Specific Heat, Enthalpy, and Entropy of Uranyl Fluoride

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The heat capacity of uranyl fluoride was measured from 13°C to 418°C K by using a vacuum-type calorimeter equipped with thermostated radiation shields. From the data so obtained, the enthalpy $H^o - H_b$ was calculated to be 63.96, 77.62, and 108.15 int. joules per gram at 298.16°C, 338.16°C, and 423.16°C 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] 1. 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-
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 58.0158 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.
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

\[ H^0 = fC^0dT, \]

while the entropy was obtained from the equation

\[ S^0 = f(C^0/T)dT. \]

The free energy was calculated from the relation

\[ F^0 = -TS^0dT \]

and also from the relation \( F^0 = H^0 - TS^0 \).

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

<table>
<thead>
<tr>
<th>( T ) (°K)</th>
<th>( C^0 ) ((\text{Int. j/g-°K}^{-1}))</th>
<th>( H^0 - H_1^0 )</th>
<th>( S^0 )</th>
<th>(- (F^0 - H_1^0))</th>
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</table>

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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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