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Correction of Specific Heat in Isobaric Expansion Data

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We have measured unusually high specific heats for liquid metals using the isobaric expansion apparatus at Lawrence Livermore National Laboratory. In an effort to improve the pyrometer used in the facility, the cause of this discrepancy was discovered. The properties of liquid tantalum have since been remeasured, which can be expressed by:

$$H = 0.15002 + 1.0164 \times 10^{-4}T + 2.1476 \times 10^{-8}T^2$$

$$V/V_0 = 1.0545 - 3.5578 \times 10^{-6}T + 9.9015 \times 10^{-9}T^2$$

$$\rho = 1.3068 - 4.6420 \times 10^{-5}T + 1.3163 \times 10^{-8}T^2$$

over the range 3270 K $\leqslant T \leqslant$ 7250 K, where H is enthalpy in $\mathrm{MJ \cdot kg^{-1}}$ relative to the value at 300 K and 0.1 GPa, ρ is the resistivity in $\mu\Omega \cdot \mathrm{m}$, and V_0 is the specific volume at STP ($6.024 \times 10^{-5}\ \mathrm{m^3 \cdot kg^{-1}}$).

KEY WORDS: electrical resistivity; high temperature; specific heat; tantalum; thermal expansion.

1. INTRODUCTION

In using the isobaric expansion (IEX) apparatus at Lawrence Livermore National Laboratory to measure high temperature thermophysical properties of metals [1–7], a consistent pattern in the specific heats in the liquid range (the principal region of measurement for the apparatus) was observed: they were surprisingly high. In an effort to improve the pyrometer used in the IEX apparatus, the cause of this behavior was discovered—a systematic error in the calibrating apparatus. The calibrating apparatus was

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redesigned. The data are recorded on oscilloscopes, and the recorded voltages from the pyrometer must be related to relative light intensity by a transfer function determined from calibrations made before each experiment. The transfer function for each channel is determined by using a series of neutral-density filters to attenuate the output of an argon ion laser beam at a wavelength of 514.5 nm, thus producing a series of deflection steps on the recording oscilloscopes. The absolute transfer function is not needed since results are normalized to a known temperature at a point on the data traces.

The intensity of light relative to the intensity of the argon ion laser beam was determined from the neutral density of each filter. The resulting group of relative light intensity versus output voltage points was then spline fitted to produce a transfer function. The redesigned calibration apparatus incorporated precision neutral-density filters on glass substrates to eliminate possible problems with local heating and bowing of the filters. The neutral density of each filter at the calibrating wavelength was taken from monochromator data supplied by the manufacturer.

A number of experiments on tantalum were performed using the redesigned apparatus, and a consistent discrepancy between the new results and the previous results was observed. The new specific heat data are about 14% lower than the old data. We measured the neutral densities of both new and old filters at the calibrating wavelength using a monochromator. Table I shows the results for the new filters, and Table II shows the results for the old. The measured values for the new filters are in reasonably good agreement with the manufacturer's data. The measured values for the old filters are consistently higher than the nominal values previously used. The average discrepancy is about 8%. As an experiment, the new tantalum data

Table I. Neutral Densities of New Filters at 514.5 nm

Nominal	Measured	Manufacturer's data	% Difference
0.1	0.106	0.100	+ 5.66
0.2	0.193	0.197	− 2.07
0.3	0.263	0.274	− 4.18
0.6	0.595	0.607	− 2.02
1.0	0.982	1.012	− 3.06
1.3	1.33	1.315	+ 1.13
2.0	2.00	2.025	− 1.25
2.3	2.28	2.300	− 0.877
2.6	2.60	2.585	+ 0.577
3.0	2.98	3.002	− 0.738
3.3	3.22	3.242	− 0.683
3.6	3.61	3.635	− 0.693

Table II. Neutral Densities of Old Filters at 514.5 nm

Nominal	Measured	% Difference
0.3	0.32	+6.67
0.6	0.66	+ 10.0
1.0	1.10	+ 10.0
1.3	1.43	+ 10.0
1.6	1.73	+8.12
2.0	2.10	+5.00
2.3	2.47	+7.39
2.6	2.80	+7.69
3.0	3.25	+8.33
3.3	3.50	+6.06
3.6	3.90	+8.33

were reprocessed using neutral density values that were reduced by 8%. The results were in good agreement with the old data, indicating that the observed discrepancy in specific heat is attributed to an error in the calibration of the filters.

