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Publication Date
1964-02-19

UCRL-11190

University of California

Ernest O. Lawrence Radiation Laboratory

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February 1964

Berkeley, California

Submitted for publication in
J. Chem. and Eng. Data

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AEC Contract No. W-7405-eng-48

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(Abstract)

High-temperature heat contents of niobium were measured over the temperature range 298° to 1415° K, using a diphenyl ether calorimeter. The results are well represented by the analytical expressions:

$$H^\circ_T - H^\circ_{298.15} = 6.564T - 1.81 \times 10^{-4}T^2 + 5.12 \times 10^4 T^{-1} - 2113 \quad (298^\circ - 500^\circ K)$$

$$H^\circ_T - H^\circ_{298.15} = 5.672T + 5.06 \times 10^{-4}T^2 - 1736 \quad (500^\circ - 1400^\circ K)$$

Smoothed values of the thermal properties of niobium, $H^\circ_T - H^\circ_{298}$, Cp, $S^\circ_T - S^\circ_{298}$, and $(F^\circ_T - H^\circ_{298})/T$, have been derived and are tabulated at even 100° intervals.

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Growing interest in niobium as a high-temperature refractory metal plus the availability of a sample of high purity material have made it desirable to determine the high-temperature thermal properties of niobium by means of heat content measurements. The only previously reported measurements of the high-temperature thermal properties of niobium are those by Jaeger and Veenstra (3), 1934, ($H^\circ_T - H^\circ_{295}$, 670° - 1828° K), and by Lowenthal (8), 1963, (Cp, 1471° - 2259° K). This paper reports the results of heat content measurements in the temperature range 298° to 1415° K.

EXPERIMENTAL

Electron-beam melted niobium supplied by the Temescal Metallurgical Corporation was used in the study. The stated maximum impurity levels indicate the sample to have a purity of 99.99+ percent Nb.

Heat content measurements were made using a diphenyl ether Bunsen-type drop calorimeter. The apparatus and experimental procedures have been described in detail previously (1, 6) and will be mentioned only briefly here. The specimen, consisting of 1.2795 grams of niobium enclosed in 0.5016 grams of platinum foil, was heated in an argon atmosphere in a vertical tube furnace to a measured temperature, then dropped into the calorimeter. Heat from the specimen entered a surrounding chamber containing liquid and solid diphenyl ether at its melting point, 300.0° K, melting some of the solid isothermally. The resulting increase in volume was measured by displacement of mercury from the bottom of the calorimeter chamber into a horizontal calibrated capillary tube. The heat effect was obtained from the measured volume change using the calibration factor determined by Jessup (4) and routinely checked throughout the measurements by dropping a solid platinum specimen in the calorimeter (6). Corrections were made for the heat content of the platinum capsule and the heat lost during the drop using data previously reported (6), and for the small difference between the calorimeter temperature, 300° K, and the standard reference temperature, 298.15°K, using the Cp at 298.15°K selected by Hultgren et al. (2) from low-temperature data.

Starting with the runs at 995°K and continuing at higher temperatures, the specimen gained small amounts of weight due to oxygen absorption.. The total increase in weight, reached after the highest temperature runs (1415°K) was 0.0021 grams, amounting to 0.16 percent by weight. Correction was made for oxidation using the apparent heat content of oxygen in niobium, calculated from heat content data for NbO_2 (7) and Nb_2O_5 (5). After completion of the high-temperature runs, two final runs (indicated in Table I) were repeated at a lower temperature in order to check the method of correction. The results, after correction, were in good agreement with the values found before extensive oxidation had occurred.

RESULTS

The experimental results, after correction for oxygen absorption, are listed in Table I and are shown plotted in terms of the function $(H^\circ_T - H^\circ_{298.15})/(T - 298.15)$ in Figure 1. The smooth curve drawn through the measured values is well represented by the analytical expressions:

$$H^\circ_T - H^\circ_{298.15} = 6.564T - 1.81 \times 10^{-4}T^2 + 5.12 \times 10^4 T^{-1} - 2113 \quad (298° - 500°K)$$

$$H^\circ_T - H^\circ_{298.15} = 5.672T + 5.06 \times 10^{-4}T^2 - 1736 \quad (500° - 1400°K)$$

The selected curve joins smoothly in both Cp and (dCp/dT) with the low-temperature Cp values selected by Hultgren et al. (2). The heat content values of Jaeger and Veenstra (3), also shown plotted in Figure 1, are on the average about 0.5 percent lower than those found here. Heat capacity values of Lowenthal (8), determined from optical emission measurements on electrically heated filaments in the range 1471° - 2259° K, appear to be about 3 percent high.

Smoothed values of the thermal properties of niobium corresponding to the selected curve are tabulated in Table II. Values of the free energy function are based on $S^\circ_{298.15} = 8.70 \pm 0.1$ as given by Hultgren et al. (2).

NOMENCLATURE

T	Temperature, °K
Cp	Heat capacity at constant pressure, cal./deg. g. atom.
$S^\circ_{298.15}$	Standard entropy at 298.15° K, cal./deg. g. atom
$H^\circ_T - H^\circ_{298.15}$	Heat content (enthalpy) increment between 298.15° K and temperature T
$S^\circ_T - S^\circ_{298.15}$	Entropy increment between 298.15° K and temperature T
$(F^\circ_T - H^\circ_{298.15})/T$	Free energy function with respect to 298.15° K

ACKNOWLEDGMENTS

This work was conducted with the support of the U. S. Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Radiation Laboratory. The authors wish to thank Dr. K.K. Kelley and Dr. Leo Brewer for helpful discussions, and Dr. Victor Zackay for providing the sample.

