

## Heat capacity of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ from 5 to 350 K <sup>a</sup>

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The heat capacity of crystalline  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  has been determined by adiabatic calorimetry primarily to enable evaluation of the standard partial molar entropy and heat capacity of aqueous thorium(IV) ion. No thermal anomalies were detected, and at 298.15 K  $C_p(T)$ ,  $S^\circ(T)$ , and  $-\{G^\circ(T) - H^\circ(0)\}/T$  are  $114.9 \pm 0.1$ ,  $129.8 \pm 0.1$ , and  $63.87 \pm 0.06$  cal<sub>th</sub> K<sup>-1</sup> mol<sup>-1</sup>, respectively.

### 1. Introduction

The low-temperature heat capacity of thorium nitrate pentahydrate<sup>(1)</sup> was ascertained primarily for the purpose of making possible the evaluation of the thermodynamic properties of the Th(IV) ion in aqueous solution from additional measurements made at Rutgers University.<sup>(2)</sup> A secondary reason was the provision of data on hydrated actinide compounds since relatively few examples of such compounds have been studied.

### 2. Experimental

#### PROVENANCE OF SAMPLE

A sample of "thorium nitrate, 99.9 per cent" from Research Organic/Inorganic Chemical Corporation was dissolved in conductivity water containing 5 mass per cent  $\text{HNO}_3$ . After the solution had been filtered, several crops of crystals were grown by slow cooling, collected, pressed between filter papers, crushed in a glass mortar, and stored over a saturated solution of  $\text{CaCl}_2$  for several weeks.

Analysis for thorium by ignition to thorium dioxide yielded 40.69, 40.69, 40.70, and 40.74 mass per cent (theoretical, 40.70 mass per cent). Analysis for water by the

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Karl Fischer method yielded  $(15.72 \pm 0.16)$  mass per cent (theoretical, 15.80 mass per cent).

Preliminary determinations of vapor pressure measured over mercury were 0.7 Torr at 298 K, 1.2 Torr at 315 K, and 10.7 Torr at 341 K.† It was observed that the sample did not gain mass as long as the relative ambient laboratory humidity was under 60 per cent. Preparation and characterization of the sample were performed at Rutgers University.

### CRYOSTAT AND CALORIMETER

Heat-capacity measurements were made at the University of Michigan in the Mark II cryostat utilizing a gold-plated, copper calorimeter (laboratory designation W-52) with an internal volume of  $50 \text{ cm}^3$  and a gold-gasketed mechanical closure. It is provided with four vanes radiating vertically from the re-entrant axial thermometer-heater well. The heat capacity of the empty calorimeter was determined in a separate set of measurements in which identical amounts of Apiezon-T grease were used for thermal contact between the heater + thermometer assembly and the well. Helium gas at a pressure of 52 Torr was used to accelerate thermal equilibration within the sample space. The crystals of the pentahydrate averaged a few tenths of a mm in average dimension and were loaded in a relative humidity of 34 per cent at 298 K. Under these conditions they did not gain or lose mass during the weighing process. The calorimeter was placed in a stainless-steel loading chamber, evacuated quickly over a period of approximately 1.5 min to 0.1 Torr; a pressure of 500 Torr of purified helium gas was added and the loading chamber again re-evacuated quickly to 0.1 Torr and the conduction helium added. The mass of the calorimetric sample was 99.0426 g. Buoyancy corrections were made on the basis of the density of the sample as  $2.80 \text{ g cm}^{-3}$ .<sup>(3)</sup> Weighings indicated no detectible water loss upon evacuation. Temperatures were determined with a capsule-type strain-free platinum-resistance thermometer (laboratory designation A-5) calibrated against IPTS-48 and are considered to accord with the thermodynamic temperature scale to within 0.03 K from 10 to 90 K and within 0.04 K from 90 to 350 K. The temperature increments may, of course, be determined with more precision than absolute temperatures and are probably correct within a few tenths of a mK after correction for quasi-adiabatic drift. A  $150 \Omega$  constantan heater was bifilarly wound on a grooved cylindrical copper sleeve closely fitted to the resistance thermometer. All measurements of resistance, potential, temperature, time, and mass are referred to calibrations performed by the National Bureau of Standards.

### 3. Results and discussion

The experimental heat capacities are presented in chronological order at the mean temperatures of the determination in table 1; hence, the approximate values of  $\Delta T$  used in the heat-capacity determinations can usually be deduced from the increments between the adjacent mean temperatures. These results are presented in terms of

† Throughout this paper Torr =  $(101.325/760)$  kPa and  $\text{cal}_{\text{th}} = 4.184 \text{ J}$ .

an ice point of 273.15 K, and a molar mass of 570.134 g mol<sup>-1</sup> for the pentahydrate. The results have been corrected for curvature, *i.e.* for the difference between the measured  $\Delta H/\Delta T$  and the limit as  $\Delta T \rightarrow 0$ . These heat capacities are considered to have a standard deviation decreasing from less than 4 per cent at 5 K to 1 per cent

TABLE 1. Heat capacity of thorium nitrate pentahydrate  
(cal<sub>th</sub> = 4.184 J)

