacity function or near overlap temperatures of the different experimental techniques.

The coefficients of this cubic spline function for C_p $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ and the values of the knot temperatures are as follows:

$$
\begin{aligned}
a_0 &= +\,1.6078753 \times 10^{+1}\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}} \\
a_1 &= +\,4.2064833 \times 10^{-2}\ \mathrm{J \cdot mol^{-1} \cdot K^{-2}} \\
a_2 &= -\,6.4321802 \times 10^{-5}\ \mathrm{J \cdot mol^{-1} \cdot K^{-3}} \\
a_3 &= +\,3.8567377 \times 10^{-8}\ \mathrm{J \cdot mol^{-1} \cdot K^{-4}} \\
b_1 &= -\,3.2183846 \times 10^{-8}\ \mathrm{J \cdot mol^{-1} \cdot K^{-4}};\ \Theta_1 = 500\ \mathrm{K} \\
b_2 &= -\,6.2727966 \times 10^{-9}\ \mathrm{J \cdot mol^{-1} \cdot K^{-4}};\ \Theta_2 = 1000\ \mathrm{K} \\
b_3 &= +\,6.5829329 \times 10^{-10}\ \mathrm{J \cdot mol^{-1} \cdot K^{-4}};\ \Theta_3 = 1500\ \mathrm{K} \\
b_4 &= +\,3.2467912 \times 10^{-8}\ \mathrm{J \cdot mol^{-1} \cdot K^{-4}};\ \Theta_4 = 2400\ \mathrm{K}
\end{aligned}
\tag{6}
$$

The standard deviation of residues of the heat-capacity data for this spline function is 0.058 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, based on 62 degrees of freedom. An equivalent representation of the heat-capacity data can be obtained by expanding this spline function and collecting terms to yield functions of the form,

$$C_p = \sum_{\nu=0}^{3} c_\nu T^\nu \tag{7}$$

corresponding to each of the five temperature intervals defined by the four knots. The coefficients of the heat-capacity functions given by equation (7) for C_p $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ are presented in table 9. The enthalpy of SRM-781 molybdenum relative to its enthalpy at 273.15 K can be obtained by integration of the heat-capacity functions, equation (7). This integration yields enthalpy functions of the form,

$$H_T - H_{273.15} = K_\mu + \sum_{\nu=0}^{4} d_\nu T^\nu \tag{8}$$

in which K_μ is the enthalpy at the (knot) temperature starting the μ^{th} interval relative to the enthalpy at 273.15 K. The enthalpy at 273.15 K is assigned the value zero. The coefficients of the enthalpy functions given by equation (8) for H $\mathrm{J \cdot mol^{-1}}$ and the values of the constants K_μ are given in table 10. Values of enthalpy and heat capacity for SRM-781 molybdenum at a series of temperatures in the range 273.15 to 2800 K have been computed from equations (8) and (7) and are given in table A5. Figures 1, 2, and 3 show the deviations of the NBS-measured and smoothed enthalpy and heat-capacity data (tables 5, 6, 7 and 8 and equations (2), (3), and (4)) from the spline representations (equations (8) and (7)). In figure 1, there is a systematic difference of about 0.2 percent between the enthalpy curve representing equation (3) (above 1200 K) and the unified spline representation (baseline). This is a result of the spline-fitting process which simultaneously gave weight to

Table 9

Coefficients of the spline representation of heat capacity (equation (7)) of SRM-781 molybdenum for $C_p/\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$

Temperature[a] Interval	$\frac{c_0}{\mathrm{J \cdot mol^{-1} \cdot K^{-1}}}$	$\frac{c_1}{\mathrm{J \cdot mol^{-1} \cdot K^{-1}}}$	$\frac{c_2}{\mathrm{J \cdot mol^{-1} \cdot K^{-1}}}$	$\frac{c_3}{\mathrm{J \cdot mol^{-1} \cdot K^{-1}}}$
273.15-500 K	$+1.6078753 \times 10^{+1}$	$+4.2064833 \times 10^{-2}$	$-6.4321802 \times 10^{-5}$	$+3.8567377 \times 10^{-8}$
500-1000 K	$+2.0101733 \times 10^{+1}$	$+1.7926949 \times 10^{-2}$	$-1.6046033 \times 10^{-5}$	$+6.3835310 \times 10^{-9}$
1000-1500 K	$+2.6374530 \times 10^{+1}$	$-8.9144148 \times 10^{-4}$	$+2.7723563 \times 10^{-6}$	$+1.1073453 \times 10^{-10}$
1500-2400 K	$+2.4152790 \times 10^{+1}$	$+3.5520382 \times 10^{-3}$	$-1.8996343 \times 10^{-7}$	$+7.6902795 \times 10^{-10}$
2400-2800 K	$-4.2468363 \times 10^{+2}$	$+5.6459755 \times 10^{-1}$	$-2.3395893 \times 10^{-4}$	$+3.3236940 \times 10^{-8}$

[a] IPTS-68 [13].

Table 10

Coefficients and constants of the spline representation of relative enthalpy (equation (8)) of SRM-781 molybdenum for $H/\mathrm{J\cdot mol^{-1}}$

Temperature Interval[a]	μ[b]	K_{μ}[c] / $\mathrm{J\cdot mol^{-1}}$	d_0 / $\mathrm{J\cdot mol^{-1}}$	d_1 / $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	d_2 / $\mathrm{J\cdot mol^{-1}\cdot K^{-2}}$	d_3 / $\mathrm{J\cdot mol^{-1}\cdot K^{-3}}$	d_4 / $\mathrm{J\cdot mol^{-1}\cdot K^{-4}}$
273.15-500 K	0	0.00	$-5.5778746 \times 10^{+3}$	$+1.6078753 \times 10^{+1}$	$+2.1032417 \times 10^{-2}$	$-2.1440601 \times 10^{-5}$	$+9.6418443 \times 10^{-9}$
500-1000 K	1	5642.15	$-1.1722893 \times 10^{+4}$	$+2.0101733 \times 10^{+1}$	$+8.9634745 \times 10^{-3}$	$-5.3486777 \times 10^{-6}$	$+1.5958828 \times 10^{-9}$
1000-1500 K	2	19231.66	$-2.6880612 \times 10^{+4}$	$+2.6374530 \times 10^{+1}$	$-4.4572074 \times 10^{-4}$	$+9.2411877 \times 10^{-7}$	$+2.7683633 \times 10^{-11}$
1500-2400 K	3	34169.02	$-4.0984820 \times 10^{+4}$	$+2.4152790 \times 10^{+1}$	$+1.7760191 \times 10^{-3}$	$-6.3321143 \times 10^{-8}$	$+1.9225699 \times 10^{-10}$
2400-2800 K	4	66884.04	$+1.9560201 \times 10^{+5}$	$-4.2468363 \times 10^{+2}$	$+2.8229878 \times 10^{-1}$	$-7.7986310 \times 10^{-5}$	$+8.3092350 \times 10^{-9}$

[a] IPTS-68 [13].

[b] μ is an index denoting the temperature interval.

[c] K_{μ} is the enthalpy at the initial temperature of the μ^{th} interval relative to the enthalpy at 273.15 K, in units $\mathrm{J\cdot mol^{-1}}$.

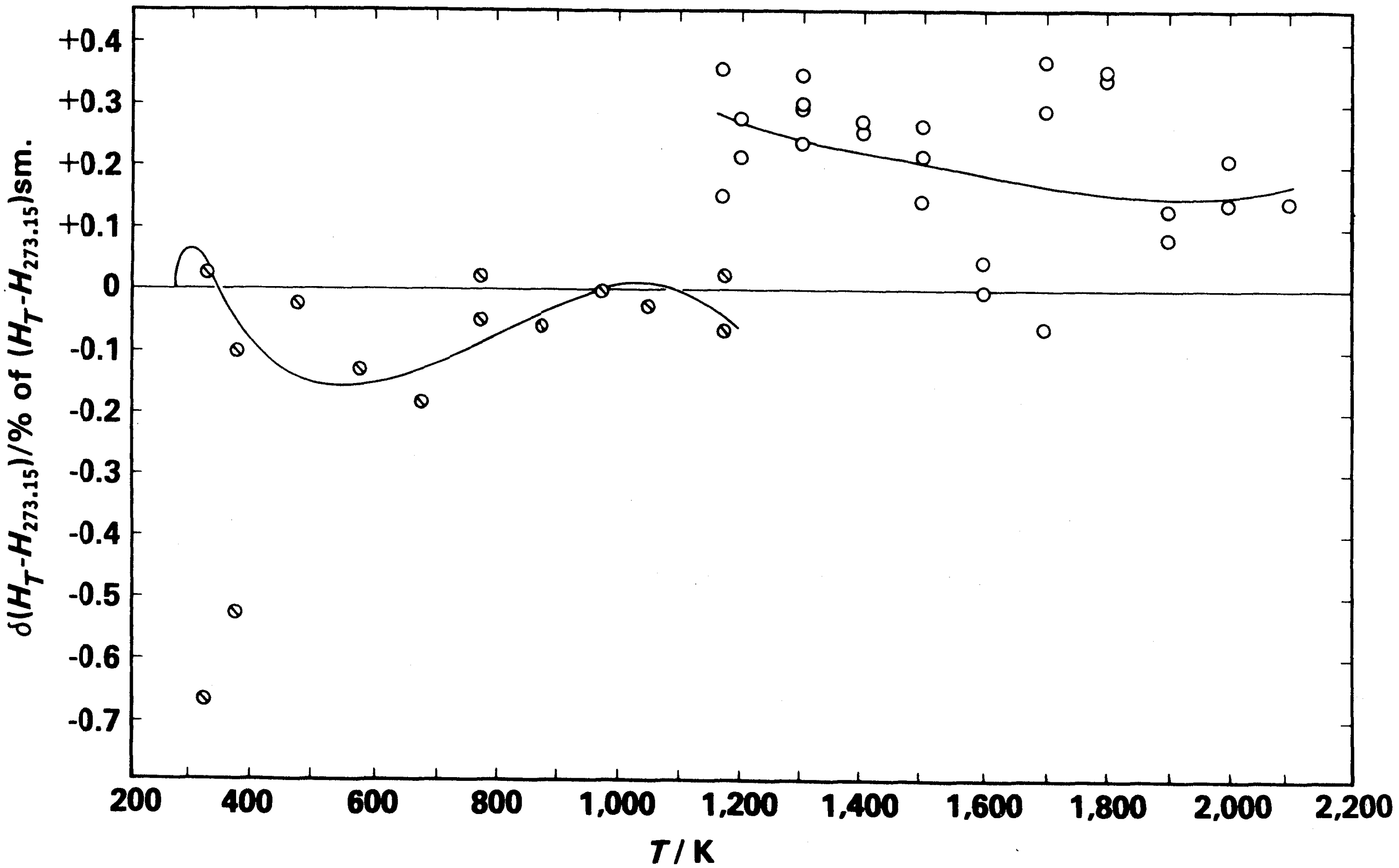

Figure 1. Deviation of NBS relative enthalpy data on SRM-781 molybdenum from unified spline representation. Baseline is equation (8). ⊘, ice-calorimeter data; smooth curve below 1200 K, equation (2); ○, adiabatic calorimeter data; smooth curve above 1200 K, equation (3).