2. NEW RESULTS

New data for the properties of tantalum were combined with the previously reported volume and resistivity data [3]. The new measurements were made at a pressure of 0.3 GPa and the previous ones at a pressure of 0.1 GPa; but this is of no consequence since the compressibility of tantalum is too low to allow one to distinguish between the two different isobars. Properties in the solid range remained unchanged. They were chosen to give good agreement with the 1973 Hultgren tables [8] since the accuracy of the pyrometer near the threshold is difficult to judge. Table III gives the new results. One resistivity value at 2750 K was revised since it appeared to represent a typographical error. An extra, though not significant, decimal place was retained in the volumes for smooth plotting. The revised properties for the liquid range are described adequately by

$$H = 0.15002 + 1.0164 \times 10^{-4}T + 2.1476 \times 10^{-8}T^2 \tag{1}$$

$$V/V_0 = 1.0545 - 3.5578 \times 10^{-6}T + 9.9015 \times 10^{-9}T^2 \tag{2}$$

$$\rho = 1.3068 - 4.6420 \times 10^{-5}T + 1.3163 \times 10^{-8}T^2 \tag{3}$$

$$(3270 \text{ K} \leqslant T \leqslant 7250 \text{ K})$$

where V_0 is the specific volume at STP (6.024×10^{-5} m$^3 \cdot$ kg^{-1}), H is the

Table III. Thermophysical Data for Tantalum[a]

H (MJ · kg^{-1})	T (K)	V/V_0	ρ ($\mu\Omega \cdot$ m)
0.30	2200	1.050	0.87
0.40	2750	1.066	1.00
0.50	3200	1.086	1.13
0.52(s)	3270	1.091	1.14
0.72(l)	3270	1.150	1.29
0.80	3616	1.172	1.31
0.90	4011	1.199	1.34
1.00	4378	1.227	1.36
1.10	4718	1.257	1.38
1.20	5036	1.287	1.41
1.30	5334	1.316	1.43
1.40	5619	1.346	1.46
1.50	5892	1.378	1.49
1.60	6160	1.411	1.52
1.70	6425	1.443	1.55
1.80	6693	1.476	1.58
1.90	6966	1.511	1.62
2.00	7250	1.545	1.67
2.10	—	1.580	1.71
2.20	—	1.617	—
2.30	—	1.653	—

[a] $V_0 = 6.024 \times 10^{-5}$ m$^3 \cdot$ kg^{-1}; $T_m = 3270$ K; $\rho_0 = 0.125$ $\mu\Omega \cdot$ m; $P = 0.1$ GPa.

enthalpy in MJ · kg^{-1} relative to the value at 300 K and 0.1 GPa, ρ is the electrical resistivity in $\mu\Omega \cdot$ m, and temperatures (T) are in degrees kelvin.

The data corresponding to three successive experiments are shown in Fig. 1. The solid curve in the liquid range represents the values in Table III. The dotted curve marked "old result" corresponds to the values reported in ref. 3. Also shown in Fig. 1 are the Hultgren table [8] values for the solid range, along with the results of Berezin and Chekhovskoi [9] in the temperature interval 2400 K to melt. The heat of fusion is compared with the result of Lebedev et al. [10]. Figure 2 shows the thermal expansion results. The curve in the solid range corresponding to Table III is compared with the x-ray data of Waseda et al. [11], the interferometric measurements of Miiller and Cezairliyan [12], and the dilatometric measurements of V'yugov and Gumenyuk [13]. Figure 3 shows the electrical resistivity. The measurements of Cezairliyan et al. [14] are shown for comparison.

3. DISCUSSION

The discovery of a systematic error in the pyrometry results reported in refs. 1–7 suggests that a moderately easy correction could be developed.

