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High-temperature calorimetric studies on the thermal properties of $Rb_2U(SO_4)_3(s)$

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Abstract

Measurements of the enthalpy increment, $(H^{\ominus}_T - H^{\ominus}_{298\,15})$ for $Rb_2U(SO_4)_3$ were carried out in the range 370–800 K using a high-temperature Calvet calorimeter. Solid state transitions were observed at 625 ± 3 K and 763 ± 2 K, with respective enthalpies of transitions of 5.998 and 13.585 kJ mol^{-1}. The $H^{\ominus}_T - H^{\ominus}_{298\,15}$ values were plotted against temperature and can be given in J mol^{-1} by $H^{\ominus}_T - H^{\ominus}_{298\,15} \pm 694/(\mathrm{J\,mol^{-1}}) = -1.117 \times 10^5 + 368.9T/\mathrm{K} + 0.0199T^2/\mathrm{K}^2$ (from 370 to 628 K); $H^{\ominus}_T - H^{\ominus}_{298\,15} \pm 405/(\mathrm{J\,mol^{-1}}) = 3.279 \times 10^3 + 13.4T/\mathrm{K} + 0.3063T^2/\mathrm{K}_2$ (from 630 to 760 K); and $H^{\ominus}_T - H^{\ominus}_{298\,15} \pm 433/(\mathrm{J\,mol^{-1}}) = -6.671 \times 10^5 + 1140T/\mathrm{K}$ (from 765 to 803 K).

The thermodynamic properties of $Rb_2U(SO_4)_3(s)$ were derived using the estimated value of $S^{\ominus}_{298\,15}$.

INTRODUCTION

Quality control of nuclear fuel is of prime importance in the nuclear industry for the safe and sustained operation of nuclear reactors. This demands strict control on chemical specifications. In order to check the accuracy of the analytical methods it is essential to employ standard reference materials which have constant stoichiometry, and good stability and solubility. Rubidium uranium trisulphate ($Rb_2U[SO_4]_3$) was suggested as a chemical standard for the determination of uranium [1]. U_3O_8 [2] and high-purity uranium metal [3] are available from NIST as a chemical standard reference material for uranium. Some physicochemical properties of these compounds have been studied by Singh Mudher et al. [4]. Studies on the thermal properties have not been reported so far. The thermal properties of $Rb_2U(SO_4)_3$ are important to characterize the material for its stability at high temperatures. Hence, enthalpy increment measurements

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on $Rb_2U(SO_4)_3$ were carried out using a high-temperature Calvet calorimeter and other thermal properties were derived from the $H_T^\ominus - H_{298\,15}^\ominus$ values.

EXPERIMENTAL

Materials

The double sulphate of rubidium and uranium, ($Rb_2U[SO_4]_3$), was obtained by crystallization from aqueous solution. Uranyl sulphate solution was obtained by the dissolution of nuclear-grade UO_3 in dilute H_2SO_4 and the UO_2^{2+} state was reduced to U^{4+} electrolytically. A solution of Rb_2CO_3 (99% pure from Aldrich Chemical) in 0.5 M H_2SO_4 was then added to the uranium solution and the resultant solution was concentrated gradually to obtain green crystals of $Rb_2U(SO_4)_3$ [1]. Chemical reagents such as H_2SO_4, HNO_3 and NH_4OH used for the preparation of $Rb_2U(SO_4)_3$ were of analytical reagent grade. The impurity content in the sample was analysed by atomic emission spectrometry. The total impurity content in the sample was less than 300 ppm as shown in Table 1. The uranium and sulphate contents were analysed chemically. The analysis of uranium was carried out using the Davies and Gray method [5]. The sulphate content was analysed gravimetrically as $BaSO_4$ after separating uranium from the solution as hydroxide [1]. The concentrations of uranium and sulphate determined in the $Rb_2U(SO_4)_3$ samples were 34.12 ± 0.12 wt.% and 41.28 ± 0.14 wt.%, respectively. The expected theoretical concentrations were 34.15 wt.% and 41.32 wt.%. The X-ray powder diffraction pattern taken on a Siemens diffractometer using Ni-filtered Cu Kα radiation, agreed with that reported earlier. $Rb_2U(SO_4)_3$ samples were made in the form of pellets of 3 mm in diameter, and 2 mm in thickness at a pressure of 50 MPa. The pellets were

TABLE 1

Results of the impurity analysis of $Rb_2U(SO_4)_3$

Element	ppm	Element	ppm
Al	70	B	<0.1
Be	<0.3	Ca	<10
Cd	<0.1	Cr	12
Cu	<5	Fe	<20
Mg	<5	Mo	40
Na	20	Ni	<5
Si	<60	Sn	<2
V	27	Zn	<10
Co	<5	Mn	<2
Pb	<5	W	<40

dried at 400 K for 2–3 h and stored in a desiccator before use for high-temperature enthalpy increment measurement.