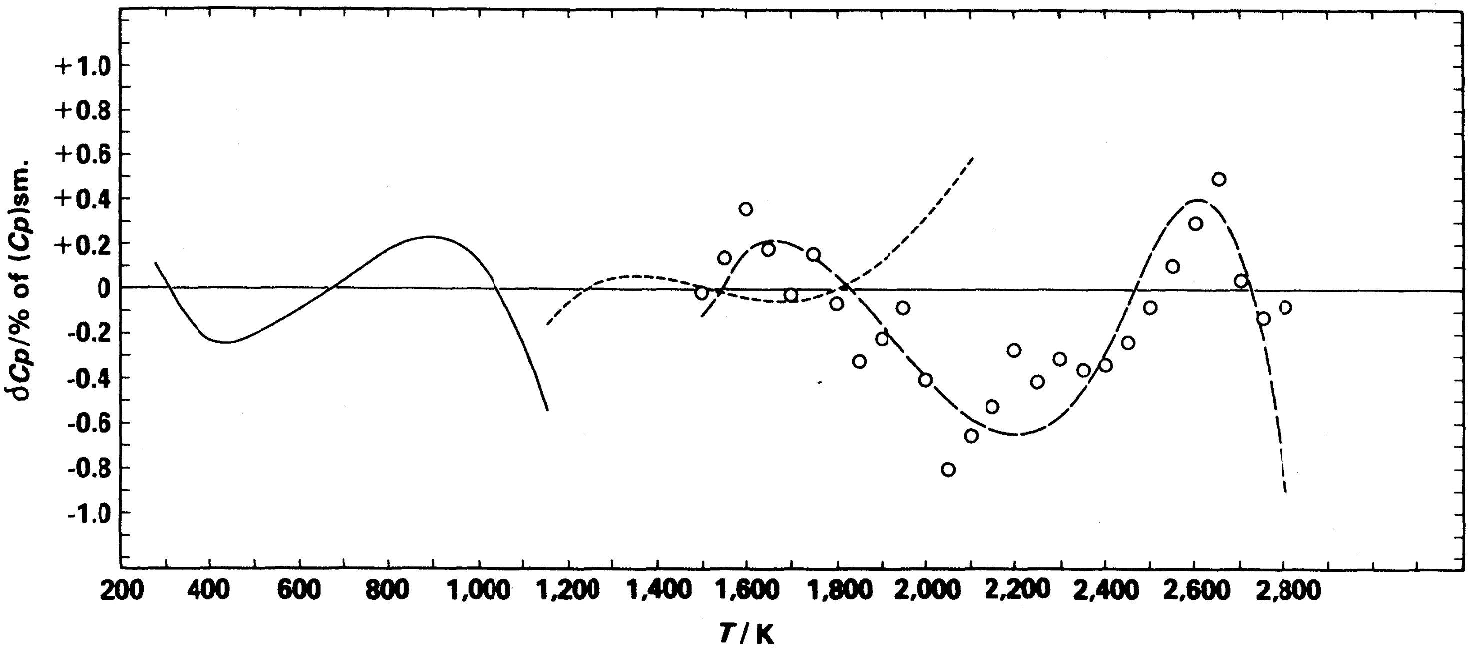

Figure 2. Deviation of NBS heat-capacity data on SRM-781 molybdenum from unified spline representation. Baseline is equation (7). ———, derived from ice-calorimeter data by differentiating equation (2); – – – – – , derived from adiabatic calorimeter data by differentiating equation (3); ○, averaged pulse-calorimeter data; —— —— ——, equation (4).

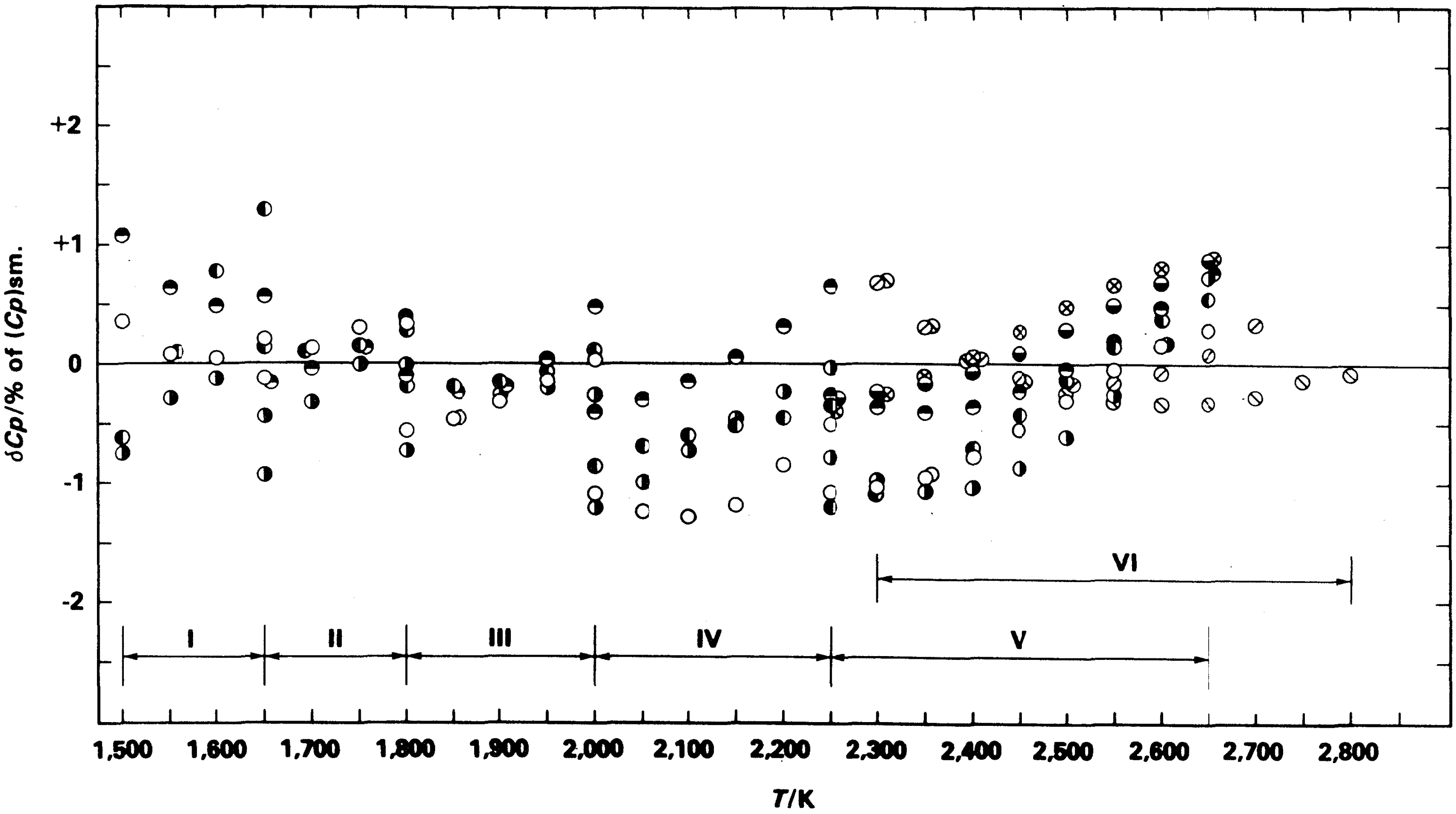

Figure 3. Deviation of all NBS pulse-calorimeter, heat-capacity data on SRM-781 molybdenum from unified spline representation. Baseline is equation (7). ○ , Series D1-F; ◐ , Series D1-S; ◑ , Series D2-F; ◓ ,Specimen D3; ◒ , Specimen D1, experiment 11; ⊗ ,Specimen D1, experiment 12; ⊘ ,Specimen D1, experiment 13; ⦸ , Specimen D1, experiment 14. Vertical lines delimit the six temperature ranges of the optical pyrometer system (see sec. 3.3.b).

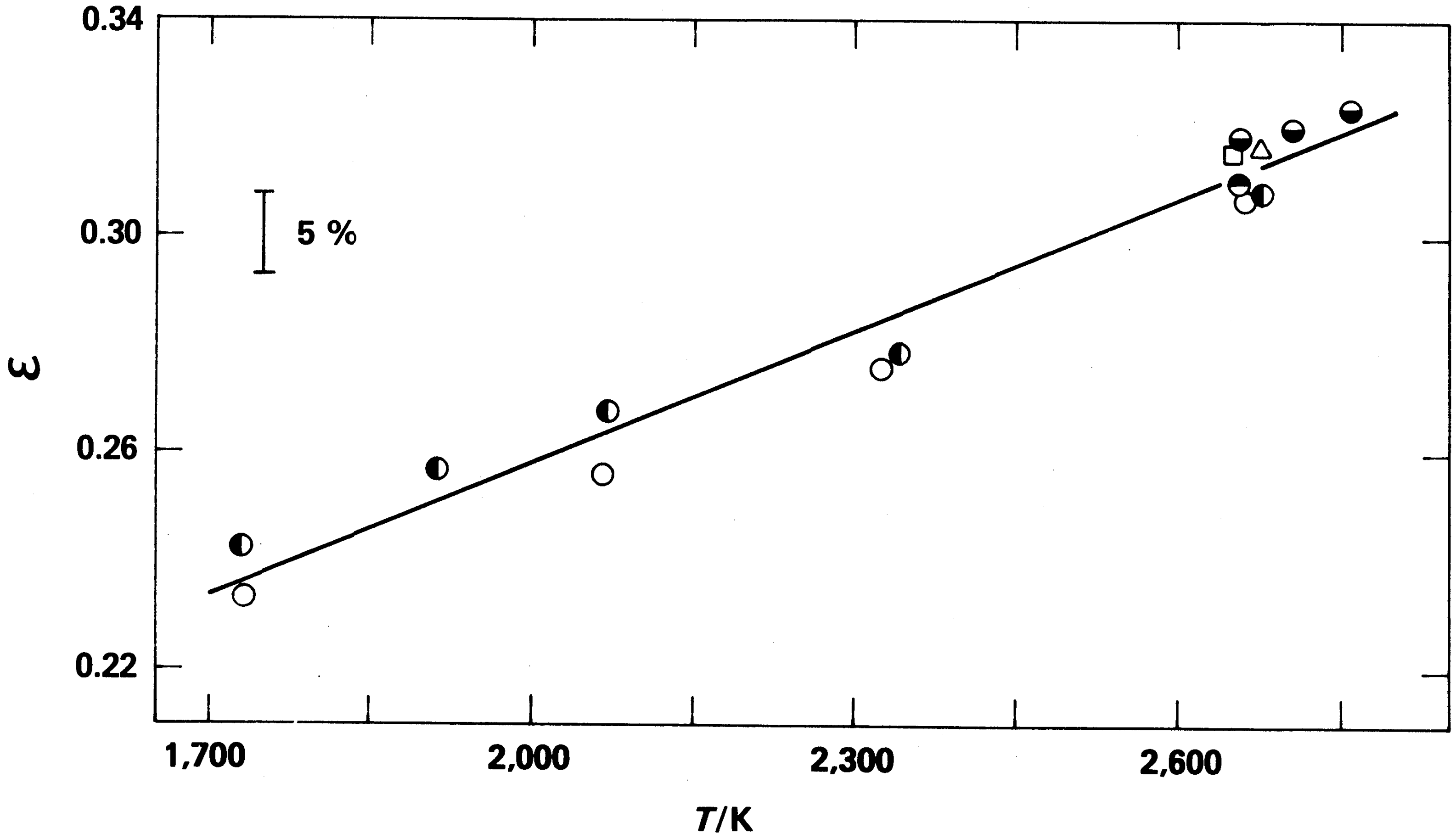

Figure 4. Total hemispherical emissivity of SRM-781 molybdenum measured in pulse-calorimeter experiments. ○, Series D1-F, experiments 1 and 3-5; ◐ , Series D1-S, experiments 6-10; □ , Series D2-F, experiment 19; △ Specimen D 3, experiment 31; ◓ , Series D1-T, experiment 11; ◒ ,Series D1-T, experiments 12-14.

pulse-calorimetrically measured heat-capacity data of this study above 1500 K as well as the smooth heat-capacity values derived from equations (2) and (3).

The hemispherical total-emittance data (table A3) were fitted with a linear function of temperature (IPTS-68 [13]) using the method of least squares. This function is:

$$\varepsilon = 9.40 \times 10^{-2} + 8.21 \times 10^{-5} T, \qquad (9)$$

in which the range of applicability is 2700 K > T > 1700 K. Figure 4 shows the emittance data and smooth values calculated from equation (9).

