Specific Heat, Enthalpy, and Entropy of Uranyl Fluoride[1][2]

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The heat capacity of uranyl fluoride was measured from 13° to 418° K by using a vacuum-type calorimeter equipped with thermostated radiation shields. From the data so obtained, the enthalpy $H° - H_0°$ was calculated to be 63.96, 77.62, and 108.15 int. joules per gram at 298.16°, 338.16°, and 423.16° K, respectively, and the entropy was calculated to be 0.4400, 0.4830, and 0.5635 int. joules per degree-gram at the same temperatures. No evidence of a transition was found. The values of the specific heat, enthalpy, entropy, and free energy are tabulated at 5-degree intervals of temperature.

I. Introduction

This investigation of the thermodynamic properties of uranyl fluoride was undertaken in connection with the Manhattan project and is a part of the program carried on during the war by the Heat and Power Division of the National Bureau of Standards.

II. Material

The uranyl fluoride used in this investigation was prepared by H. F. Priest of Columbia University. The material, after being dried at 130°C for 4 hours, was placed in the sample container. Air was removed by pumping until a high vacuum was obtained, helium was admitted at a pressure of 20 mm Hg, and the container was sealed with solder. The helium was added to promote the rapid attainment of thermal equilibrium. The observed heat capacity was adjusted for the presence of this helium.

Before the material was used in the calorimeter, an analysis made by the SAM Laboratories of the Carbide and Carbon Chemicals Corporation showed the sample to contain 77.19 weight percent of uranium and 12.6 weight percent of fluorine. Following the calorimetric measurements, the Uranium Section of the National Bureau of Standards found the sample to contain 77.28 percent of uranium and 12.1 percent of fluorine. The theoretical percentages are 77.28 and 12.33. Spectroscopic tests for 34 elements showed less than 0.07 weight percent impurity. The difficulties in fluorine analysis are such that it is probably improper to base any conclusions regarding purity of the sample on observed fluorine content.

III. Apparatus and Procedure

The calorimeter used in this investigation was of the adiabatic, vacuum type described by Southard and Brickwedde [1][3]. The sample container was the one used in the determination of the heat capacities of GR-S rubber [2] and polyvinyl chloride [3].

The system, including the measuring circuits, was very similar to that used by Scott, Meyers, Rands, Brickwedde, and Bekkedahl [4] to determine the heat capacity of butadiene, except for the following: The apparatus was designed for measuring the heat capacities of solids and so had no filling tube or attendant parts. The shield was suspended by means of fine wire, and the sample container was in turn suspended from the shield by means of linen cord. A copper, rather than an aluminum, shield was used on the bottom of the sample container to prevent heat losses from the exposed ends of the heater. The sample-

[3] Figures in brackets indicate the literature references at the end of this paper.

container heater was located in the thermometer well, which was filled with lead-tin eutectic solder. The side and bottom shield heaters were controlled individually. In order to improve the ease of controlling the radiation shields at temperatures above the ice point, an auxiliary heater was wrapped on the outer wall of the vacuum chamber, and the chamber was surrounded by a stirred oil bath. The auxiliary heater was used to keep this wall at a temperature only slightly below that of the shields and sample container. Its use resulted in a substantial improvement in shield control. Temperatures were measured with platinum resistance thermometer L15 (thermometer P), whose calibration is described in reference [5].

The methods of measurement and of calculation were similar to those described in the paper on butadiene [4]. The tare-heat capacity measurements were made on the empty sample container, and the gross-heat capacity measurements were made with 58.015_8 grams of uranyl fluoride in the container. Because of the negligible vapor pressure of the material, it was unnecessary to correct the heat capacities for vaporization. Specific heat measurements were regularly made with both high and low heating rates, the rates varying as much as from 0.63 to 2.18 degrees per minute. This procedure provided a test for a large proportion of the errors that might occur in the measurement of heat capacity, but would not have revealed an error whose magnitude per unit time was proportional to the heating rate.

IV. Calculations and Results

The observed heat capacity data were plotted as deviations from empirical equations. From the resulting deviation curves, values were read at uniform temperature intervals, and tables were constructed giving both the gross- and tare-heat capacities at 2.5-degree intervals below 115° K and at 5-degree intervals at higher temperatures. Subtraction of the tare- from the gross-heat capacity gave the net heat capacity, which was extrapolated to 0° K by means of the Debye equation $C = 0.8359\ D\ (117/T)$. This equation represented the experimental data satisfactorily at 20°, 25°, and 30° K.