Thermal analysis

Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) were carried out on $Rb_2U(SO_4)_3$ samples using an ULVAC Sinku Riko (model TGD-7000) thermal analyser. The calibration of the DTA apparatus was performed using high-purity $K_2CrO_4(s)$. The temperature calibration was carried out by determining the melting point of high-purity tin. Platinum cups were used as container material for the sample and reference. The sample size used for our experiment was 100 mg. Experiments were carried out in both the heating and cooling modes. A heating rate of 10 K min^{-1} and a cooling rate of 5 K min^{-1} were used for the studies. Preheated high-purity alumina was used as reference material. The temperatures were scanned from 300 to 973 K.

A Netzsch differential scanning calorimeter was also employed for confirming the transition temperatures of the sample. A heating rate of 15 K min^{-1} and sample size of 50 mg were used in the experiments.

The Calvet calorimetric system and experimental procedure

The enthalpy increment measurements were carried out using a Setaram high-temperature Calvet microcalorimeter. Details of the experimental procedure and calibration of the calorimeter were reported in earlier publications [6, 7]. The Calvet calorimeter has identical twin compartments surrounded by thermopiles kept inside a massive fritted alumina calorimetric block whose temperature is monitored and controlled. The calorimetric block is heated by a Kanthal wound furnace. Two closed-end long alumina tubes are inserted into the two compartments to act as sample and reference holders, respectively. The closed-end alumina tube helps in maintaining any type of gas environment over the sample. The compartments exchange heat with the block. Thermopiles surrounding the two compartments are connected in opposition to minimize thermal disturbance. The differential signal from the thermopile is proportional to the heat evolved/absorbed in any one compartment. This exchange of heat gives an electrical signal from the thermopile which is amplified and fed into a recorder or a computer for data acquisition and processing. The twin alumina compartments were evacuated to 100 Pa and flushed with high-purity argon before the start of the experiment. The enthalpy increment measurements were carried out by dropping the samples from a thermostated enclosure kept at 298.15 K into the closed-end alumina tube. The measurements were made at different isothermal temperatures from 370 to 800 K at intervals of 10–15 K. At each isothermal temperature, two or three samples were dropped one after another to obtain precise values. The accuracy of the measurements was checked by dropping NIST alumina samples (synthetic sapphire SRM-720) at the beginning and end of each experiment. From the calibration runs, it was found that the precision of the measurements was ±0.5% and accuracy was better than ±0.5%.

RESULTS

Thermal analysis

Figure 1 shows the DTA annd TG curves for $Rb_2U(SO_4)_3$. Two endotherms are indicated, one at 628 K and another at 780 K, before the decomposition starts at 893 K. TG curve shows a weight loss in the range 893–953 K. The weight loss can be attributed to the loss of SO_2 according to the reaction given below. The products $Rb_2UO_2(SO_4)_2$ and SO_2 were not confirmed by any chemical analysis

$$Rb_2U(SO_4)_3 \rightarrow Rb_2UO_2(SO_4)_2 + SO_2$$

The expected weight loss according to the above reaction is 9.18 wt.% which is in very good agreement with the observed value of 9.17 wt.% in the TG curve.

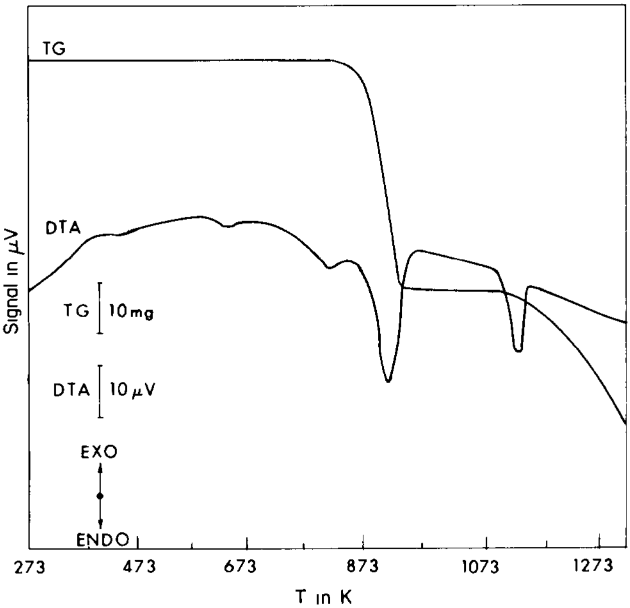

Fig. 1. DTA and TG traces showing the transitions and decomposition of $Rb_2U[SO_4]_2$. Sample weight 517 mg.

