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The Heat Capacity and Entropy of Thorium from 18 to 300°K.

BY MAURICE GRIFFEL AND RICHARD E. SKOCHDOPOLE

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The heat capacity of thorium has been measured from 18 to 300°K. and tabulated along with entropy, enthalpy and Gibbs function as a function of temperature. The entropy, excluding spin and nuclear effects is 12.76 cal. deg.$^{-1}$ at 298.16°K.

In 1917 Lewis and Gibson[2] estimated the entropy of thorium as $S^0_{298.16} = 13.58$ based on measurements by Dewar[3] of the average atomic heat between the boiling points of hydrogen and nitrogen. This value has not been further checked and is presented in the standard compilations of Kelley[4] and of the Bureau of Standards.[5] We have measured the heat capacity for the purpose of securing the data and for comparison with the specific heat measurements on uranium[6] and on the rare earth metals, especially cerium.[7]

Apparatus.—The calorimeter used is of the adiabatic type first built by Blue and Hicks.[8] No detailed description of its construction or of the electrical circuits will be given since complete descriptions of similar designs have recently appeared.[9]

Our temperature scale is that of the Bureau of Standards[10,11] which calibrated our platinum-resistance thermometer. The platinum-resistance thermometer is of the capsule type made by Leeds and Northrup and has a nominal resistance of 25 ohms at room temperature. Measurements of thermometer resistance and of power input were made using conventional circuitry, a calibrated White double-potentiometer and a calibrated standard cell. The duration of energy input was regulated by a Standard Electric Time Company pendulum clock and bench control unit together with a Stevens–Arnold millisec. relay. Time measurements were calibrated against a standard WWV frequency and are accurate to at least 0.002 second. Control of the temperature of the adiabatic shield was by circuits similar to those previously described.[9a]

The thorium, in the shape of a cylinder, was not contained in a calorimeter vessel but was directly suspended in the adiabatic chamber. The 130-ohm heater was of #38 constantan wire non-inductively wound in a helical groove of a copper shell which fitted tightly into a hole drilled along the axis of the cylinder. The platinum resistance thermometer in turn was slipped into the heater shell. A slight amount of Lubriseal stopcock grease was used for added assurance of good thermal contact. Leads from the thermometer and from the heater were wrapped around a small ring which fitted into a re-entrant well directly under the thermometer and which was held to the block by small screws.

The heat capacity of the thorium is obtained by subtraction of the experimentally determined heat capacity of the heater-thermometer core and other small parts such as the ring and small copper blocks holding the thermocouples. For this auxiliary run the heater-thermometer core and other parts were fitted into a thin copper shell having the same inside dimensions as the well in the thorium cylinder. Subtraction of the heat capacity of the weighed shell as determined by measurements of Giauque and Meads[12] (confirmed by our own redetermination) gave the net heat capacity of the remainder. The thermochemical calorie is taken as 4.1840 absolute joules.

Materials.—The thorium cylinder, 3″ high and 1.5″ in diameter, was machined from extruded thorium made by the Ames Laboratory. It weighed 954.066 g. ≡ 4.1102 moles. Analysis showed it to contain 0.04% nitrogen, 0.06% oxygen, 0.025% silicon. Aluminum, calcium, cadmium, iron, magnesium and zinc were present to at the most 100 parts per million.

Experimental Results

The results of our measurements are given in Table I. The values of C_p were taken from a smooth curve of the heat capacities determined using heating intervals of 3 or 4 degrees. Above 30°K. the application of Osborne's[13] method of cal-

TABLE I

HEAT CAPACITY OF THORIUM, CAL. DEG.$^{-1}$ (G. ATOM)$^{-1}$

Atomic wt. = 232.12, 0°C. = 273.16°K.