Due to graphical methods involved in getting the table of net-heat capacities, small irregularities could be detected in the higher differences. To reduce these, an analytical smoothing process was applied. The smoothed value corresponding to a given unsmoothed value was found by multiplying the unsmoothed value and the four adjacent unsmoothed values on either side of it by a set of coefficients. A number of such smoothing processes have been devised. The one adopted in the present work was developed by Harold W. Woolley. In it the coefficients were chosen to minimize the squares of the random parts of the first differences
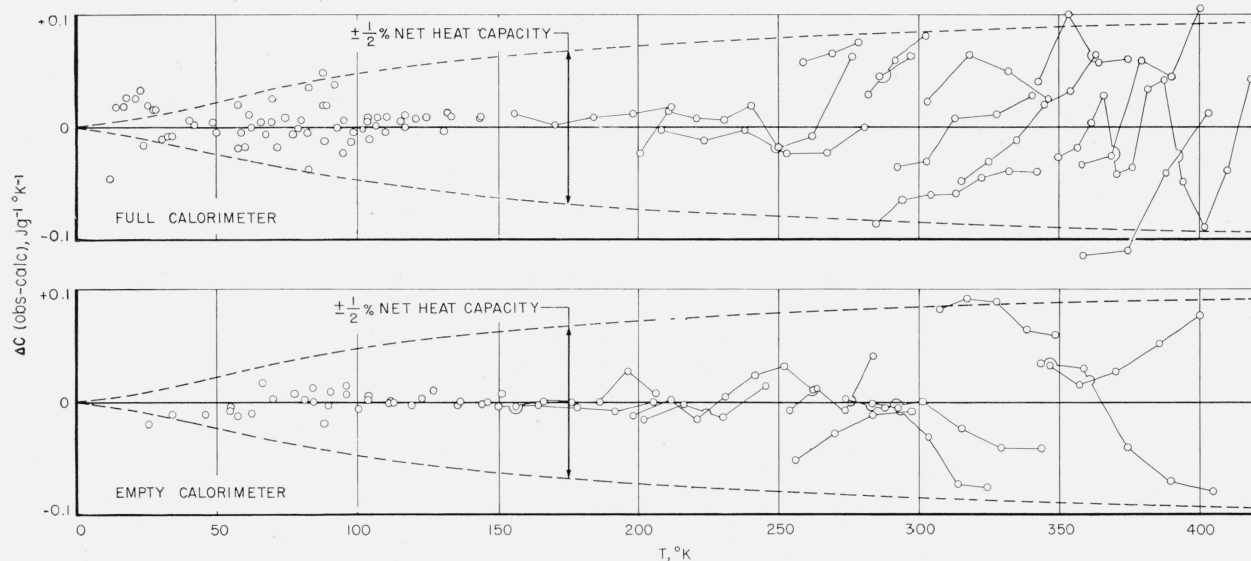

FIGURE 1. *Observed heat capacities.*

The dashed lines indicate deviations from the tables of gross and tare heat capacities equal to ±0.5 percent of the net heat capacity.

in such a manner that the process would make no significant change in functions for which the fourth and higher differences were negligible. The smoothing operation introduced no changes in the table as large as the probable experimental error.

The enthalpy was calculated from the formula $H° = \int C° dT$, while the entropy was obtained from the equation $S° = \int (C°/T) dT$. The free energy was calculated from the relation $F° = -\int S° dT$ and also from the relation $F° = H° - TS°$.

This provided a check on the accuracy of the integrations. Simpson's rule was used at the higher temperatures. Between 20° and 115°K, a tabular integration formula involving four rather than three successive tabular entries was used, and below 20°, the integrals were obtained directly from the Debye equation. The results are presented in table 1. The dashed lines in figure 1, representing 0.5 percent of the heat capacity, show the temperature trend of the specific heat.