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Table I. Experimental Results

T, °K	$H^\circ_T - H^\circ_{298.15}$ Cal. /G. atom	T, °K	$H^\circ_T - H^\circ_{298.15}$ Cal. /G. atom
358.3	350	813.2	3226
358.3	357	813.3	3216
397.6	594	892.2	3703
397.7	597	892.5	3729
440.2	859	892.5	3731
440.9	840	995.3	4416
502.2	1251	1002.5	4454
502.4	1239	1002.8	4472
502.4	1244	1006.0*	4500
585.7	1758	1006.2*	4521
586.0	1751	1102.9	5133
611.4	1919	1103.0	5139
611.4	1933	1203.2	5792
703.3	2515	1203.2	5821
703.4	2500	1302.9	6505
703.4	2502	1303.1	6518
715.0	2578	1414.5	7312
788.4	3039	1414.7	7348
788.5	3039		

*Runs made to confirm method of correcting for oxygen absorption (see text).

Table II. Thermal Properties of Niobium

		Cal. / Deg. g. atom		
T, °K	$H^\circ_T - H^\circ_{298.15}$ Cal. /G. atom	Cp	$S^\circ_T - S^\circ_{298.15}$	$-\frac{F^\circ_T - H^\circ_{298.15}}{T}$
298.15	0	5.88	0.00	8.70
400	611	6.09	1.76	8.93
500	1226	6.18	3.13	9.38
600	1849	6.28	4.27	9.88
700	2482	6.38	5.24	10.40
800	3126	6.48	6.10	10.89
900	3778	6.58	6.87	11.37
1000	4442	6.68	7.57	11.83
1100	5116	6.79	8.21	12.26
1200	5799	6.88	8.81	12.67
1300	6493	6.99	9.36	13.06
1400	7196	7.09	9.88	13.44

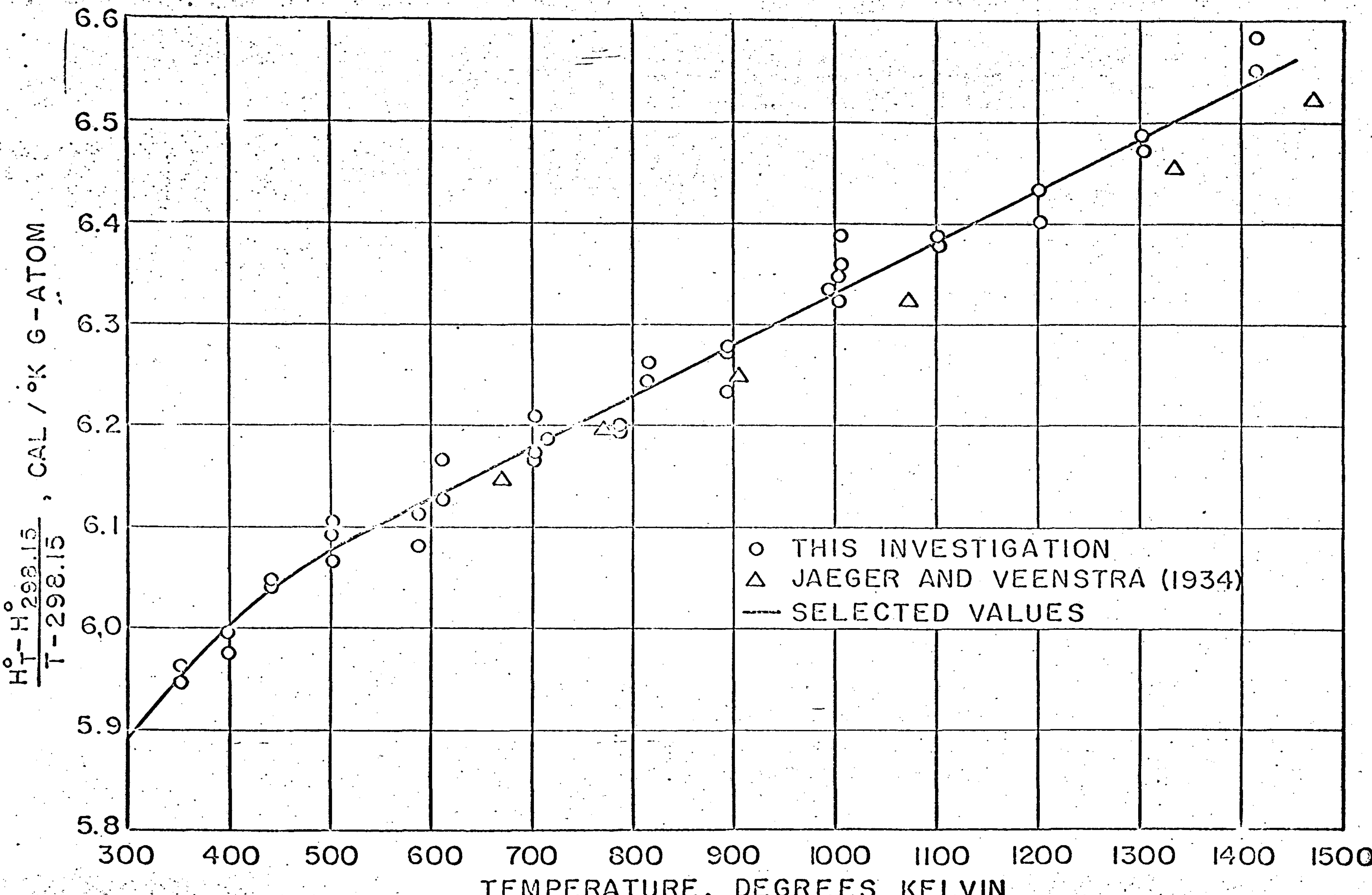

Figure 1. Heat content of niobium expressed in terms of the function $(H^\circ_T - H^\circ_{298.15})/(T - 298.15)$.