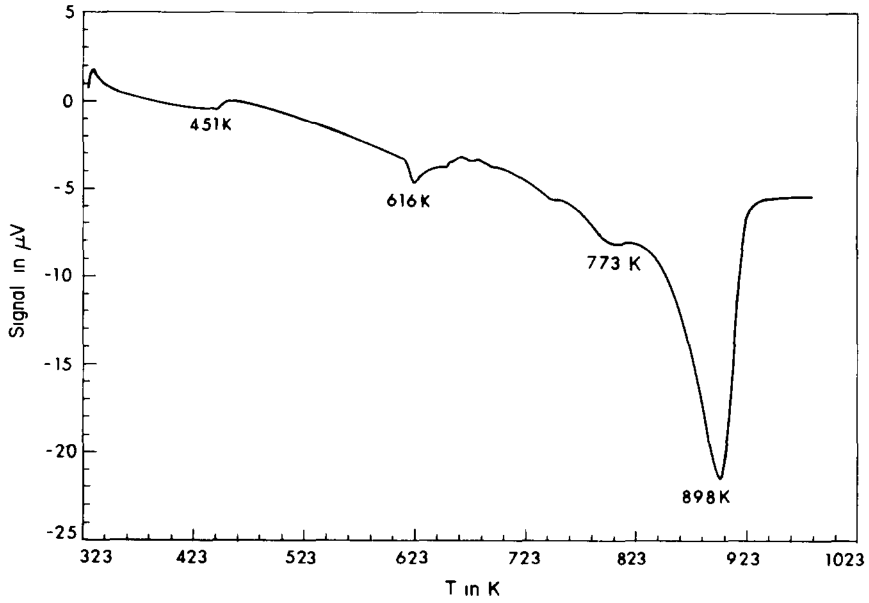

Fig. 2. DSC curves showing the transitions of $Rb_2U(SO_4)_3$.

Figure 2 shows the differential scanning calorimetric results. The first endothermic peak is at 616 K and the second at 773 K. The third peak in the DSC curve at 898 K corresponds to the decomposition of $Rb_2U(SO_4)_3$.

Calorimetric results

The enthalpy increment values of $Rb_2U(SO_4)_3$ at various temperatures are given in Table 2. The enthalpy increments were least-squares fitted with temperature into three separate linear segments. The equations obtained were

$$H^{\ominus}_T - H^{\ominus}_{298.15} \pm 694/(\mathrm{J\,mol^{-1}}) = -1.117 \times 10^5 + 368.9T/\mathrm{K} + 0.0199T^2/\mathrm{K}^2$$

(from 370 to 628 K)

$$H^{\ominus}_T - H^{\ominus}_{298.15} \pm 405/(\mathrm{J\,mol^{-1}}) = 3.279 \times 10^3 + 13.4T/\mathrm{K} + 0.3063T^2/\mathrm{K}^2$$

(from 630 to 760 K)

$$H^{\ominus}_T - H^{\ominus}_{298.15} \pm 433/(\mathrm{J\,mol^{-1}}) = -6.671 \times 10^5 + 1140T/\mathrm{K}$$

(from 765 to 800 K)

The dependence of the enthalpy increment values on temperature is compared with the fit values in Fig. 3. It can be seen from the fit that there are two solid state transitions: one at 625 ± 3 K and the other at 763 ± 2 K. The corresponding enthalpies of transition were calculated as 5.998 and 13.585 kJ $\mathrm{mol^{-1}}$, respectively.