TABLE 1.—*Heat capacity, enthalpy, entropy, and free energy of uranyl fluoride*

T	$C°$	$H° - H_0°$	$S°$	$-(F° - H_0°)$	T	$C°$	$H° - H_0°$	$S°$	$-(F° - H_0°)$
($°K$)	(*Int. j/g*) $°K^{-1}$	*Int. j/g*	(*Int. j/g*) $°K^{-1}$	*Int. j/g*	($°K$)	(*Int.j/g*) $°K^{-1}$	*Int. j/g*	(*Int.j/g*) $°K^{-1}$	*Int. j/g*
0	0.00000	0.00000	0.00000	0.00000	215	0.2949	37.626	0.33687	34.802
5	.00051	.00064	.00017	.00021	220	.2979	39.107	.34368	36.503
10	.00403	.01014	.00135	.00339	225	.3008	40.604	.35041	38.238
15	.01231	.0492	.00440	.01690	230	.3037	42.116	.35705	40.006
20	.02333	.1378	.00943	.0508	235	.3064	43.641	.36361	41.808
25	.03386	.2803	.01575	.1133	240	.3090	45.179	.37009	43.643
30	.04478	.4768	.02288	.2096	245	.3116	46.731	.37649	45.518
35	.05567	.7280	.03060	.3431	250	.3142	48.295	.38281	47.400
40	.06637	1.0331	.03874	.5163	255	.3166	49.872	.38905	49.337
45	.07747	1.3925	.04719	.7310	260	.3190	51.462	.39523	51.298
50	.08909	1.8086	.05595	.9887	265	.3214	53.063	.40133	53.290
55	.10191	2.2855	.06503	1.2910	270	.3237	54.676	.40735	55.310
60	.11549	2.8292	.07448	1.6396	275	.3259	56.300	.41331	57.362
65	.12713	3.4371	.08420	2.0363	280	.3280	57.934	.41920	59.443
70	.13573	4.0951	.09395	2.4817	285	.3300	59.579	.42503	61.555
75	.14362	4.7933	.10358	2.9756	290	.3320	61.235	.43079	63.694
80	.15261	5.5333	.11313	3.5174	295	.3339	62.900	.43648	65.862
85	.16310	6.3220	.12269	4.1070	300	.3357	64.574	.44210	68.058
90	.17378	7.1647	.13232	4.7443	305	.3374	66.256	.44767	70.284
95	.18226	8.0560	.14196	5.4302	310	.3390	67.947	.45317	72.536
100	.18847	8.9834	.15147	6.1638	315	.3406	69.647	.45860	74.814
105	.19439	9.9404	.16081	6.9446	320	.3422	71.354	.46398	77.121
110	.2007	10.928	.16999	7.7713	325	.3438	73.069	.46930	79.454
115	.2070	11.947	.17905	8.6443	330	.3454	74.792	.47456	81.814
120	.2132	12.998	.18800	9.5620	335	.3470	76.523	.47976	84.199
125	.2193	14.079	.19682	10.524	340	.3486	78.262	.48492	86.612
130	.2252	15.190	.20554	11.530	345	.3502	80.009	.49002	89.049
135	.2308	16.331	.21415	12.579	350	.3517	81.764	.49507	91.512
140	.2362	17.498	.22264	13.671	355	.3532	83.526	.50007	94.000
145	.2413	18.692	.23102	14.806	360	.3546	85.296	.50502	96.512
150	.2463	19.911	.23928	15.981	365	.3560	87.072	.50992	99.050
155	.2510	21.154	.24743	17.198	370	.3572	88.855	.51477	101.611
160	.2556	22.421	.25547	18.455	375	.3584	90.645	.51957	104.197
165	.2598	23.710	.26340	19.752	380	.3596	92.440	.52433	106.806
170	.2640	25.019	.27122	21.089	385	.3607	94.241	.52904	109.440
175	.2679	26.349	.27893	22.464	390	.3617	96.046	.53370	112.098
180	.2717	27.698	.28653	23.878	395	.3627	97.858	.53831	114.776
185	.2753	29.066	.29403	25.330	400	.3638	99.674	.54288	117.480
190	.2788	30.451	.30141	26.818	405	.3648	101.495	.54741	120.206
195	.2822	31.854	.30870	28.343	400	.3658	103.321	.55189	122.954
200	.2854	33.273	.31589	29.906	415	.3668	105.153	.55633	125.725
205	.2886	34.708	.32297	31.502	420	.3678	106.989	.56073	128.518
210	.2917	36.159	.32997	33.135	425	.3688	108.831	.56508	131.330

V. Discussion

Although tests were made for transitions, none were found.

The probable error in the tabulated values of the specific heat of the sample used in this investigation is estimated to be 0.1 percent from 40° to 250° K. Below 40° K the error is larger, perhaps reaching 1 percent at 20° K. As radiation becomes an important source of error above room temperature, the probable error above 250° K may become as large as 0.5 percent. These estimates do not include errors due to impurities in the sample. Although there is probably no reliable evidence for more than 0.07 weight percent impurity in the sample, the lack of detailed knowledge of the purity does introduce some uncertainty in the results.

VI. References

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