6. Reliability of the NBS Data

The overall inaccuracy of the relative-enthalpy and heat-capacity data for the SRM-781 molybdenum sample (insofar as these data are considered to represent pure molybdenum metal) contains a component arising from chemical impurities in the sample as well as the usual random and systematic components associated with each of the three individual calorimeters used in the heat measurements. The effect of sample impurity will be considered first and it will be shown that this source of error is smaller than other sources of error. This will be followed below by consideration of heat-measuring errors. These error estimates will then be combined to yield values for the overall inaccuracy of each of the three sets of heat data.

6.1 Error Due to Sample Impurity

All calculations of the enthalpy and heat-capacity data (tables 8, 5, 6, and 7) were made assuming a sample purity of 100 percent. The small amount of impurities actually present (tables 1, 2, and A1) introduce error chiefly by making the real sample one or more phases whose average heat capacity per unit mass differs slightly from that of the nominal pure material (molybdenum). This assumes that no latent heats of phase change are introduced by the impurities. A simple way to estimate the order of magnitude of this "error" is to make the approximation that all the impurity elements have the same heat capacity per gram atom as molybdenum. Thus if one were to replace all the impurities, atom-for-atom, by molybdenum, the percentage change in sample mass should be a measure of the change in both the enthalpy and heat-capacity. The effect on this basis can be calculated from table 2: the "elements measured" indicate a net error of +0.02 percent and the upper limits of the "elements showing interference", and additional +0.03 percent, for a total error of +0.05 percent. Hydrogen, which was not analyzed for, could produce a much greater error. One hundred ppm hydrogen impurity, for instance, would introduce an error on the order of +1 percent. However, molybdenum is not known to form stable hydrides and it is believed that hydrogen was present at a much lower level. As noted in table A1, the electronic characterization of samples A and B was interpreted as indicating a greater impurity level (0.2% by mass) than did the other two analytical techniques. However, the amounts of impurities postulated in the interpretation (table A1) would, on the above basis, introduce a total error of only +0.01% due to their high atomic weights.

6.2 Bunsen-Ice-Calorimeter Data

A detailed estimate of possible systematic errors for enthalpy measurements made with the ice calorimeter has been given in a previous publication (see section 4 of reference [2].) Since the measuring system of the present study is identical to that described in reference [2], the same quantitative estimate applies. To briefly summarize, systematic error may arise from the calibrations of the potentiometer and the resistance bridge used with the furnace temperature-measuring elements, as well as from the calibrations of the measuring elements themselves. Also, calibration error in the analytical balance used to weigh the mercury reservoir before and after each experiment as well as the sample and sample container could be a source of systematic error. Two remaining sources are the calorimeter calibration constant and a possible difference in the heat loss of the full and empty containers during the drop into the calorimeter. The arithmetic sum of all the systematic errors ascribed to these sources plus that calculated above for sample impurity is 0.11 percent at 1200 K.

Figure 1 indicates that two enthalpy measurements at 323.15 and 373.15 K deviate considerably from all the others in the series (up to three times the standard deviation of residues). A re-calculation of the standard deviation of the ice-calorimeter data, neglecting these two measurements, yields 0.06 percent for this index of the imprecision of the measurements. Adding this index, taken at a 99-percent confidence level, to the estimated maximum systematic error (0.11 percent at 1200 K) yields 0.3 percent as an estimate of the overall inaccuracy of the enthalpy data. The inaccuracy in the heat-capacity values obtained by differentiating equation (2) is believed not to exceed 0.5 percent up to 1000 K.

Comparison of the heat capacity at 273.15 K derived from equation (2) with the value of heat capacity at 273.15 K derived from a careful analysis of all the low-temperature (below 300 K) heat-capacity data reported for molybdenum in the literature [18] yields a difference in heat capacity at this temperature of 0.01 percent. Although the low-temperature samples were undoubtedly of a different composition and history than SRM-781, such close agreement does lend confidence to the validity of the present measurements.

6.3 Adiabatic Receiving-Calorimeter Data

Past experience with this calorimeter has indicated that the major source of inaccuracy in enthalpy measurements above 1200 K arises from error in measuring the average temperature of the sample in the furnace. An approximation commonly made (and it is followed in this discussion) is to assume that the error in pyrometrically determined temperatures is proportional to the square of the absolute temperature. The estimated pyrometric uncertainties listed in section 3.2.a approximately obey this temperature dependence and yield an uncertainty of 2.5 K at 2300 K. To this must be added the additional error in realizing the average temperature of the sample. On the basis of an earlier determination of the temperature profile of the furnace core at 2300 K, an approximate calculation indicated that near 2300 K, the temperature of the bottom of the sample container (which is what the pyrometer measures) may be as much as 0.5 K different from the average temperature of the sample. Assuming, therefore, an overall temperature error of 3 K at 2300 K and of the same sign and proportional to the square of the temperature at other temperatures, the smoothed results of the enthalpy measurements (equation (3)) indicate an error in $(H_T - H_{298.15})$ varying from 0.1 percent at 1200 K to 0.15 percent at 2000 K and an error in C_p varying from 0.15 percent at 1200 K to 0.3 percent at 2000 K.

Some of the error in pyrometric temperature measurements may be due to the calibration of the absorbing filters used for the different ranges. In proceeding to successively higher temperatures a point is reached at which a calibrated absorbing filter is required in the radiation path and the adjusted pyrometer current abruptly assumes a much lower value. It is then instructive to examine a monotonically-varying property (e.g. enthalpy) to see if a discontinuity appears at this point. In the present study, such a current change did occur between 1500 and 1600 K. Examination of the unsmoothed enthalpy data in this temperature range (figure 1) discloses no enthalpy differences which exceed the usual precision of measurement. Therefore, there is no evidence for the existence of a filter-dependent pyrometer error. A second such current shift took place between 2000 and 2100 K but it is felt that the lack of enthalpy data at more than one temperature in the range 2100 K and above would make any conclusions about an enthalpy discontinuity between 2000 K and 2100 K unreliable.

Further evidence of the reliability of the optical pyrometry in the present study can be obtained from the measurements on a specimen of α-Al_2O_3 (NBS SRM-720 [16].) The enthalpy of this material was measured once at 1170 K (before experiment 1) and once at 1700 K (after experiment 27). The results agreed with the highly consistent earlier results [16] to 0.05 percent or better, providing evidence that the pyrometry did not substantially deteriorate during the measurements on molybdenum.

Addition of the observed standard deviation of residues for the enthalpy data (from equation (3); taken at a 99-percent confidence level) to the maximum estimated inaccuracy in enthalpy due to temperature error (0.15 percent at 2000 K) and the estimated inaccuracy due to sample impurity (0.05 percent) yields an estimate of the overall inaccuracy in the enthalpy measurements of 0.6 percent. The inaccuracy in the heat-capacity values derived from equation (3) by differentiation is believed to be about 1 percent.

Although error in sample-temperature measurements certainly seems to be the most serious one in heat measurements similar to those of the present study, there is a remote chance that a substantial part of the large disagreement among the many investigators of the enthalpy and heat capacity of molybdenum (see section 7) is due to a real difference between some samples of the pure, annealed metal. The present enthalpy data on molybdenum include an enthalpy measurement on a sample with a very different history (sample E; see section 2) at each of the temperatures 1170, 1699 and 1900 K (table 6). The agreement within 0.15 percent between Samples A (SRM-781) and E at these three temperatures is some evidence that the massive annealed metal has a reproducible enthalpy and heat capacity.

6.4 Pulse-Calorimeter Data

The procedural details for estimating the errors in the measured and computed quantities in high-speed experiments using the present measurement system have been given in a prior publication [21]. In the present work, specific terms in the error estimates were recomputed whenever circumstances warranted. The error estimates, summarized in table 11, indicate an estimated overall inaccuracy in the heat capacity not exceeding 3 percent. This figure represents twice the sum of two components: the standard deviation of residues of the best fit to the heat-capacity data (equation (4)) and the estimated systematic errors (table 11) combined in quadrature.

The rate at which the tubular specimen is heated in a pulse-calorimetric heat-capacity measurement has a significant effect upon the heat capacity calculated from the potential-drop, current and temperature data. The effect of specimen-heating rate was investigated in the series of experiments 20 through 26 in temperature Range IV (see section 3.3.b). The results at 2000 K are representative of those over the entire temperature range and are given in table 12 and figure 5. Low heating rates, $dT/d\tau$, (below 4000 $K{\cdot}s^{-1}$) yield larger values of the calculated heat capacity. This effect is believed to be related to the existence of larger temperature gradients in the specimen at low heating rates and to the fact that the specimen temperature and its time derivative measured at the mid-region differ from the corresponding effective values for the entire specimen. To take experimental data at heating rates less than 4000 $K{\cdot}s^{-1}$ would introduce a source of systematic error. All the heat-capacity data of tables 7 and 8, upon which equations (4) and (7) are based were taken at heating rates in excess of 5000 $K{\cdot}s^{-1}$.

Table 11

Summary of error estimates for pulse-calorimeter data on SRM-781 molybdenum

Measured or Derived Quantity	Imprecision[a]	Inaccuracy[b]
Temperature (at 2000 K)	0.3 K	5K
Specimen current	0.03%	0.1%
Specimen potential drop	0.04%	0.1%
Hemispherical total emittance	2%	5%
Heat capacity		

[a] Imprecision of a set of data for some property measured as a function of temperature refers to the standard deviation of residues of a smooth function of temperature fitted to the data set by the method of least squares.

[b] Inaccuracy refers to twice the arithmetic sum of the imprecision and the estimated systematic errors (systematic errors combined in quadrature).

Table 12

Heat-capacity results[a] on SRM-781 molybdenum (specimen D2) at 2000 K, as a function of specimen heating rate

$\frac{dT/d\mathrm{T}}{\mathrm{K \cdot s^{-1}}}$	$\frac{C_p}{\mathrm{J \cdot mol^{-1} \cdot K^{-1}}}$
1230	37.89
2040	37.12
2840	36.91
3920	36.77
5270	36.77
6510	36.72
8010	36.75

[a] These are experiments 20-26.

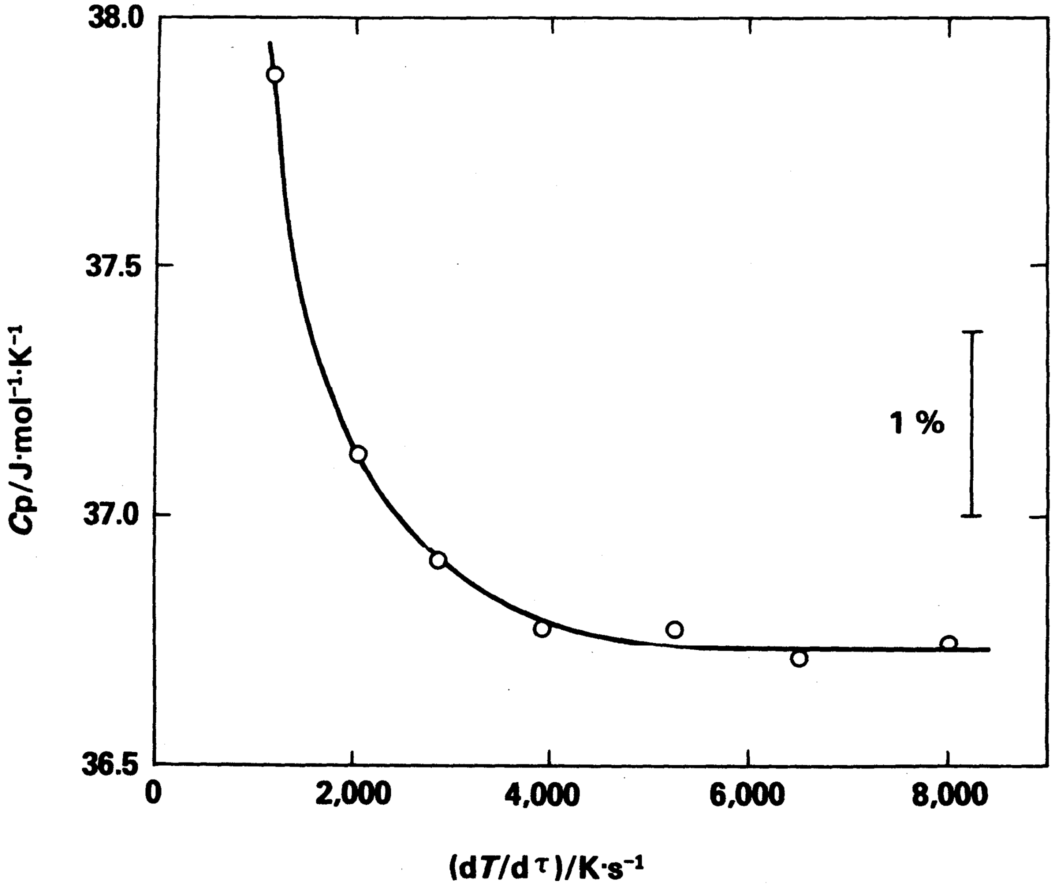

Figure 5. Dependence at 2000 K of calculated heat-capacity of SRM 781 molybdenum (specimen D2) on specimen-heating rate.