$T$ K	$C_p$ cal <sub>th</sub> K <sup>-1</sup> mol <sup>-1</sup>	$T$ K	$C_p$ cal <sub>th</sub> K <sup>-1</sup> mol <sup>-1</sup>	$T$ K	$C_p$ cal <sub>th</sub> K <sup>-1</sup> mol <sup>-1</sup>	$T$ K	$C_p$ cal <sub>th</sub> K <sup>-1</sup> mol <sup>-1</sup>
Mark II Cryostat							
Series I		Series II		Series III		9.48	0.91
113.36	59.24	242.69	99.96	57.43	30.00	10.50	1.20
120.49	62.05	252.47	102.69	62.61	33.52	11.62	1.56
128.33	64.93	262.04	105.32	68.30	37.10	12.86	1.968
137.23	68.12	271.42	107.75	74.85	40.96	14.20	2.491
146.66	71.37	281.03	110.40	81.82	44.94	15.63	3.097
156.60	74.50	290.88	112.92	89.56	48.97	18.01	4.172
167.19	77.88	300.53	115.71	98.29	52.95	20.78	5.563
178.06	81.29	310.40	118.09	107.71	56.95	22.95	6.745
188.55	84.70	320.50	120.80	117.68	60.94	26.25	8.660
198.70	87.72	330.58	123.57			30.41	11.273
208.56	90.56	338.42	125.61	Series IV		36.96	15.698
218.49	93.42	344.48	127.42	5.72	0.21	43.36	20.15
228.51	96.15	349.31	128.63	6.46	0.27	48.45	23.76
238.57	98.90			7.52	0.43	53.61	27.39
248.67	101.63			8.49	0.66	58.92	31.02

at 10 K and to less than 0.08 per cent above 50 K. Because heat capacities of Calorimetry Conference standard samples of benzoic acid and synthetic sapphire have been determined in the calorimeter, the accuracy of the measurements should be closely parallel with the precision.

Heat capacities and thermodynamic functions at selected temperatures, as presented in table 2, are obtained from the heat capacities by a least-squares fitted curve through the experimental points (carefully compared with a large scale plot of the results) and the integration thereof. Both the curve fitting and the quadrature were performed by digital computer programs. Thermodynamic functions are considered to have a precision indicated by standard deviation less than 0.07 per cent above 100 K. An additional digit beyond those significant is frequently given in table 2 for internal consistency and to permit interpolation and differentiation. The entropies and Gibbs energies have not been adjusted for nuclear spin and for isotopic mixing contributions and are, hence, practical values for use in chemical thermodynamic calculations.

Combining data from the table at 298.15 K with the entropy of thorium metal<sup>(4)</sup> and with those of other elementary substances involved<sup>(5)</sup> enables us to evaluate the entropy of formation  $\Delta S_f^\circ$  for the pentahydrate at this temperature as  $-(547.0 \pm 0.1)$  cal<sub>th</sub> K<sup>-1</sup> mol<sup>-1</sup>. Inclusion of the enthalpy of formation of the pentahydrate<sup>(2)</sup> yields

TABLE 2. Thermodynamic properties of  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$   
 ( $\text{cal}_{\text{th}} = 4.184 \text{ J}$ )

$T$ K	$C_p$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$\{S^\circ(T) - S^\circ(0)\}$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$\{H^\circ(T) - H^\circ(0)\}$ $\text{cal}_{\text{th}} \text{mol}^{-1}$	$-\{G^\circ(T) - H^\circ(0)\}/T$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$
5	0.136	(0.043)	(0.170)	(0.009)
10	1.044	0.352	2.654	0.086
15	2.824	1.089	12.046	0.286
20	5.163	2.211	31.819	0.620
25	7.919	3.652	64.37	1.077
30	11.003	5.364	111.56	1.645
35	14.330	7.307	174.81	2.313
40	17.80	9.446	255.10	3.069
45	21.33	11.747	352.93	3.904
50	24.86	14.177	468.41	4.809
60	31.74	19.32	751.8	6.795
70	38.13	24.70	1101.6	8.967
80	43.92	30.18	1512.4	11.276
90	49.10	35.66	1978.0	13.681
100	53.74	41.08	2492.6	16.15
110	57.96	46.40	3051.4	18.66
120	61.84	51.61	3650.7	21.19
130	65.50	56.71	4287.5	23.73
140	68.99	61.69	4960.1	26.26
150	72.37	66.57	5667	28.79
160	75.66	71.34	6407	31.30
170	78.88	76.03	7180	33.79
180	82.02	80.62	7985	36.26
190	85.08	85.14	8820	38.72
200	88.05	89.58	9686	41.15
210	90.95	93.95	10581	43.56
220	93.78	98.24	11505	45.95
230	96.56	102.47	12456	48.32
240	99.30	106.64	13436	50.66
250	102.02	110.75	14442	52.98
260	104.72	114.80	15476	55.28
270	107.41	118.81	16537	57.56
280	110.09	122.76	17624	59.82
290	112.76	126.67	18739	62.06
300	115.41	130.54	19879	64.27
310	118.05	134.37	21047	66.47
320	120.70	138.16	22240	68.65
330	123.38	141.91	23461	70.82
340	126.10	145.63	24708	72.96
350	128.81	149.33	25983	75.09
273.15	108.26	120.06	16876	58.27
298.15	114.92	129.83	19666	63.87

a standard Gibbs energy of formation of  $-(556.1 \pm 0.1) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ . The evaluation of the partial molar thermodynamics of the aqueous ion has been presented elsewhere.<sup>(2)</sup>

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