U.S. Department of Commerce
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National Bureau of Standards
Certificate

Standard Reference Material 781

Molybdenum - Heat Capacity

Relative Enthalpy and Heat Capacity from 273.15 to 2800 K

T[a]	$H_T-H_{273.15}$	C_p	T	$H_T-H_{273.15}$	C_p
K	$J\cdot mol^{-1}$[b]	$J\cdot mol^{-1}\cdot K^{-1}$	K	$J\cdot mol^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$
273.15	0.00	23.56	420	3596.9	25.26
280	161.72	23.66	440	4103.6	25.42
290	399.07	23.81	460	4613.6	25.57
298.15	593.59	23.92	480	5126.5	25.72
300	637.87	23.95	500	5642.2	25.85
320	1119.6	24.22	550	6942.8	26.17
340	1606.4	24.46	600	8258.7	26.46
360	2097.9	24.69	650	9588.4	26.73
380	2593.7	24.89	700	10931	26.98
400	3093.4	25.08	750	12286	27.21

(Table continued on inside of certificate)

[a]Temperature expressed on IPTS-68 scale.
[b]Relative atomic mass (atomic weight) = 95.94.

The tabulated enthalpy values up to 1200 K are believed to have an inaccuracy not exceeding ±0.3 percent, while in this temperature range, the inaccuracy in the heat capacity is not thought to exceed ±0.5 percent. Between 1200 K and 1850 K, the inaccuracies in the enthalpy and heat capacity are estimated not to exceed ±0.6 percent and ±1.0 percent, respectively. The inaccuracy in the heat capacity at 2000 K is estimated to be no greater than ±2 percent and at 2800 K, no greater than ±3 percent. These limits on inaccuracy of the measured data represent a linear sum of random error calculated at a 99-percent confidence level and the estimated maximum systematic error.

These smoothed enthalpy and heat-capacity values were derived from enthalpy measurements in the range 273.15 to 2100 K, made by D. A. Ditmars, S. Ishihara and T. B. Douglas, and from heat-capacity measurements in the range 1500 to 2800 K, made by A. Cezairliyan, all of the NBS Physical Chemistry Division.

The technical and support aspects involved in the preparation, certification and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis and R. K. Kirby.

Washington, D.C. 20234
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J. Paul Cali, Chief
Office of Standard Reference Materials

Relative Enthalpy and Heat Capacity (continued)

T^a	$H_T - H_{273.15}$	C_p	T	$H_T - H_{273.15}$	C_p
K	$J \cdot mol^{-1}$ [b]	$J \cdot mol^{-1} \cdot K^{-1}$	K	$J \cdot mol^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$
800	13652	27.44	1800	44062	34.42
850	15030	27.67	1850	45796	34.94
900	16419	27.89	1900	47557	35.49
950	17819	28.12	1950	49346	36.06
1000	19232	28.37	2000	51163	36.65
1050	20656	28.62	2050	53011	37.26
1100	22094	28.90	2100	54890	37.90
1150	23546	29.18	2150	56801	38.55
1200	25013	29.49	2200	58746	39.24
1250	26495	29.81	2250	60725	39.94
1300	27994	30.14	2300	62740	40.67
1350	29510	30.50	2350	64793	41.43
1400	31044	30.86	2400	66884	42.21
1450	32597	31.25	2450	69015	43.03
1500	34169	31.65	2500	71188	43.89
1550	35762	32.07	2550	73406	44.84
1600	37376	32.50	2600	75673	45.88
1650	39012	32.95	2650	77996	47.05
1700	40671	33.42	2700	80381	48.37
1750	42354	33.91	2750	82836	49.87
			2800	85371	51.57

[a]Temperature expressed on IPTS-68 scale.

[b]Relative atomic mass (atomic weight) = 95.94.

The enthalpy and heat-capacity values are tabulated at intervals such that three-point interpolation will produce an error of less than one in the last figure. NOTE: More significant figures have been stated than are justified by the accuracy of the measurements.

This molybdenum was obtained from the General Electric Company where it was made by sintering high-purity powder, swaging and grinding to final diameter (two diameters are available: 3.2 mm, SRM 781-D1; and 6.4 mm, SRM 781-D2), and annealing at 1725 K under high vacuum. Spark source mass spectrometry measurements indicate a purity of at least 99.95 wt. %. The residual electrical resistance ratio was found to be about 70.

All enthalpy and heat-capacity measurements were made on specimens chosen at random from the lot of material available for SRM 781. The enthalpy measurements were made with two different receiving calorimeters. Ten measurements were made between 273.15 and 1173.15 K with a Bunsen ice calorimeter [1,2] and 24 measurements were made between 1170.4 and 2102.4 K with an adiabatic receiving calorimeter [3]. Heat-capacity measurements were made in the range 1500 to 2800 K using a high-speed (millisecond) pulse-heating technique [4].