In order to detect significant differences among the heat-capacity values for the three different specimens and also for different experimental series (see tables 7 and 8), the heat-capacity data in the range 1500 to 2650 K were fitted separately for each experimental series and each specimen. The fitting procedure employed a third-degree polynomial in temperature with the method of least squares and resulted in four heat-capacity functions. The standard deviation of residues for each of these four functions was in the range 0.3 to 0.5 percent. The percent differences of these heat-capacity functions, taken pairwise, is given in table 13. In this table, the differences are tabulated in pairs. Each upper pair member represents the average algebraic percent difference between the pair of functions indicated in the table margins. Each lower pair member represents the average absolute percent difference between the same pair of functions. These differences all lie in the range 0.1 to 0.6%. Since these differences are comparable to the imprecision of the heat-capacity measurements, it is concluded that no significant differences exist between the heat-capacity data of different specimens and different experimental series.

The electrical resistivity of all specimens was measured before and after the pulse experiments (but after the pre-experimental pulse conditioning; see section 3.3.b). These resistivity data agreed within 0.1 percent, indicating that no significant irreversible structural or chemical changes had taken place in the specimens as a result of their being heated to temperatures in excess of 2650 K.

7. Comparison of NBS Heat Data on SRM-781 Molybdenum with Data on Molybdenum Metal of Previous Investigators and Compilers

Interest in the thermodynamic properties of molybdenum has had many different motivations and has spanned a period of nearly a century and a half. As a result, there now exists in the literature a considerable body of enthalpy and heat-capacity data for this material. The earliest thermal measurements known to the present authors were made by Regnault [27] and by De la Rive and Marcet [26]. These were part of an attempt by these early investigators to verify and extend the foundations of the efforts by Dulong and Petit to correlate the heat-capacity behavior of the elements. Almost a century later, the refractory qualities of molybdenum were valued and the metal was widely studied for applications in thermionic devices [86, 87]. Most recently, it has found use as a structural and alloying component in applications for advanced power-generating and propulsion systems [46, 88]. It has also been considered as a candidate high-temperature standard reference material [68], the application to which the present investigation is addressed. Finally, there has been a continuing concern with the deviation of its high-temperature heat capacity from the classical Debye heat capacity [86, 66, 21, 89]. Attempts to explain the deviation have included the contributions of anharmonicity, point defects and electronic excitations at temperatures well above Θ_D. Most of the heat-capacity studies have been carried out on the solid phase above room temperature. A very few extend down to liquid helium temperature and still fewer include the liquid phase. There have also been several attempts to correlate all the heat-capacity data available at a given time.

Table 13

Average percent difference[b] over the range 1500 to 2650 K between smooth representations[d] of heat capacity of different SRM-781 molybdenum specimens and different experiment series

i^{a} j	D3	D2-F	D1-S
D1-F	0.48[c] 0.48	-0.07 0.16	0.18 0.21
D1-S	0.31 0.35	-0.24 0.24	——
D2-F	0.55 0.55	——	——

[a] The indices *i* and *j* refer to the experiment series listed in the table margins and summarized in table 7.

[b] $\frac{\overline{\Delta C_p}}{C_p} = \frac{100}{N} \sum_{\nu=1}^{N} [({}^{i}C_p(T_\nu) - {}^{j}C_p(T_\nu))/{}^{j}C_p(T_\nu)]$; N temperatures, T_ν, are uniformly spaced in the range 1500 to 2650 K.

[c] Upper figures are average *algebraic* percent differences, lower figures are average *absolute* percent differences.

[d] These smooth representations not given in text.

One task of the present study of molybdenum as a standard reference material has been the compilation of a comprehensive bibliography giving all known literature references to date containing either original or compiled and critically-evaluated data on the enthalpy or heat capacity of this material in the solid range above 273.15 K. This bibliography is contained within section 9 and further information on each individual investigation is given in table 14. In some instances, as this table shows, data have been repeated by the same author(s) in several citations, sometimes in a different guise. For completeness, all such citations have been included and the duplication of data has been noted in the last column of this table. This does not apply to the data compilations (pre-starred entries of columns 1 and 2). For these, only the most recent data compilation by each author in question has been cited. Columns 4 and 5 of table 14 indicate which property (enthalpy or heat capacity) was actually measured or compiled by each investigator.

The smoothed, composite enthalpy and heat capacity of SRM-781 molybdenum derived in the present study (equations (8) and (7), respectively) have been compared with most of the original measured enthalpy and heat-capacity data appearing in the references of table 14. (Some of the earliest references were considered unreliable due to uncertainties in temperature measurements and sample purity and were therefore omitted.) These comparisons are given in figures 6, 7, 8, and 9. Figures 6 and 7 present, respectively, the comparisons for measured values of the enthalpy of molybdenum relative to 273.15 K and measured values of the heat capacity of molybdenum taken from the literature. In both these figures, the original data points have been represented insofar as possible. A few investigators, however, have given their data exclusively in the form of smooth functions and these have been included as well. In no case do the curves appearing in figures 6 and 7 represent smooth versions of any set of data points concurrently appearing in these figures. In a few instances in which the representation of multiple measurements at very closely-spaced temperatures (< 50 K apart) by a single investigator would have obscured the figures, these data were averaged to preserve the overall trend in the investigator's data while still giving a clear representation. An example of this is the data of [81] (figure 7) which comprise 37 individual measurements of heat capacity in a 500 K interval. A few data points fell outside the chosen ordinate limits of these figures. The deviations of these points have been printed directly above or below them. All data have been corrected [12] to their values on the temperature scale IPTS-68 [13]. A convenient table (A4) for effecting such corrections for molybdenum in those cases in which the data are expressed on IPTS-48, was calculated using reference [12] with equation (7) of the present work and appears in the present Appendix. All enthalpy data which were originally referred to 298.15 K have been referred to 273.15 K using the enthalpy increment $(H_{298.15\ \mathrm{K}} - H_{273.15\ \mathrm{K}}) = 593.6\ \mathrm{J\ mol^{-1}}$ (see section 4.2). The NBS-measured heat data on SRM-781 molybdenum have been omitted from figures 6 and 7 but the range of these NBS-measured enthalpy and heat-capacity data have been indicated by the dotted horizontal lines. It seems unlikely to the present authors that the great dispersion of the literature enthalpy and heat-capacity data can be ascribed wholly to variations in sample purity. This dispersion probably arises from large systematic errors in temperature measurement.

Table 14

Chronological compilation of literature references containing original or compiled data on the enthalpy or heat capacity of molybdenum metal chiefly in the temperature range 273.15 K to 2800 K

Year	Author(s)	Ref.	Property cited or measured		Temperature Range, K	Plotted in Figure:	Remarks (Method, sample purity, etc.)
			ΔH	C_p			
1840	De la Rive & Marcet	[26]	X		288	------	Drop method.
1840	Regnault	[27]	X		373	------	Drop method; < 1% error in measuring $\overline{C_p}$ of H_2O.
1901	Defacqz & Guichard	[28]	X		358-717	------	Drop method: 12 to 20% above NBS values.
1905	Stücker	[29]	X		373-923	------	Drop method: 5 to 20% above NBS values.
1918	Wüst, *et al*.	[30]	X		373-1773	6	Ice calorimeter.
1928	Stern	[31]	X		373,715	------	Ice calorimeter: $\overline{C_p}$ deviates from NBS values by +0.4 and -0.8%.
1929	Bronson & Chisholm	[32]		X	293-553	------	Drop method; original enthalpy data unpublished.
1929	Cooper & Langstroth	[33]	X		195-563	7	Drop method: enthalpy reference temp. uncertain; C_p plotted.
1933	Bronson, *et al*.	[34]	X		323-775	6	Drop method; same specimen as [33].
1934	Jaeger & Veenstra	[35]	X		671-1828	6	Drop method; imprecision $\leq$ 0.2%.
1934	Jaeger & Veenstra	[36]	X		671-1828	------	(Repeats smooth data of [35]).
1951	Redfield & Hill	[37]	X		481-1359	6	Ice calorimeter; est. error = 4%.
*^{e}1955	* Stull & Sinke	[39]		X	298-2800	9	--------------------
1956	Lucks & Deem	[40]	X		306-1882	6	Ice calorimeter: also measured Al_2O_3.
1956	Rasor & McClelland	[41]			1073-2813	7	(Data repeated in [44].)
1957	Kothen	[38]	X		298-2623	6	Drop method; smooth data only given.

Table 14 (continued)

Chronological compilation of literature references containing original or compiled data on the enthalpy or heat capacity of molybdenum metal chiefly in the temperature range 273.15 K to 2800 K

Year	Author(s)	Ref.	Property cited or measured		Temperature Range, K^{a}	Plotted in Figure:	Remarks (Method, sample purity, etc.)
			ΔH	C_p			
1960	Boggs & Wiebelt	[42]		X	1050-1750	7	DTA; purity = 99.9%.
*1960	* Kelley	[23]	X	X	400-2890	8,9	--------------------
1960	Lehman	[43]		X	300-2800	7	Pulse method; est. error = 2.5%.
1960	Rasor & McClelland	[44]		X	1073-2813	7	DC heating method; est. error = 5%; purity = 99.65%; see [41].
1960	Rudkin	[45]		X	1548-2175	7	DC heating method.
*1961	* Goldsmith, *et al*.	[46]		X	280-2830	9	--------------------
1961	Kirillin, *et al*.	[47]	X		972-2610	6	Drop method; est. error <1.2%; purity = 99.95%.
1961	Lazareva, *et al*.	[48]	X		1154-2462	6	Drop method; est. error <1%; purity = 99.98%.
1961	Taylor & Finch	[49]		X	300-2860	7	Pulse method; est. error <7%; graph repeated in [58].
1962	Chekhovskoi	[50]	X		972-2610	------	(Repeats data of [47].)
1962	Kirillin, *et al*.	[51]	X		972-2610	------	(Repeats data of [47].)
1962	Rudkin, *et al*.	[52]		X	1548-2175	------	(Repeats data of [45].)
*1962	* Schick	[53]	X	X	298-2800	8,9	Compiled 1962, published 1966.
*1963	* Kirillin, *et al*.	[54]	X	X	273-2673	8,9	--------------------
1963	Lowenthal	[55]		X	1200-2100	7	AC heating method; purity = 99.93%; est. error <3%.