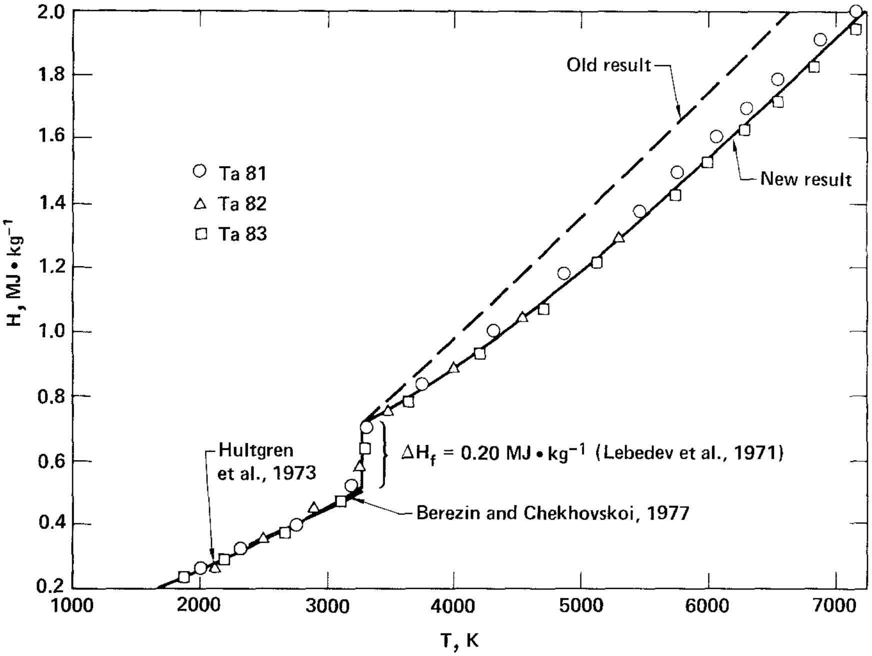

Fig. 1. Enthalpy vs temperature for tantalum. In the liquid range, the dashed curve corresponds to the results reported in ref. 3. The solid curve is described by Eq. (1). The heat of fusion is compared with that in ref. 10. The results in the solid range are compared with those in refs. 8 and 9.

The signal seen at the output of a single channel of the pyrometer used in the IEX apparatus may be described by

$$I(T) = G\int \epsilon(\lambda, T)D(\lambda)B(\lambda)W(\lambda, T)\,d\lambda \tag{4}$$

where $W(\lambda, T)$ is the blackbody spectrum; $D(\lambda)$ is the relative response of the detector; $B(\lambda)$ describes the response in the passband of the narrow-band filter used; $\epsilon(\lambda, T)$ is the emissivity of the radiator; and G is a proportionality constant that includes geometric attenuation, scattering losses, etc. The limits of integration are determined by the passband of the filter.

We may assume the emissivity is constant with wavelength in the passband and remove it outside the integrand, assigning a value corresponding to the central wavelength in the passband. As a result, we may rewrite the expression as

$$I(T) = G\epsilon(\bar{\lambda}, T)F(T) \tag{5}$$

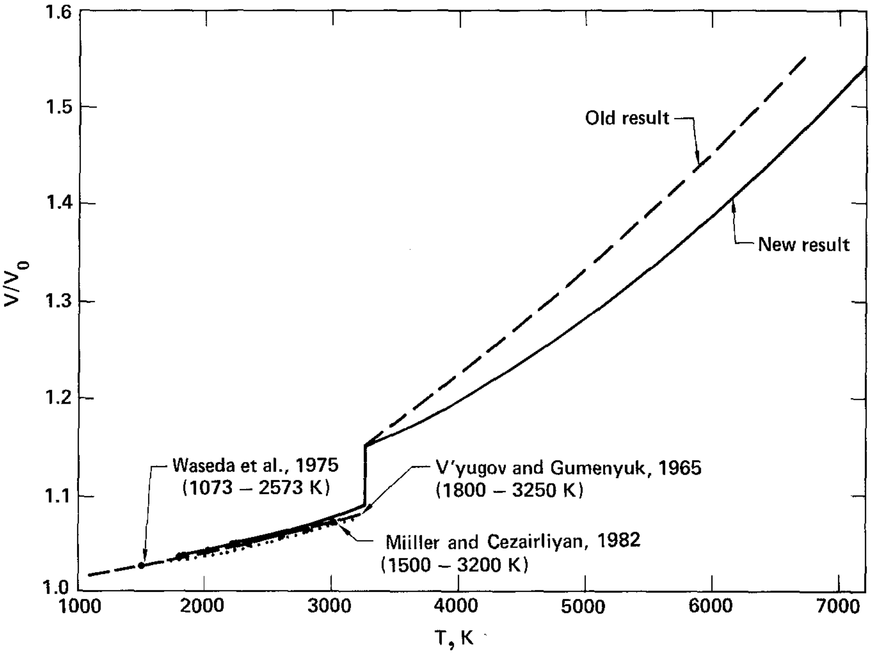

Fig. 2. Thermal expansion of tantalum. In the liquid range, the dashed curve corresponds to the results reported in ref. 3. The solid curve is described by Eq. (2). The solid region is compared with that reported in refs. 11–13.

