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Heat Capacities, Entropies and Enthalpies of Tantalum between 12 and 550°K.[1,2]

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Heat capacities of tantalum have been measured between 12 and 550°K. with a precision of 0.15% or better. The Third Law Entropy at 25° is found to be 9.92 ± 0.01 e.u./g. atom, in good agreement with earlier work. Differences ranging up to 3% were observed between present heat capacity results and those previously published for temperatures above 325°K. Agreement between low temperature heat capacities reported here and elsewhere is somewhat better.

Several studies of intermediate metallic phases containing tantalum are under way in this Laboratory. In the course of this work it has become necessary to have precise heat capacity data for elemental tantalum in the range 10 to 550°K. Examination of the literature showed that published data, particularly for temperatures above 300°K., did not have the required precision and so the measurements reported in this paper were begun.

Experimental Details

The apparatus employed and method of measurement have been described previously.[3,4] The tantalum was purchased from the Fansteel Metallurgical Corp. and was stated to be 99.9+% pure. It was in the form of annealed, mill quality 0.006 in. thick foil. The foil was wound into a compact roll and tied with 0.003 in. strips. The strips were tantalum in the series of measurements above 320°K. but in the low temperature series molybdenum strips were inadvertently used. The mass of molybdenum used was 1.871 g. or 0.01950 g. atoms. The mass of tantalum in the low temperature series was 659.919 g. or 3.6484 g. atoms and in the high temperature series was 662.616 g. (including the tantalum strips) or 3.6633 g. atoms.

The high temperature series consisted of 37 determinations extending from 295 to 552°K. Temperature intervals ranged from 5 to 12 degrees. The low temperature series was composed of 70 determinations covering the range from 11 to 323°K. Temperature increments used were 2 degrees from 11 to 25°K., 5 degrees from 25 to 200°K. and 6 degrees from 200 to 320°K. In both series measurements were made in such a way that there was no gap between successive determinations; that is, the final temperature of one experiment was the initial temperature of the next experiment.

Correction for the molybdenum present was made using the data of Simon and Zeidler.[5]

Results

The smoothed heat capacities obtained are given in Table I. For the low temperature series the average deviation of the individual determinations from a smooth curve was 0.05% or less down to

TABLE I

SMOOTHED HEAT CAPACITIES OF TANTALUM

Temp., °K.	C_p,[a] cal./deg. g. atom	Temp., °K.	C_p,[a] cal./deg. g. atom
12	0.074	20	.338
14	.115	22	.443
15	.143	24	.564
16	.175	25	.631
18	.250	26	.703
28	0.857	290	6.029
30	1.006	295	6.039
35	1.411	298.16	6.045
40	1.824	300	6.049
45	2.228	305	6.058
50	2.592	310	6.067
55	2.936	315	6.075
60	3.245	320	6.084
65	3.520	325	6.092
70	3.755	330	6.100
75	3.972	335	6.109
80	4.170	340	6.117
85	4.348	345	6.126
90	4.499	350	6.135
95	4.623	355	6.144
100	4.737	360	6.152
105	4.841	365	6.160
110	4.941	370	6.167
115	5.026	375	6.173
120	5.106	380	6.179
125	5.177	385	6.185
130	5.242	390	6.191
135	5.302	395	6.197
140	5.360	400	6.203
145	5.404	405	6.209
150	5.449	410	6.216
155	5.492	415	6.222
160	5.533	420	6.229
165	5.569	425	6.236
170	5.603	430	6.244
175	5.633	435	6.252
180	5.661	440	6.259
185	5.689	445	6.266
190	5.715	450	6.274
195	5.739	455	6.282
200	5.761	460	6.289
205	5.783	465	6.296
210	5.804	470	6.304
215	5.822	475	6.311
220	5.839	480	6.318
225	5.855	485	6.326
230	5.872	490	6.334
235	5.888	495	6.341
240	5.903	500	6.348
245	5.917	505	6.355
250	5.931	510	6.362
255	5.943	515	6.368
260	5.955	520	6.375
265	5.967	525	6.382
270	5.980	530	6.390
273.16	5.987	535	6.397
275	5.992	540	6.404
280	6.005	543.16	6.408
285	6.017		

[a] The cal. is the defined calorie, which equals 4.1840 absolute joules.

(1) From a thesis submitted by K. F. Sterrett in partial fulfillment of the requirements for the Ph.D. degree at the University of Pittsburgh, June, 1957.

(2) This work was assisted by the U. S. Atomic Energy Commission.

(3) W. V. Johnston, K. F. Sterrett, R. S. Craig and W. E. Wallace, THIS JOURNAL, **79**, 3633 (1957).

(4) C. A. Krier, R. S. Craig and W. E. Wallace, *J. Phys. Chem.*, **61**, 522 (1957).