Table 14 (continued)

Chronological compilation of literature references containing original or compiled data on the enthalpy or heat capacity of molybdenum metal chiefly in the temperature range 273.15 K to 2800 K

Year	Author(s)	Ref.	Property cited or measured		Temperature Range, K^a	Plotted in Figure:	Remarks (Method, sample purity, etc.)
			ΔH	C_p			
1964	Conway, *et al.*	[56]	X		1400-2520	6	Drop method.
1964	Kraftmakher	[57]		X	1300-2500	------	(Data in graph form; See [79] for tabulated data.)
1964	Taylor & Finch	[58]		X	300-2880	------	Smooth curve only; data in [49].
1965	Cezairliyan	[59]	X	X	1250-1600	6,7	Pulse method; purity >99.9%; est. error <5%.
1965	Filippov & Yurchak	[60]		X	1123	7	Periodic heating.
*1965	* Hultgren, *et al.*	[24]	X	X	0-2890	8,9	Compiled 1965, published 1973.
*1966	* (JANAF Tables)	[61]	X	X	0-2800	8,9	Compiled 1966, published 1971.
1967	Kraftmakher, Ya. A.	[62]		X	1300-2500	------	(Repeats data of [57].)
1968	Chekhovskoi & Petrov	[63]	X		973-2834	------	(Repeats data and equations of [66].)
1968	Filippov, *et al.*	[64]		X	601-2501	7	Periodic heating.
1968	Khusainova & Filippov	[65]		X	550-1200	------	Periodic heating; data only given in small scale plot.
1968	Kirillin, *et al.*	[66]	X		973-2834	6	Drop method; purity = 99.95%.
*1968	* Reilly & Furukawa	[18]	X	X	0-300	8,9	--------------------
1969	Kirillin, *et al.*	[67]	X		973-2834	------	(Repeats data and equations of [66].)

Table 14 (continued)

Chronological compilation of literature references containing original or compiled data on the enthalpy or heat capacity of molybdenum metal chiefly in the temperature range 273.15 K to 2800 K

Year	Author(s)	Ref.	Property cited or measured		Temperature Range, K^a	Plotted in Figure:	Remarks (Method, sample purity, etc.)
			ΔH	C_p			
1970	Cezairliyan, et al.	[21]		X	1900-2800	7	Pulse method; purity >99.94%; est. error <3%.
1970	Chekhovskoi, et al.	[68]	X		2094-2869	6	Drop method/levitation; purity >99.97%.
1970	Makarenko, et al.	[69]		X	1100-2400	7	Two pulse methods; est. error <10%; 99.99% purity. Only smooth data given.
1970	Sheindlin, et al.	[70]	X	X	300-2300	------	(Repeats equations of [66].)
*1970	* Touloukian & Buyco	[71]		X	0.4-2860	------	(Lists data of 25 sources; gives no recommended values).
1971	Berezin, et al.	[72]	X		1962-2869	6	Drop method/ levitation; est error <0.33%. Includes data of [68].
1971	Chekhovskoi & Berezin	[73]	X		2094-2684	------	(Repeats data of [72].)
1971	Dikhter & Lebedev	[74]		X	2200-2850	------	Exploding wire method; deviates 18 to 34% from equation (8).
1971	Ishihara & Douglas	[75]^b	X		1170-2102	1,2	Drop method; at least 99.8% purity.
1972	Oetting & Navratil	[76]	X		696-1381	6	Drop method; 99.98% purity.
1973	Bondarenko, et al.	[77]	X		1200-2500	6	Drop method; only equation given; est. error <0.8%.
1973	Douglas & Ditmars	[78]^c	X		273-1173	1,2	Ice calorimeter; same sample as [75].
1973	Kraftmakher	[79]		X	1300-2500	7	Modulated power method; only smooth data given.
1973	Mebed, et al.	[80]		X	1300-2500	7	Periodic heating; "technical grade" specimen.

Table 14 (continued)

Chronological compilation of literature references containing original or compiled data on the enthalpy or heat capacity of molybdenum metal chiefly in the temperature range 273.15 K to 2800 K

Year	Author(s)	Ref.	Property cited or measured		Temperature Range, K[a]	Plotted in Figure:	Remarks (Method, sample purity, etc.)
			ΔH	C_p			
1975	Chekhovskoi & Kalinkina	[81]		X	317-834	7	Continuous adiabatic heating; 99.95% purity.
1975	Fedorov	[82]		X	1500-2500	------	Pulse method; data only given in small-scale plot.
1976	Cezairliyan	d		X	1500-2800	2,3	Pulse method: same sample as [75] and [78].

[a] In the drop method, the calorimeters were generally at room temperature. In those cases in which the initial temperature of the range is substantially above room temperature, enthalpy data is missing between room temperature and the initial temperature. Single temperatures indicate existence of one or more data at each of those temperatures. All temperatures IPTS-68 [13].

[b] This data reproduced as table 6 of the present work.

[c] This data reproduced as table 5 of the present work.

[d] Present work (tables 7 & 8).

[e] Citations preceded by an asterisk (*) are major data compilations.

These literature enthalpy and heat-capacity data for molybdenum provide, in any event, a formidable task for the data compiler. Nine such compilations are known to the present authors and these are compared (with the exception of compiler reference [71]; see table 14) to the present NBS results on SRM-781 molybdenum in figures 8 (enthalpy) and 9 (heat-capacity). With regard to figure 8, note that the compilations of Goldsmith, et al. [46] and Stull and Sinke [39] have been omitted; the former, because no values were given; the latter, for clarity since the values given by Stull and Sinke are virtually identical with those of Schick [53] below 1500 K and with those of Kelley [23] above 1500 K. In figure 9, reference [39] is only displayed in the interval 1400-1600 K for the same reasons. Note that the deviations of some compilations (notably, those of Kelley [23], Hultgren [24] and Kirillin [54]) are negative and very large (on the order of 20 percent) near the melting point. The present NBS measurements agree very well with the most recent correlation [61].

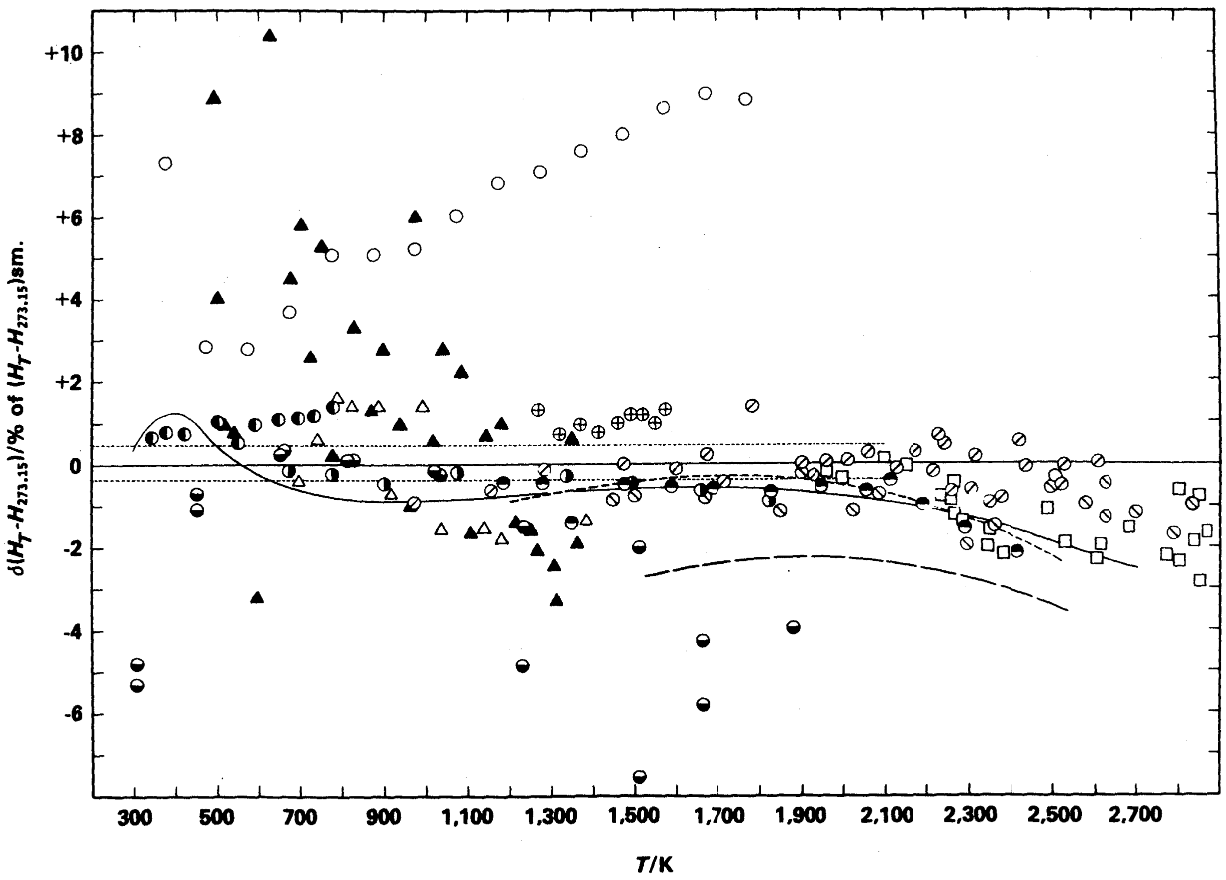

Figure 6. Deviation of directly-measured molybdenum enthalpy data appearing in the literature from unified spline representation of present NBS data for SRM-781 molybdenum. Base line is equation (8). Dotted lines indicate limits of dispersion of NBS relative-enthalpy data. See table 15 for explanation of symbols.

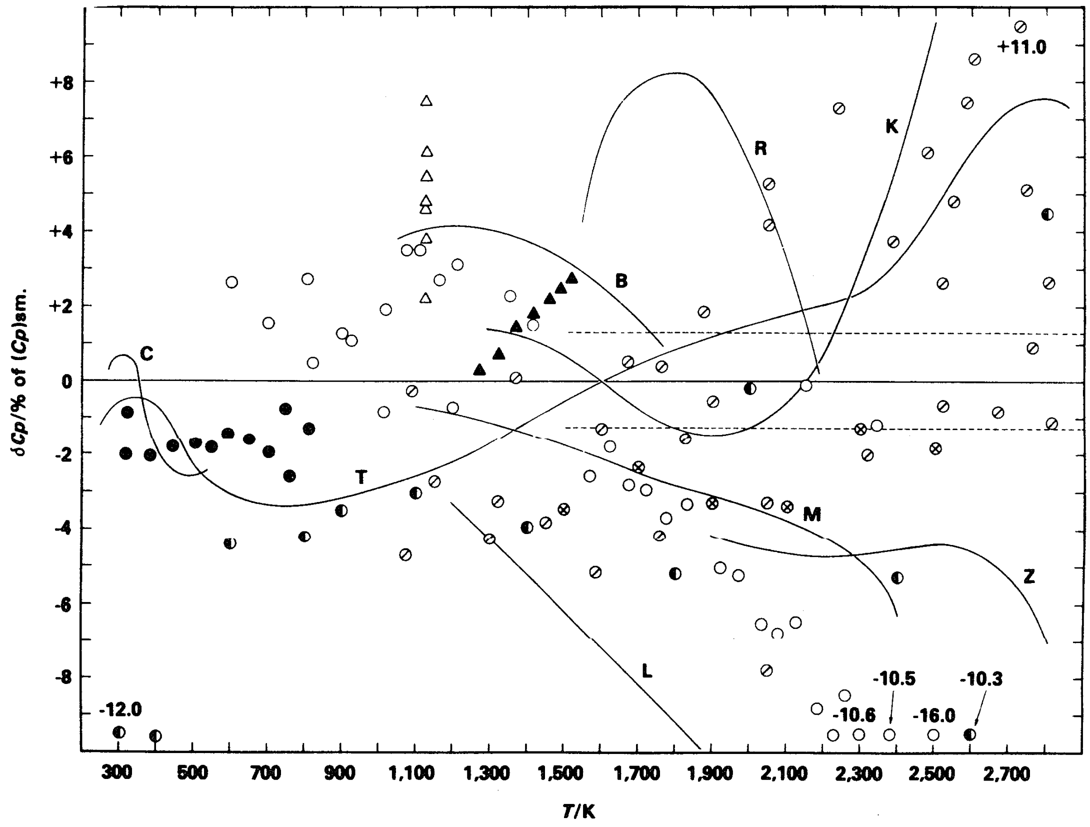

Figure 7. Deviation of directly-measured molybdenum heat-capacity data appearing in the literature from unified spline representation of present NBS data for SRM-781 molybdenum. Baseline is equation (7). Dotted lines indicate limits of dispersion of NBS pulse-calorimetric, heat capacity data. See table 16 for explanation of symbols.