T, °K.	C_p	C_v	T, °K.	C_p	C_v
20	1.106	1.106	165	6.055	6.011
25	1.801	1.800	170	6.083	6.039
30	2.397	2.396	175	6.109	6.062
35	2.910	2.899	180	6.133	6.084
40	3.355	3.352	185	6.155	6.105
45	3.733	3.728	190	6.177	6.125
50	4.048	4.042	195	6.197	6.143
55	4.309	4.302	200	6.217	6.161
60	4.529	4.520	205	6.237	6.180
65	4.723	4.713	210	6.256	6.197
70	4.878	4.866	215	6.275	6.214
75	5.011	4.997	220	6.293	6.230
80	5.132	5.117	225	6.310	6.245
85	5.248	5.231	230	6.330	6.264
90	5.342	5.323	235	6.347	6.279
95	5.415	5.395	240	6.362	6.292
100	5.482	5.460	245	6.379	6.307
105	5.547	5.524	250	6.392	6.318
110	5.607	5.582	255	6.407	6.332
115	5.664	5.637	260	6.422	6.345
120	5.717	5.689	265	6.437	6.358
125	5.767	5.737	270	6.453	6.372
130	5.815	5.783	275	6.468	6.385
135	5.857	5.824	280	6.483	6.398
140	5.895	5.860	285	6.497	6.410
145	5.931	5.894	290	6.510	6.421
150	5.965	5.927	295	6.524	6.434
155	5.996	5.956	298.16	6.532	6.441
160	6.026	5.984	300	6.538	6.446

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(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

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(3) J. Dewar, *Proc. Roy. Soc.* (*London*), **89A**, 158 (1913).

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culating dQ/dT from values of $\Delta Q/\Delta T$ resulted in a negligibly small correction. Below 30°K. the correction did not exceed 0.3%. In the temperature range 135–155°K. the experimental points deviated from the smoothed curve more than anywhere else, some points being as much as 0.1 to 0.2% from the curve. This interval was repeated but the points still scattered more than on either side of the interval. The reason for this is not known. Along the remainder of the curve all the experimental points lie within 0.1% of the smooth curve with most points much closer than this. At the higher temperatures the deviations tend to increase but remain well within the 0.1% limit.

Due to the decreasing sensitivity of the thermometer the accuracy is limited to 1% at 20°K., 0.3% at 30°K. Above 35°K. the accuracy is believed to be 0.1%.

The values of C_v listed in column 3 were calculated with the aid of the thermodynamic relation $C_p - C_v = TV\alpha^2/\beta$ in which α is the coefficient of cubical expansion, β is the compressibility and V is the volume per gram atom. At 25° the density was taken to be 11.61[14] corresponding to $V = 19.99$ cc./g. atom. The value of β, 16.4×10^{-13} cm.²/dyne, was computed from the measurements by Reynolds[15] of the Young modulus and Poisson ratio. We have chosen this value instead of the direct experimental result of Bridgman,[16] 18.55×10^{-13} cm.²/dyne, since the material used by Reynolds was also made at the Ames Laboratory and Bridgman's measurements were made when thorium metal was not readily obtainable in as high a purity as presently.

The thermal expansion coefficient was taken as 32.58×10^{-6} deg.$^{-1}$ from the work of Erfling.[17] At 298.16°K. we obtain $C_p - C_v = 0.0917$ cal./mol. deg. Since values of the various parameters are not known as a function of temperature we have calculated $C_p - C_v$ at other temperatures by means of the empirical equation of Lindemann and Nernst: $C_p - C_v = AC_p^2T$, A being $7.20_4 \times 10^{-6}$.

In Table II are listed the entropy, the enthalpy and the Gibbs function. The extrapolation below 20°K. was by means of a Debye curve with $\Theta = 141.6$; this is the mean value in the range 18–28°K.

TABLE II

THERMODYNAMIC PROPERTIES OF THORIUM

T, °K.	$S°$, cal./deg. × g. atom	$\frac{H° - H°_0}{T}$, cal./deg. × g. atom	$\frac{-(F° - H°_0)}{T}$, cal./deg. × g. atom
20	0.410	0.304	0.106
50	2.770	1.801	0.969
100	6.135	3.369	2.766
150	8.460	4.164	4.296
200	10.215	4.648	5.567
250	11.623	4.980	6.643
298.16	12.760	5.220	7.540
300	12.799	5.228	7.571

Discussion

Thorium does not exhibit any anomalies in its heat capacity; the slight irregularity found in the range 135–155°K. is so much less than the irregularity exhibited by cerium[6] in the range 130–180°K. that it may be neglected. In the range over which it has been investigated,[6] uranium likewise shows no anomalies in contradistinction to the behavior of neodymium.[7]

It seems premature to try to fit this in with a theory of the electronic structures of these metals until other types of data as well as specific heats at still lower temperatures have been obtained for all of them. We intend to pursue some of this work in the near future.

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