TABLE 2

Enthalpy increments of $Rb_2U(SO_4)_3$ at various temperatures

T in K	$H_T^\ominus - H_{298.15}^\ominus$ in J mol^{-1}	T in K	$H_T^\ominus - H_{298.15}^\ominus$ in J mol^{-1}
298.15	0.0	First transition	
370.2	26717 ± 150	630.0	133291 ± 450
388.4	33681 ± 180	639.8	137268 ± 340
418.0	45850 ± 276	658.2	144756 ± 876
437.6	52072 ± 325	668.5	148919 ± 610
458.1	60091 ± 432	678.6	152985 ± 241
498.1	77112 ± 310	693.2	160068 ± 720
518.6	85018 ± 543	708.3	167147 ± 870
539.0	93256 ± 498	752.5	185656 ± 900
559.7	100608 ± 870	760.0	190381 ± 1020
580.2	109278 ± 765		
593.6	112436 ± 981	Second transition	
604.9	117789 ± 1076	763.7	203966 ± 1015
617.1	123162 ± 670	773.0	213847 ± 1190
623.2	125479 ± 698	788.0	231062 ± 786
625.4	127293 ± 1439	803.0	248643 ± 943

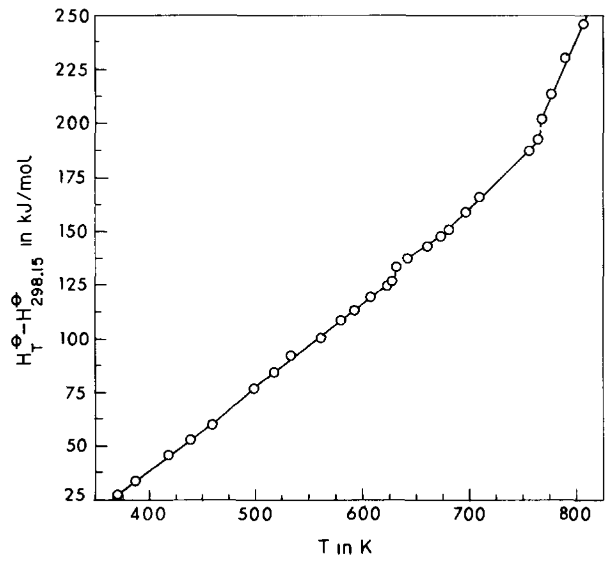

Fig. 3. Dependence of enthalpy increment on temperature for $Rb_2U(SO_4)_3(s)$ samples.

TABLE 3

Thermal properties of $Rb_2U(SO_4)_3(s)$

T in K	$H_T^\ominus - H_{298.15}^\ominus$ in J mol^{-1}	$C_p^\ominus$ in JK^{-1}mol^{-1}	$S_T^\ominus$ in JK^{-1}mol^{-1}	$-(G_T^\ominus - 298.15)/T$ in JK^{-1}mol^{-1}
325	9598	384.9	384.9	354.6
350	19232	385.7	412.7	367.8
375	28886	386.5	439.4	362.3
400	38559	387.3	464.3	367.9
425	48251	388.1	487.8	374.3
450	57962	388.8	510.0	381.2
475	67692	389.6	531.1	388.6
500	77442	390.4	551.1	396.2
525	87211	391.1	570.1	404.0
550	96999	391.9	588.4	412.0
575	106806	392.7	605.8	420.1
600	116633	393.4	622.5	428.1
625	126478	394.2	638.6	436.2
Transition				
650	141401	411.6	577.0	359.5
675	151882	426.9	592.8	367.8
700	162746	442.2	608.6	376.1
725	173993	457.5	624.4	384.4
750	185623	472.9	640.2	392.7

The first differential of the enthalpy equations with respect to temperature yields the molar heat capacity. The $S_{298.15}^\ominus$ value of $Rb_2U(SO_4)_3$ is assumed to be the summation of $S_{298.15}^\ominus$ values of $Rb_2SO_4(s)$ and $U(SO_4)_2$ reported in the literature [8]. From this value, the $S_T^\ominus$ of $Rb_2U(SO_4)_3$ is calculated using the equation

$$S_T^\ominus = S_{298.15}^\ominus + \int_{298.15}^{T} (C_p^\ominus/T)\,\mathrm{d}T$$

The Gibbs free energy function $-(G_T^\ominus - H_{298.15}^\ominus)/T$ was derived from the equation

$$-(G_T^\ominus - H_{298.15}^\ominus)/T = S_T^\ominus - [(H_T^\ominus - H_{298.15}^\ominus)/T]$$

The calculated values of the thermal properties are given in Table 3.

DISCUSSION

The transition temperatures obtained by calorimetry are in reasonable agreement with the DSC and DTA results. A difference of 10 K in the second transition temperature between DSC and calorimetry may be attributed to the dynamic nature of DSC in which to some extent, the peak temperature is a function of heating rate. The decomposition temperatures obtained in DSC and DTA are in very good agreement with each other. The solid state transitions were found to be reversible. The X-ray diffraction pattern before and after the calorimetric experiments below 800 K remained the same, indicating no basic structural changes during the calorimetric study.

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