Table 15

Symbol and citation key for relative enthalpy data displayed in figure 6

Symbol	Reference	Year	Investigator(s)	Original Number of Data Points
○	[30]	1918	Wüst, et al.	15
◐	[34]	1933	Bronson, et al.	38
◑	[35]	1934	Jaeger & Veenstra	13
▲	[37]	1951	Redfield & Hill	31
◒	[40]	1956	Lucks & Deem	17
————	[38]	1957	Kothen	-
⊘	[47]	1961	Kirillin, et al.	32
◓	[48]	1961	Lazareva, et al.	58
— — —	[56]	1964	Conway, et al.	-
⊕	[59]	1965	Cezairliyan	9
⦸	[66]	1968	Kirillin, et al.	24
□	[72]	1971	Berezin, et al.	29
△	[76]	1972	Oetting & Navratil	11
---------	[77]	1973	Bondarenko, et al.	-

Table 16

Symbol and citation key for heat-capacity data displayed in figure 7

Symbol	Reference	Year	Investigator(s)	Original Number of Data Points
C————	[33]	1929	Cooper & Langstroth	-
B————	[42]	1960	Boggs & Wiebelt	-
◐	[43]	1960	Lehman	12
⊘	[44]	1960	Rasor & McClelland	36
R————	[45]	1960	Rudkin	-
T————	[49]	1961	Taylor & Finch	-
L————	[55]	1963	Lowenthal	-
▲	[59]	1965	Cezairliyan	9
△	[60]	1965	Filippov & Yurchak	8
○	[64]	1968	Filippov, et al.	32
Z————	[21]	1970	Cezairliyan, et al.	-
M————	[69]	1970	Makarenko, et al.	-
K————	[79]	1973	Kraftmakher	-
⊗	[80]	1973	Mebed, et al.	7
●	[81]	1975	Chekhovskoi & Kalinkina	37

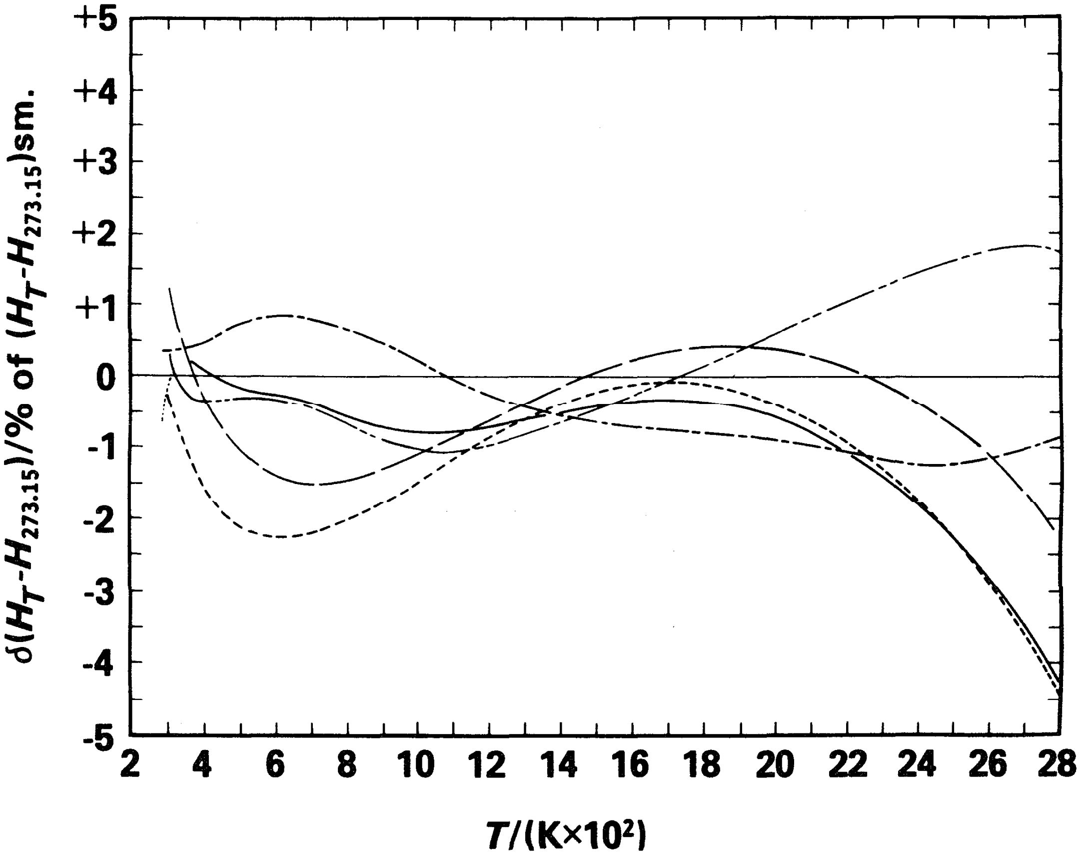

Figure 8. Deviation of enthalpy correlations appearing in the literature from unified spline representation of present NBS data for SRM-781 molybdenum. Baseline is equation (8). See table 17 for explanation of symbols.

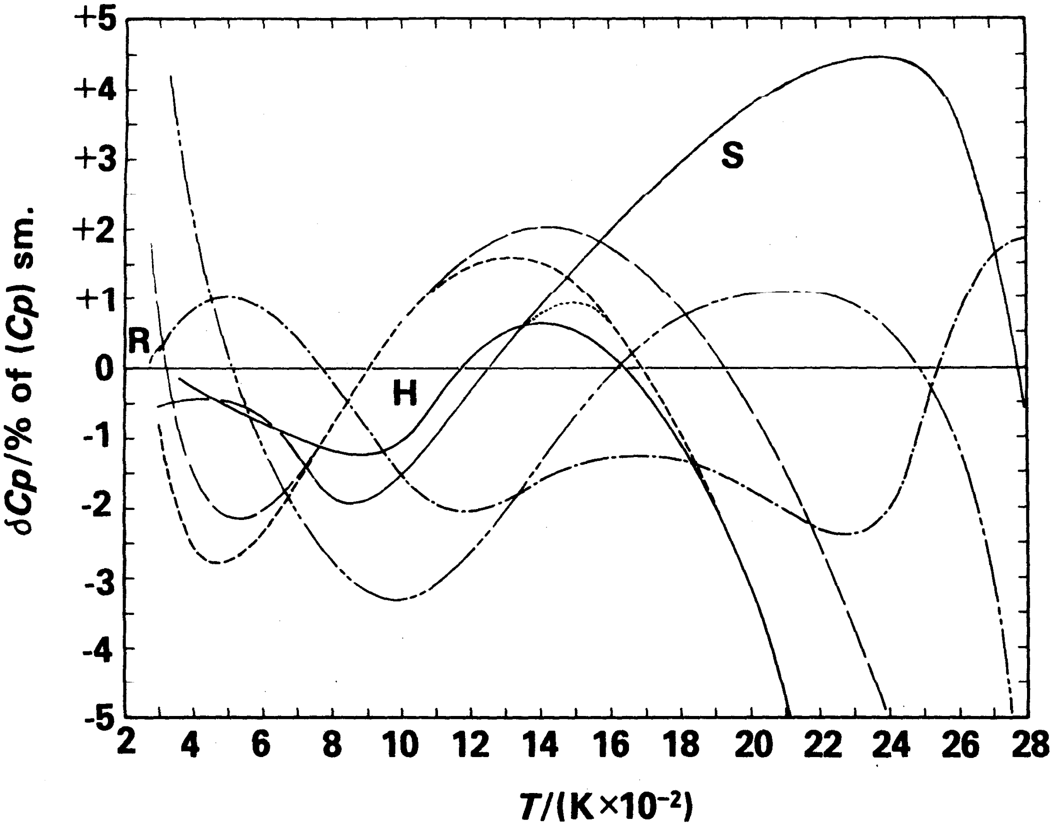

Figure 9. Deviation of heat-capacity correlations appearing in the literature from unified spline representation of present NBS data for SRM-781 molybdenum. Baseline is equation (7). See table 17 for explanation of symbols.

Table 17

Symbol and citation key for relative enthalpy and heat-capacity correlations displayed in figures 8 and 9

Relative enthalpy Symbol (fig. 8)	Heat-capacity Symbol (fig. 9)	Reference	Year	Compiler
[a]	- - - - - - - - - - -	[39]	1955	Stull & Sinke
— — — — —	— — — — —	[23]	1960	Kelley
[a]	——— - - ———	[46]	1961	Goldsmith, et al.
——— - - ———	S —————	[53]	1962	Schick
——— ——— -	——— ——— -	[54]	1963	Kirillin, et al.
—————	H —————	[24]	1965	Hultgren
——— - ——— - -	——— - ——— - -	[61]	1966	JANAF Tables
- - - - - - - - - - - - - - - -	R —————	[18]		Reilly & Furukawa

[a] Not shown on figure 8 (see section 9).

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9. References

[1] NBS Special Publication 260, Catalog of NBS Standard Reference Materials, 1975-76 Edition. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

[2] Ditmars, D. A., and Douglas, T. B., J. Res. Nat. Bur. Stand. (U.S.), 75A (Phys. and Chem.), No. 5, 401 (Sept.-Oct. 1971).

[3] Cezairliyan, A., Morse, M. S., and Beckett, C. W., Rev. Int. Hautes Tempér. et Réfract., 7, 382 (1970).

[4] Kunzler, J. E., and Wernick, J. H., Trans. Metal. Soc. AIME, 212, 856 (1958).

[5] Kunzler, J. E., Electrical Properties of Metals and the Importance of Purity, Chapter 9 in Ultra-High-Purity Metals, Am. Soc. for Metals (1961).

[6] Landolt-Börnstein, Zahlenwerte und Functionen, 6th ed., (Springer, Göttingen, 1959).

[7] Archer, R. S., Briggs, J. Z., and Loeb, C. M., Jr., Molybdenum, (Climax Molybdenum Co., 1953).

[8] Douglas, T. B., and King, E. G., High-Temperature Drop Calorimetry, Chapter 8 in Experimental Thermodynamics, Volume I, Calorimetry of Non-Reacting Systems, p. 293, J. P. McCullough and D. W. Scott, Eds. (Butterworths, London, 1968). See also NBS Special Publication No. 300, vol. 6, p. 181 (1970).

[9] Ditmars, D. A., Int. J. Appl. Rad. Isotopes, 27, 469 (1976).

[10] Ginnings, D. C., Douglas, T. B., and Ball, A. F., J. Res. Nat. Bur. Stand. (U.S.), 45, No. 1, 23 (1950), RP2110.

[11] Furukawa, G. T., Douglas, T. B., McCoskey, R. E., and Ginnings, D. C., J. Res. Nat. Bur. Stand. (U.S.), 57, No. 2, 67 (1956), RP2694.

[12] Douglas, T. B., J. Res. Nat. Bur. Stand. (U.S.), 73A (Phys. and Chem.), No. 5, 451 (Sept.-Oct. 1969).

[13] The International Practical Temperature Scale of 1968, Metrologia, 5, 35 (1969).

[14] West, E. D., and Ishihara, S., A Calorimetric Determination of the Enthalpy of Graphite from 1200 to 2600°K in Advances in Thermophysical Properties at Extreme Temperatures and Pressures, p. 146, ASME, New York, (1965). See also NBS Special Publication No. 300, vol. 6, p. 220 (1970).

[15] West, E. D., and Ishihara, S., National Bureau of Standards Report No. 9803, National Bureau of Standards, U.S. Department of Commerce, (Jan. 1, 1968).

[16] Certificate: Standard Reference Material 720, Synthetic Sapphire (Al_2O_3), National Bureau of Standards, U.S. Department of Commerce, (1970)

[17] Ishihara, S., and West, E. D., J. Res. Nat. Bur. Stand. (U.S.), 80A (Phys. and Chem.), No. 1, 65 (Jan.-Feb. 1976).