(5) F. Simon and W. Zeidler, *Z. physik. Chem.*, **123**, 383 (1926).

50°K., below which it rose gradually to 1.8% at 12°K. Between 295 and 545°K. the deviations averaged 0.14%. The raw data showed smooth joining of the data obtained in the low and high temperature sets of measurements. Since the two series of determinations involved two completely independent calorimeters, it appears that systematic errors are not significantly larger than the scatter of the individual points.

Third Law entropies and enthalpies relative to 0°K. are given in Table II. Extrapolations below 12°K. were made using the usual T-cubed law plus a linear term to allow for the electronic contribution. Uncertainties have been estimated from the scatter in the heat capacity data. The entropy at 298.16°K. is in excellent agreement with values reported by Clusius and Losa,[6] 9.90 ± 0.02 e.u./g. atom, and Kelley[7], 9.9 ± 0.1 e.u./g. atom.

TABLE II

THIRD LAW ENTROPIES AND ENTHALPIES RELATIVE TO 0°K. FOR TANTALUM

Temp., °K.	Entropy (e.u./g. atom)	$H_T - H_0$°K. (cal./g. atom)
12	0.03 ± 0.00 (extrapolation)	0.22 ± 0.02 (extrapolation)
273.16	9.39 ± .01	1207 ± 1
298.16	9.92 ± .01	1358 ± 1
543.16	13.64 ± .01	2885 ± 3

Deviations between the present heat capacity measurements and those obtained in earlier studies range up to 3%. Detailed comparison between the low temperature series results and those obtained by Clusius and Losa and by Kelley is shown in Fig. 1. Their measurements were made using the conventional intermittent heating technique, differing from that used in the present work only in that the isothermal instead of the adiabatic procedure was employed. The high temperature heat capacities of tantalum have been measured by Magnus and Holtzman,[8] Jaeger and Veenstra[9] and Spedding and Miller,[10] all using the drop method. Results obtained in these three studies differ among themselves by as much as 3% and deviate from the present work to roughly the same extent.

(6) K. Clusius and C. G. Losa, *Z. Naturforsch.*, **10A**, 939 (1955).
(7) K. K. Kelley, *J. Chem. Phys.*, **8**, 318 (1940).
(8) A. Magnus and H. Holtzman, *Ann. Physik.*, **5**, 585 (1929).
(9) F. M. Jaeger and W. A. Veenstra, *Rec. trav. chim.*, **53**, 677 (1934).
(10) F. H. Spedding and C. F. Miller, U. S. Atomic Energy Commission Report ISC-167 (1951).

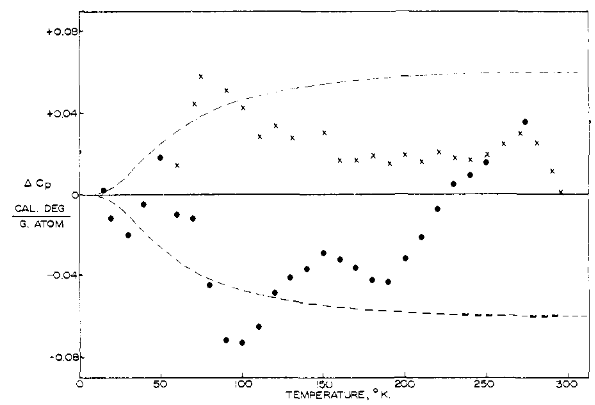

Fig. 1.—Deviations of the heat capacities of tantalum measured by Kelley (x) and Clusius and Losa (●) from those reported in this study. The dotted lines indicate deviations of 1%.

The data in Table I have been used to evaluate the apparent Debye temperature at several temperatures. In making these calculations the constant-pressure heat capacities were first corrected to constant-volume conditions and then for the electronic contribution, both using data by Clusius and Losa.[6] Calculations were not extended beyond 100°K. because of difficulties in allowing for the electronic contribution. Published values for γ, the electronic specific-heat parameter, for tantalum differ[6,11,12] by a factor of two. Above 100°K. the apparent Debye temperature becomes so sensitive to errors in γ that the computed results are without significance.

The results of the present study lead to an apparent Debye temperature which averages 230°K. over the interval from 12 to 100°K. The curve of θ *versus* T exhibits a shallow minimum at 30°K. with θ equalling 225°K. at that point and rising to 238 and 234°K. at the upper and the lower and upper limits, respectively. The data of Clusius and Losa reveal a similar trend with the minimum coming at about 45°K. Their θ values average 229°K. and rise to 228 and 238°K. at 20 and 100°K., respectively. From measurements in the liquid helium range Worley, *et al.*, obtained values for θ of 213 and 225°K. for two specimens of tantalum.

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(12) W. H. Keesom and M. Desirant, *Physica*, **8**, 273 (1941).