The smooth enthalpy and heat-capacity functions and the tabulated enthalpy and heat-capacity values for SRM 781 were derived from the foregoing measurements in the following way: The enthalpy data in the range 273.15 to 1173.15 K were fitted by the method of least squares with a single smooth function having four constants and of a form chosen to minimize the standard deviation of residues in this range. Similarly, the enthalpy data in the range 1173.15 to 2102.4 K were fitted with a (different) smooth function having five constants. Differentiation of these two functions yielded heat-capacity functions corresponding to the two temperature ranges. Heat-capacity values were calculated from these functions at 50 K intervals in the range 273.15 to 2100 K. These smooth heat-capacity values were pooled with the averaged pulse-calorimetric heat-capacity data taken at 50 K intervals in the range 1500 to 2800 K. The pooled heat-capacity data were then fitted with a cubic spline function having four knots and of the form,

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

where $(T-\theta_\nu)_+ \equiv 0$ for $T \leq \theta_\nu$.

In this fitting process, the method of least squares was used. The knots, θ_ν were chosen near suspected inflection points in the heat-capacity function or near overlap temperatures of the different experimental techniques. The data were weighted inversely to their estimated overall uncertainty.

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

$a_0 = +1.6078753 \times 10^{+1}$

$a_1 = +4.2064833 \times 10^{-2}$

$a_2 = -6.4321802 \times 10^{-5}$

$a_3 = +3.8567377 \times 10^{-8}$

$b_1 = -3.2183846 \times 10^{-8}$; $\theta_1 = 500$ K

$b_2 = -6.2727966 \times 10^{-9}$; $\theta_2 = 1000$ K

$b_3 = +6.5829329 \times 10^{-10}$; $\theta_3 = 1500$ K

$b_4 = +3.2467912 \times 10^{-8}$; $\theta_4 = 2400$ K

The standard deviation of residues of the heat-capacity data for this spline function is 0.058 $J{\cdot}mol^{-1}{\cdot}K^{-1}$, 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,

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

corresponding to each of the five temperature intervals defined by the four knots. These functions for C_p units $J{\cdot}mol^{-1}{\cdot}K^{-1}$ are given below:

273.15 to 500 K; $C_p = 16.079 + 4.2065{\cdot}10^{-2}\,T - 6.4322{\cdot}10^{-5}T^2 + 3.8567{\cdot}10^{-8}T^3$

500 to 1000 K; $C_p = 20.102 + 1.7927{\cdot}10^{-2}T - 1.6046{\cdot}10^{-5}T^2 + 6.384{\cdot}10^{-9}T^3$

1000 to 1500 K; $C_p = 26.374 - 8.914{\cdot}10^{-4}T + 2.772{\cdot}10^{-6}T^2 + 1.107{\cdot}10^{-10}T^3$

1500 to 2400 K; $C_p = 24.153 + 3.552{\cdot}10^{-3}T - 1.900{\cdot}10^{-7}T^2 + 7.6903{\cdot}10^{-10}T^3$

2400 to 2800 K; $C_p = -424.684 + 5.645976{\cdot}10^{-1}T - 2.3395893{\cdot}10^{-4}T^2 + 3.323694{\cdot}10^{-8}T^3$

The enthalpy of SRM 781 relative to its enthalpy at 273.15 K can be obtained by integration of these heat-capacity functions. This integration yields enthalpy functions of the form,

$$H_T - H_{273.15} = \sum_{\nu=0}^{4} d_\nu T^\nu .$$

These functions for H units $J \cdot mol^{-1}$ are given below:

273.15 to 500 K; $H_T - H_{273.15} = -5577.87 + 16.07875\ T + 2.10324 \cdot 10^{-2} T^2 - 2.14406 \cdot 10^{-5} T^3 + 9.6418 \cdot 10^{-9} T^4$

500 to 1000 K; $H_T - H_{273.15} = -6080.74 + 20.10173\ T + 8.96347 \cdot 10^{-3} T^2 - 5.34868 \cdot 10^{-6} T^3 + 1.59588 \cdot 10^{-9} T^4$

1000 to 1500 K; $H_T - H_{273.15} = -7648.95 + 26.37453\ T - 4.4572 \cdot 10^{-4} T^2 + 9.2412 \cdot 10^{-7} T^3 + 2.76836 \cdot 10^{-11} T^4$

1500 to 2400 K; $H_T - H_{273.15} = -6815.80 + 24.15279\ T + 1.77602 \cdot 10^{-3} T^2 - 6.33211 \cdot 10^{-8} T^3 + 1.92257 \cdot 10^{-10} T^4$

2400 to 2800 K; $H_T - H_{273.15} = 262486.05 - 424.68363\ T + 2.8229878 \cdot 10^{-1} T^2 - 7.7986310 \cdot 10^{-5} T^3 + 8.3092350 \cdot 10^{-9} T^4$

References

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[3] E. D. West and S. Ishihara, "Advances in Thermophysical Properties at Extreme Temperatures and Pressures," pp. 146-149 (1965), The American Society of Mechanical Engineers, 345 East 47th Street, New York New York 10017.

[4] A. Cezairliyan, J. Res. Nat. Bur. Std., **75C (1), 7** (1971).