[18] Reilly, M. L., and Furukawa, G. T., Critical Analysis of the Heat-Capacity Data of the Literature and Evaluation of Thermodynamic Properties of Cr, Mo, and W from 0 to 300 K, NSRDS-NBS (to be published).

[19] Starrett, K. F., and Wallace, W. E., J. Am. Chem. Soc., 80, 3176 (1958).

[20] Cezairliyan, A., J. Res. Nat. Bur. Stand. (U.S.), 75C, (Eng. and Inst.), No. 1, 7 (Jan.-Mar. 1971).

[21] Cezairliyan, A., Morse, M. S., Berman, H. A., and Beckett, C. W., J. Res. Nat. Bur. Stand. (U.S.), 74A (Phys. and Chem.), No. 1, 65 (Jan.-Feb. 1970).

[22] Foley, G. M., Rev. Sci. Instr., 41, 827 (1970).

[23] Kelley, K. K., Contributions to the Data on Theoretical Metallurgy. XIII. High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for the Elements and Inorganic Compounds, U.S. Bureau of Mines Bull. 584, (1960).

[24] Hultgren, R., Desai, P. D., Hawkins, D. T., Gleiser, M., Kelley, K. K., and Wagman, D. D., Selected Values of the Thermodynamic Properties of the Elements, American Society for Metals, Metals Park, OH (1973).

[25] Atomic Weights of the Elements 1975, Pure and Appl. Chem., 47 (1), 75 (1976).

[26] De la Rive and Marcet, Ann. Chim. Phys. [2], 75, 136 (1840).

[27] Regnault, V., Ann. Chim. Phys. [2], 73, 5 (1840).

[28] Defacqz, E., and Guichard, M., Ann. Chim. Phys. [7], 24, 139 (1901).

[29] Stücker, N., Sitzb. König. Akad. Wiss., Wien, 114, 657 (1905).

[30] Wüst, F. A., Meuthen, A., and Durrer, R., Forsch. Gebiete. Ingenieurw., 204 (1918).

[31] Stern, T. E., Phys. Rev., 32 (2), 298 (1928).

[32] Bronson, H. L., and Chisholm, H. M., Proc. Nova Scotia Inst. Sci., 17 (4), 44 (1929).

[33] Cooper, D., and Langstroth, G. O., Phys. Rev., 33 (2), 243 (1929).

[34] Bronson, H. L., Chisholm, H. M., and Dockerty, S. M., Can. J. Res., 8, 282 (1933).

[35] Jaeger, F. M., and Veenstra, W. A., Rec. Trav. Chim. Pay-Bas, 53 (6), 677 (1934).

[36] Jaeger, F. M., and Veenstra, W. A., Proc. Roy. Acad. Sci. Amsterdam, 37, 61 (1934).

[37] Redfield, T. A., and Hill, J. H., U.S. AEC ORNL-1087, (Sept. 24, 1951).

[38] Kothen, C. W., Dissertation, Ohio State Univ., available from Univ. Microfilms (Ann Arbor, Mich.) as Publ. No. 23697, 93 pp. (1952); Smooth data also available in Dissertation Abstracts 17, 2842 (1957).

[39] Stull, D. R., and Sinke, G. C., in Thermodynamic Properties of the Elements, Advances in Chemistry Series - No. 18, Am. Chem. Soc., Washington, DC (1955).

[40] Lucks, C. F., and Deem, H. W., WADC Tech. Rept. 55-496 (1956), ASTIA Document AD 97185.

[41] Rasor, N. S., and McClelland, J. D., WADC Tech. Rept. 56-400, part I (March, 1957), ASTIA Document AD 118144.

[42] Boggs, J. H., and Wiebelt, J. A., U.S. AEC TID 5734 (Feb., 1960).

[43] Lehman, G. W., WADD Tech. Rept. 60-581 (July, 1960), ASTIA Document AD 247411, PB160804.

[44] Rasor, N. S., and McClelland, J. D., J. Phys. Chem. Solids 15, 17 (1960).

[45] Rudkin, R. L., Res. and Dev. Tech. Rept. USNRDL-TR-433 (June 20, 1960), PB 155892.

[46] Goldsmith, A., Waterman, T. E., and Hirschhorn, H. J., Handbook of Thermophysical Properties of Solid Materials, Revised Ed., V. I: Elements, Armour Research Foundation, Chicago, the MacMillan Company, New York, (1961).

[47] Kirillin, V. A., Sheindlin, A. E., and Chekhovskoi, V. Ya., Soviet Physics Doklady, 139 (3), 557 (1961); (translated from Dokl. Akad. Nauk. SSSR, 139 (3), 645 (1961)).

[48] Lazareva, L. S., Kantor, P. B., and Kandyba, V. V., Phys. Metals and Metallog. (USSR), 11 (4), 133 (1961); (translated from Fiz. Metal. i Metalloved., 11 (4), 628 (1961)).

[49] Taylor, R. E., and Finch, R. A., U.S. AEC NAA-SR-6034 (1961).

[50] Chekhovskoi, V. Ya., Inzh.-fiz. Zh. Akad. Nauk. Belorussk. SSR, 5 (6), 43 (1962).

[51] Kirillin, V. A., Sheindlin, A. E., and Chekhovskoi, V. Ya., Int. J. Heat Mass Transfer, 5, 1 (1962).

[52] Rudkin, R. L., Parker, W. J., and Jenkins, R. J., Measurements of Thermal Properties of Metals at Elevated Temperatures, in Temperature, Its Measurement and Control in Science and Industry, Vol. III, C. M. Herzfeld, Ed., Reinhold, New York, Part 2, p. 523 (1962).

[53] Schick, H. L., (Ed.) in Thermodynamics of Certain Refractory Compounds, Academic Press, New York, Vol. II, p. 161 (1966).

[54] Kirillin, V. A., Shiendlin, A. E., and Chekhovskoi, V. Ya., Enthalpy and Heat Capacity of Some Solid Materials at Extremely High Temperatures, in IUPAC High Temperature Technology, Proc. Int. Symp. High Temp. Tech. held at Pacific Grove, CA, p. 471 (1963).

[55] Lowenthal, G. C., Aust. J. Phys., 16 (1), 47 (1963).

[56] Conway, J. B., Hein, R. A., Fincel, R. M., Jr., and Losekamp, A. C., G.E. Advanced Technology Series, 1964 Ann. Mtg. Metall. Soc. AIME, Paper TM 64-2-8 (19 Feb. 1964).

[57] Kraftmakher, Ya. A., Soviet Physics-Solid State, 6 (2), 396 (1964); (translated from Fiz. Tverd. Tel., 6 (2), 503 (1964).

[58] Taylor, R. E., and Finch, R. A., J. Less-Common Metals, 6, 283 (1964).

[59] Cezairliyan, A., A High-Speed (Millisecond) Method for the Simultaneous Measurement of Enthalpy, Specific Heat, and Resistivity of Electrical Conductors at High Temperatures, in Advances in Thermophysical Properties at Extreme Temperatures and Pressures, p. 253, ASME, New York, (1965).

[60] Filippov, L. P., and Yurchak, R. P., High Temperature (USSR), 3 (6), 837 (1965); (translated from Teplofiz. Vys. Temp., 3 (6), 901 (1965)).

[61] JANAF Thermochemical Tables 2nd edition, NSRDS-NBS 37, June 1971, for sale by Superintendent of Documents, Washington, DC.

[62] Kraftmakher, Ya. A., Rab. Fiz. Tverd. Tela., 1, 37 (1967).

[63] Chekhovskoi, V. Ya., and Petrov, V. A., High Temperature (USSR), 6 (4), 717 (1968); (translated from Teplofiz. Vys. Tem., 6 (4), 752 (1968)).

[64] Filippov, L. P., Arutyunov, A. V., Makarenko, I. N., Mardykin, L. N., Trukhanova, L. N., and Khusainova, B. N., Tr. Vses. Nauch.-Tekh. Konf. Termodin. Sb. Dokl. Sekts. "Termodin. Fazovykh Perekhodov, Potoka Neobratimykh Protsessov" i "Teplofiz. Svoistva Veschestv." 3rd, p. 242 (1968, publ. 1969).

[65] Khusainova, B. N., and Filippov, L. P., High Temperature (USSR), 6 (5), 891 (1968); (translated from Teplofiz. Vys. Tem., 6 (5), 929 (1968)).

[66] Kirillin, V. A., Sheindlin, A. E., Chekhovskoi, V. Ya., and Petrov, V. A., Enthalpy and Heat Capacity of Molybdenum at Extremely High Temperatures, in Proc. 4th Symp. on Thermophys. Prop., J. R. Moszynski (Ed.), ASME, New York, p. 54 (1968).

[67] Kirillin, V. A., Sheindlin, A. E., Chekhovskoi, V. Ya., and Petrov, V. A., Tr. Vses. Nauch.-Tekh. Konf. Termodin., Sb. Dokl. Sekts. "Teplofiz. Svoistva Veshchestv" 3rd, p. 80 (1968, publ. 1969).

[68] Chekhovskoi, V. Ya., Sheindlin, A. E., and Berezin, B. Ya., High Temp.-High Press., 2 (3), 301 (1970).

[69] Makarenko, I. N., Trukhanova, L. N., and Filippov, L. P., High Temperature (USSR), 8 (2), 416 (1970); (translated from Teplofiz. Vys. Temp., 8 (2), 445 (1970)).

[70] Sheindlin, A. E., Chekhovskoi, V. Ya., and Shpil'rain, E. E., High Temp.-High Press., 2 (1), 1 (1970).

[71] Touloukian, Y. S., and Buyco, E. H., Specific Heat: Metallic Elements and Alloys, in Thermophysical Properties of Matter, The TPRC Data Series, Touloukian, Y. S., and Ho, C. Y. (Eds.), IFI, Plenum, New York (1970).

[72] Berezin, B. Ya., Chekhovskoi, V. Ya., and Sheindlin, A. E., High Temp.-High Press., 3 (3), 287 (1972).

[73] Chekhovskoi, V. Ya., and Berezin, B. Ya., Inzh.-Fiz. Zh., 21 (2), 309 (1971).

[74] Dikhter, I. Ya., and Lebedev, S. V., High Temperature (USSR), 9 (5), 845 (1971); (translated from Teplofiz. Vys. Temp., 9 (5), 929 (1971)).

[75] Ishihara, S., and Douglas, T. B., National Bureau of Standards Report No. 10481, National Bureau of Standards, U.S. Department of Commerce, (July 1, 1971).

[76] Oetting, F. L., and Navratil, J. D., J. Chem. Eng. Data, 17 (2), 230 (1972).

[77] Bondarenko, V. P., Fomichev, E. N., and Kandyba, V. V., High Temp.-High Press., 5 (1), 5 (1973).

[78] Douglas, T. B., and Ditmars, D. A., National Bureau of Standards Internal Report No. 73-280, National Bureau of Standards, U.S. Department of Commerce, (January 1, 1973).

[79] Kraftmakher, Ya. A., High Temp.-High Press., 5 (4), 433 (1973).

[80] Mebed, M. M., Yurchak, R. P., and Filippov, L. P., High Temp.-High Press., 5 (3), 253 (1973).

[81] Chekhovskoi, V. Ya., and Kalinchina, R. G., Russ. J. Phys. Chem., 49 (3), 431 (1975); (translated from Zh. Fiz. Khim., 49 (3), 740 (1975)).

[82] Fedorov, V. B., High Temperature (USSR), 13 (3), 608 (1975); (translated from Teplofiz. Vys. Temp., 13 (3), 666 (1975)).

[83] Bean, C. P., DeBlois, R. W., and Nesbitt, L. B., J. App. Phys., 30 (12), 1976 (1959).

[84] LePage, J., Bernalte, A., and Lindholm, D. A., Rev. Sci. Inst., 39 (7), 1019 (1968).

[85] Hellenthal, W., and Uelhoff, W., Z. Angew. Phys., 21 (6), 535 (1966).

[86] Eastman, E. C., Williams, A. M., and Young, T. F., J. Am. Chem. Soc., 46, 1185 (1924).