where

$$F(T) = \int D(\lambda) B(\lambda) W(\lambda, T)\, d\lambda \tag{6}$$

The function $F(T)$ is calculated in advance and is fixed for a given choice of detector and filter. It is described by numerical tables accessible to the data-reduction computer code. We assume the temperature dependence of the emissivity to be linear:

$$\epsilon(\bar{\lambda}, T) = \epsilon(\bar{\lambda}, T_c)[1 + b(T - T_c)] \tag{7}$$

where T_c is a known temperature corresponding to a specified point of the data trace. We may use the experimentally measured value of I at this point with Eq. (5) to write

$$G\epsilon(\bar{\lambda}, T_c) = I(T_c)/F(T_c) \tag{8}$$

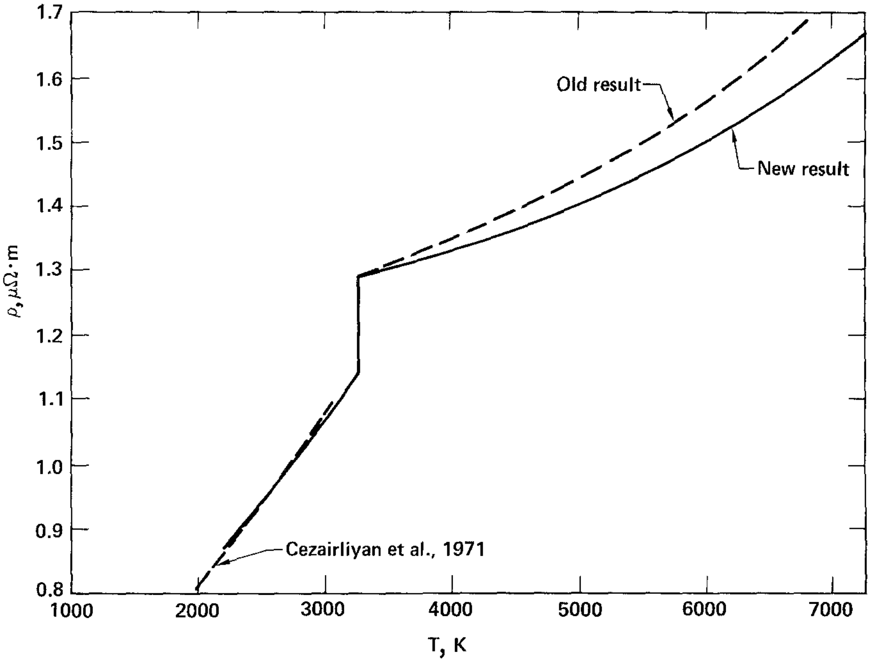

Fig. 3. Electrical resistivity of tantalum. In the liquid range, the dashed curve corresponds to the results reported in ref. 3. The solid curve is described by Eq. (3). The solid region is compared with that reported in ref. 14.

and

$$\frac{I(T)}{I(T_c)} = \frac{\epsilon(\bar{\lambda},T)}{\epsilon(\bar{\lambda},T_c)}\,\frac{F(T)}{F(T_c)} \tag{9}$$

so that

$$\frac{I(T)}{I(T_c)} = \left[1 + b(T - T_c)\right]\frac{F(T)}{F(T_c)}\,. \tag{10}$$

The left side of Eq. (10) is the experimentally determined intensity relative to the value at the calibrating point. We assign parameter b a trial value, and then use root finding methods to solve the equation for the brightness temperature at each point of the data trace. Two such channels are analyzed at the same time, considering a range of b parameters for the two channels. The combination of b values that results in the best overall agreement between the two channels is retained.

If we multiply the neutral density values in the calibrating apparatus by a constant factor β, we would, by the definition of neutral density, raise the left side of Eq. (10) to the power β. The resulting shift in the location of the root results in a new temperature. The nature of the calculation makes it difficult to predict the behavior of the root in the general case. It is evident that the temperature curve will remain pinned to the calibrating point and that some rotation of the curve will occur, but the extent of the change in shape is not evident.

In most cases, the original data are no longer available for the materials reported in refs. 1–7. As an alternative, recent data on aluminum and copper (to be published) were reprocessed to see what effect an 8% change in the neutral density filter values would have on the results. In each case the result was the same as it was for tantalum. Since there is no evident material dependence, it seems reasonable to assume that we can adjust the previously published results [1–7] by decreasing the specific heat in the liquid range by 14%.

4. SUMMARY

The pyrometer used in the IEX apparatus at Lawrence Livermore National Laboratory had a systematic error in calibration that caused unusually high specific heats. We have corrected this problem and have remeasured the data for liquid tantalum. It appears that previously reported results on specific heats in the liquid range [1–7] can be reduced by 14%.

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