[87] Van Voorhis, C. C., Phys. Rev., 30, 318 (1927).

[88] Campbell, I. E., (Ed.), High Temperature Technology, John Wiley and Sons, Inc., 1956.

[89] Hoch, M., High Temp.-High Press., 1 (5), 531 (1969).

APPENDIX

Table A1

Calculation[a] of estimated impurity levels in OSRM SRM-781
6.35-mm-O.D. molybdenum rod, specimen no. 12[d]

Element	Impurity Level		Atomic contribution to resistivity at 4 K[b]	Total contribution to resistivity at 4 K
	mass %	atom %	μΩ·cm/at.%	μΩ·cm
Fe	0.01	0.017	0.8	0.0136
Ni	0.01	0.016	0.8	0.0128
Co	0.01	0.016	0.8	0.0128
Al	0.01	0.036	0.3	0.0108
				Σ = 0.0500
W	0.0586	0.0307		
Ta	0.0579	0.0307		
Nb	0.0297	0.0307		
Zr	0.0292	0.0307		
	Σ = 0.216 mass %.			

$$RRR = \frac{\rho_{273\,K}}{\rho_{4\,K}} = \frac{4.84}{0.05 + (0.3)\cdot 4x} = 55.8\,[c]$$

$$x = 0.0307 \text{ at.\%}$$

[a] See text, section 2.1.c, for a description of the assumptions underlying this calculation.

[b] Value for Ni from reference [6].
Values for Fe, Co, Al estimated.

[c] Value for $\rho_{273\,K}$ of W from reference [7].

[d] This specimen number refers to table 3.

Table A2

Enthalpy data for two empty (90 Pt-10 Rh) containers

T^a/K	$(H_T-H_{273.15})$(meas.)/J		ΔH(meas.)-ΔH(smooth)^b/J	T^a/K	$H_T-H_{273.15}$ (meas.)/J		ΔH(meas.)-ΔH(smooth)^b/J
	Container 1	Container 2			Container 1	Container 2	
323.15	— —	90.67 90.21	+0.79 +0.33	773.15	955.15 954.75	— —	+1.09 +0.59
359.15	156.26 155.69	— —	+0.46 -0.11	823.15	— —	1050.18 1052.21	-4.32 -2.29
423.15	— —	273.57 273.92	-1.26 -0.91	873.15	1156.64 1156.24	— —	+0.83 +0.43
473.15	369.79 370.00	— —	+0.64 +0.85	923.15	— —	1259.54 1260.75	+1.54 +2.75
523.15	— —	464.00 464.57	-0.46 +0.11	973.15	1360.59 1360.38	— —	-0.50 -0.71
573.15	560.37 559.35	— —	-0.32 -1.34	1023.15	— —	1465.60 1464.14	+0.48 -0.98
623.15	— —	659.13 657.64	+1.35 -0.14	1073.15	1570.19 1569.03	— —	+0.09 -1.07
673.15	756.37 756.97	— —	+0.67 +1.27	1123.15	— —	1676.96 1676.14	+0.89 +0.07
723.15	— — — —	854.99 854.56 853.88 854.21	+0.53 +0.10 -0.58 -0.25	1173.15	1783.31 1782.61	— —	+0.25 -0.45

[a] International Practical Temperature Scale of 1968 [13].

[b] $\Delta H = H_T - H_{273.15}$; the "smooth" values are those given by equation (1).

Table A3

Hemispherical total emittance of the SRM-781 molybdenum specimen in the temperature range 1730 to 2760 K

Code Symbol[a]	$\frac{T}{\mathrm{K}}$[b]	ε	Code Symbol	$\frac{T}{\mathrm{K}}$	ε
B	1730	0.242	D	2655	0.318
A	1733	0.233	E	2658	0.316
B	1912	0.257	A	2663	0.308
A	2066	0.256	B	2671	0.308
B	2068	0.268	F	2673	0.316
A	2323	0.276	D	2706	0.321
B	2344	0.278	D	2760	0.324
C	2655	0.310			

[a] Indicates the experiments from which the emittance data were derived according to the following code:

A: Specimen D1, experiments 1, 3-5
B: Specimen D1, experiments 6-10
C: Specimen D1, experiment 11
D: Specimen D1, experiments 12-14
E: Specimen D2, experiment 19
F: Specimen D3, experiment 31

[b] IPTS-68[13].

Table A4

Corrections for molybdenum (s) to convert enthalpy and heat-capacity data between IPTS-48 and IPTS-68 temperature scales[a]

T_{48} or T_{68}	$H_{48}-H_{68}$	$(C_p)_{48}-(C_p)_{68}$	T_{48} or T_{68}	$H_{48}-H_{68}$	$(C_p)_{48}-(C_p)_{68}$
K	$J\cdot mol^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$	K	$J\cdot mol^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$
300	- 0.2	-0.004	1550	+ 57.2	+0.071
350	- 0.2	-0.006	1600	+ 60.9	+0.075
400	+ 0.3	+0.011	1650	+ 64.7	+0.078
450	+ 0.8	+0.012	1700	+ 68.7	+0.082
500	+ 1.4	+0.010	1750	+ 72.9	+0.086
550	+ 1.8	+0.006	1800	+ 77.3	+0.090
600	+ 2.0	+0.003	1850	+ 81.9	+0.094
650	+ 2.1	0.000	1900	+ 86.7	+0.099
700	+ 2.0	-0.001	1950	+ 91.7	+0.104
750	+ 2.1	+0.003	2000	+ 97.0	+0.108
800	+ 2.4	+0.012	2050	+102.6	+0.114
850	+ 3.4	+0.029	2100	+108.4	+0.119
900	+ 5.4	+0.054	2150	+114.5	+0.125
950	+ 9.2	+0.078	2200	+120.9	+0.131
1000	+13.2	+0.081	2250	+126.7	+0.137
1050	+17.3	+0.083	2300	+134.6	+0.144
1100	+21.5	+0.086	2350	+142.0	+0.151
1150	+25.8	+0.089	2400	+149.7	+0.158
1200	+30.3	+0.091	2450	+157.8	+0.166
1250	+35.0	+0.094	2500	+166.3	+0.177
1300	+39.8	+0.098	2550	+175.5	+0.190
1350	+44.2	+0.059	2600	+185.4	+0.206
1400	+47.3	+0.062	2650	+196.2	+0.225
1450	+50.4	+0.065	2700	+208.0	+0.248
1500	+53.7	+0.068	2750	+221.0	+0.274
			2800	+235.5	+0.304

[a] Calculated from reference [12].

Table A5

Enthalpy relative to 273.15 K and heat capacity of SRM-781 molybdenum computed from equations (8) and (7)

T^a/K	$C_p^{\circ b}$/$J \cdot mol^{-1} \cdot K^{-1}$	$H_T^\circ - H^\circ_{273.15}$/$J \cdot mol^{-1}$	T/K	C_p°/$J \cdot mol^{-1} \cdot K^{-1}$	$H_T^\circ - H^\circ_{273.15}$/$J \cdot mol^{-1}$
273.15	23.56	0.00	720	27.07	11472.
275	23.58	43.60	740	27.17	12014.
280	23.66	161.72	760	27.26	12558.
285	23.74	280.21	780	27.35	13104.
290	23.81	399.07	800	27.44	13652.
295	23.88	518.29	820	27.53	14202.
298.15	23.92	593.59	840	27.62	14754.
300	23.95	637.87	860	27.71	15307.
305	24.02	757.80	880	27.80	15862.
310	24.09	878.06	900	27.89	16419.
315	24.15	998.66	920	27.98	16978.
320	24.22	1119.6	940	28.08	17538.
325	24.28	1240.8	960	28.17	18101.
330	24.34	1362.4	980	28.27	18665.
335	24.40	1484.2	1000	28.37	19232.
340	24.46	1606.4	1020	28.47	19800.
345	24.52	1728.8	1040	28.57	20370.
350	24.58	1851.6	1060	28.68	20943.
355	24.63	1974.6	1080	28.78	21517.
360	24.69	2097.9	1100	28.90	22094.
370	24.79	2345.3	1120	29.01	22673.
373.15	24.82	2423.4	1140	29.12	23255.
380	24.89	2593.7	1160	29.24	23838.
390	24.99	2843.1	1180	29.36	24424.
400	25.08	3093.4	1200	29.49	25013.
410	25.17	3344.7	1250	29.81	26495.
420	25.26	3596.9	1300	30.14	27994.
430	25.34	3849.8	1350	30.50	29510.
440	25.42	4103.6	1400	30.86	31044.
450	25.50	4358.2	1450	31.25	32597.

Table A5 (Continued)

Enthalpy relative to 273.15 K and heat capacity of SRM-781 molybdenum computed from equations (8) and (7)

$\frac{T^a}{K}$	$\frac{C_p^{\circ b}}{J \cdot mol^{-1} \cdot K^{-1}}$	$\frac{H_T^{\circ} - H_{273.15}^{\circ}}{J \cdot mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p^{\circ}}{J \cdot mol^{-1} \cdot K^{-1}}$	$\frac{H_T^{\circ} - H_{273.15}^{\circ}}{J \cdot mol^{-1}}$
460	25.57	4613.6	1500	31.65	34169.
470	25.64	4869.7	1550	32.07	35762.
480	25.72	5126.5	1600	32.50	37376.
490	25.78	5384.0	1650	32.95	39012.
500	25.85	5642.2	1700	33.42	40671.
510	25.92	5901.0	1750	33.91	42354.
520	25.98	6160.5	1800	34.42	44062.
530	26.05	6420.6	1850	34.94	45796.
540	26.11	6681.4	1900	35.49	47557.
550	26.17	6942.8	1950	36.06	49346.
560	26.23	7204.8	2000	36.65	51163.
570	26.29	7467.4	2050	37.26	53011.
580	26.35	7730.6	2100	37.90	54890.
590	26.40	7994.3	2150	38.55	56801.
600	26.46	8258.7	2200	39.24	58746.
610	26.52	8523.5	2250	39.94	60725.
620	26.57	8789.0	2300	40.67	62740.
630	26.62	9054.9	2350	41.43	64793.
640	26.68	9321.4	2400	42.21	66884.
650	26.73	9588.4	2450	43.03	69015.
660	26.78	9856.0	2500	43.89	71188.
670	26.83	10124.	2550	44.84	73406.
680	26.88	10392.	2600	45.88	75673.
690	26.93	10661.	2650	47.05	77996.
700	26.98	10931.	2700	48.37	80381.
			2750	49.87	82836.
			2800	51.57	85371.

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[a] IPTS-68 [13].

[b] Atomic weight = 95.94 [25].

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16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

The relative enthalpy of NBS Standard Reference Material No. 781 (99.95 mass-percent pure, polycrystalline molybdenum: a metallic, high-temperature enthalpy and heat-capacity standard) has been measured with two differently designed, receiving-type calorimeters in the temperature ranges 273 to 1173 K and 1173 to 2100 K, respectively. The smoothed enthalpy data derived from these measurements are believed to have an inaccuracy not exceeding 0.6 percent at any temperature in these ranges. The heat capacity of Standard Reference Material No. 781 has also been measured in the temperature range 1500 to 2800 K using a millisecond - resolution pulse technique with resistive self-heating. This technique measured, in addition, hemispherical total emittance. In this highest temperature range, the smoothed heat-capacity data are believed to be in error by no more than 3 percent. A complete description of all the NBS experimental techniques and a detailed analysis of all suspected sources of errors are presented. Equations representing the smoothed NBS enthalpy and heat-capacity data for SRM-781 molybdenum in the range 273.15 to 2800 K are presented along with a table of these data calculated from the equations at selected temperatures. A bibliography of all known publications on the enthalpy and heat capacity of molybdenum has been compiled. The NBS-measured enthalpy and heat-capacity data for molybdenum have been compared with those of all the principal investigators and compilers reported in the literature.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)* Drop calorimetry; emittance; enthalpy; heat capacity; high-speed measurements; high temperature; molybdenum; pulse calorimetry; standard reference material; thermodynamic functions.

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