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THERMODYNAMIC FUNCTIONS OF ALKALINE EARTH MONOURANATES FROM CALORIMETRIC MEASUREMENTS

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ABSTRACT

High temperature differential calorimetry was used to determine the enthalpy increments of $BaUO_4$, α-$SrUO_4$ and $CaUO_4$ relative to room temperature The measurements covered the temperature range 1000–1735 K From these enthalpy values other thermodynamic functions, such as $C_{pT}^{\ominus}$, $S_T^{\ominus}$ and $-(G_T^{\ominus} - H_{298}^{\ominus})/T$, were deduced using $C_{p298}^{\ominus}$ and $S_{298}^{\ominus}$ from the literature The high temperature $C_{pT}^{\ominus}$ values for the monouranates obtained in this study are discussed in relation to the low temperature data available in the literature

INTRODUCTION

As part of a programme to obtain thermodynamic data on compounds of fission products that are likely to be formed in reactor fuels, we have already reported the results of studies on zirconates and cerates of the alkaline earth elements, barium and strontium [1,2]. In this paper we report measurements on alkaline earth monouranates Barium and strontium are produced in the fission of ^{235}U with yields of 6 6 and 9.1%, respectively They are known to precipitate as a separate zirconate phase in the hot zones of the mixed oxide fuel in a fast reactor [3] BaO and SrO may also form a solid solution in UO_2 and, under favourable conditions of temperature and oxygen potentials, form the monouranates $BaUO_4$ has indeed been observed in irradiated fuel [4]. In this study the monouranates of Ca, Sr and Ba were synthesised and calorimetric measurements were carried out in order to derive thermodynamic data.

EXPERIMENTAL

Preparation and characterisation of samples

The uranates were prepared by mixing stoichiometric amounts of the appropriate alkaline earth carbonate and ammonium diuranate, and heating

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the mixture at 1270 K in air for 30–40 h The formation of the uranates was confirmed by X-ray diffraction analyses The samples used for calorimetric measurements were in the form of small pellets

Calorimetric technique

The experimental technique used was drop calorimetry Samples at ambient temperature were dropped into the calorimeter furnace A Setaram microcalorimeter (model HT-1500) was used for this purpose The parameter measured was enthalpy increment $H_T^\ominus - H_{298}^\ominus$ Calibration was achieved by comparison of the measured heat flow with that of a standard α-Alumina (NBS SRM 720) was used as the standard material The sandwich technique was employed a measurement was taken on a sample in between two standard measurements

RESULTS

The measured enthalpy increment values thus obtained were fitted by the least-squares method to give smoothed values, from which other thermodynamic parameters such as $C_{pT}^\ominus$, $S_T^\ominus$ and $-(G_T^\ominus - H_{298}^\ominus)/T$ were computed

The standard error for the fit is given by

$$\text{Standard error} = \sqrt{\frac{\Sigma(\text{Residual})^2}{(\text{No of observations} - \text{No of coefficients})}}$$

$BaUO_4$

The $H_T^\ominus - H_{298}^\ominus$ values for $BaUO_4$ were measured in the temperature range 1006–1660 K These were fitted to the expression

$$H_T^\ominus - H_{298}^\ominus = 36\ 7546T + (1\ 0969 \times 10^{-3})T^2 + (6\ 6390 \times 10^5)T^{-1} - 13\,283$$

in cal mol^{-1} (298–1660 K) The standard error of this fit was 2% Other thermodynamic functions were derived from the above expression using $C_{p298}^\ominus$ and $S_{298}^\ominus$ values taken from O'Hare et al [5] Table 1 shows all these functions listed as functions of temperature

Alpha-$SrUO_4$

The measurements on this system were carried out between 1065 and 1735 K The data were fitted to obtain the expression

$$H_T^\ominus - H_{298}^\ominus = 24\ 5627T + (8\ 2504 \times 10^{-3})T^2 - (1\ 5410 \times 10^5)T^{-1} - 7540$$

TABLE 1

Thermodynamic functions of $BaUO_4$

Temp (K)	$H_T^\ominus - H_{298}^\ominus$ (measured) (cal mol^{-1})	$H_T^\ominus - H_{298}^\ominus$ (from fit) (cal mol^{-1})	Temp (K)	$H_T^\ominus - H_{298}^\ominus$ (cal mol^{-1})	$C_p^\ominus$ (cal K^{-1} mol^{-1})	$S_T^\ominus$ (cal K^{-1} mol^{-1})	$-(G_T^\ominus - H_{298}^\ominus)/T$ (cal K^{-1} mol^{-1})
1006	25584	25462	298	0	29 9402	36 7997	36 7997
1051	27083	27189	300	55	30 04	36 985	36 80
1098	29119	29001	400	3254	33 48	46 16	38 02
1145	30754	30819	500	6696	35 20	53 84	40 45
1236	34420	34359	600	10271	36 23	60 35	43 23
1282	36327	36157	700	13931	36 94	65 99	46 09
1325	38100	37844	800	17653	37 47	70 96	50 89
1368	39119	39535	900	21422	37 91	75 40	51 60
1412	41020	41272	1000	25234	38 28	79 42	54 19
1443	42157	42498	1100	29078	38 62	83 08	56 65
1479	44033	43925	1200	32955	38 93	86 45	58 99
1526	45680	45794	1300	36862	39 21	89 58	61 22
1570	47568	47548	1400	40798	39 49	92 50	63 36
1624	49807	49708	1500	44780	39 75	95 23	65 39
1667	51832	51433	1600	48747	40 01	97 80	67 33
			1700	52760	40 25	100 24	69 20

TABLE 2

Thermodynamic functions of α-$SrUO_4$

Temp (K)	$H_T^\ominus - H_{298}^\ominus$ (measured) (cal mol^{-1})	$H_T^\ominus - H_{298}^\ominus$ (from fit) (cal mol^{-1})	Temp (K)	$H_T^\ominus - H_{298}^\ominus$ (cal mol^{-1})	$C_p^\ominus$ (cal K^{-1} mol^{-1})	$S_T^\ominus$ (cal K^{-1} mol^{-1})	$-(G_T^\ominus - H_{298}^\ominus)/T$ (cal K^{-1} mol^{-1})
1065	29008	27833	298	0	31 216	36 601	36 601
1111	31346	29794	300	58	31 23	36 79	36 60
1201	33639	33732	400	3220	32 13	45 89	37 84
1248	34535	35841	500	6496	33 43	53 19	40 20
1300	37335	38216	600	9911	34 89	59 41	42 89
1337	38428	39933	700	13477	36 43	64 91	45 65
1427	41909	44204	800	17198	38 00	69 87	48 38
1469	43335	46242	900	21078	39 60	74 44	51 02
1553	47929	50405	1000	25119	41 22	78 70	53 58
1581	51146	51819	1100	29322	42 84	82 70	56 05
1607	54136	53143	1200	33688	44 47	86 50	58 43
1651	56824	55409	1300	38216	46 11	90 12	60 73
1697	59498	57812	1400	42909	47 74	93 60	62 95
1735	61175	59823	1500	47765	49 38	96 95	65 11
			1600	52785	51 02	100 19	67 20
			1700	57970	52 67	103 33	69 23

TABLE 3

Thermodynamic functions of $CaUO_4$

Temp (K)	$H_T^\ominus - H_{298}^\ominus$ (measured) (cal mol^{-1})	$H_T^\ominus - H_{298}^\ominus$ (from fit) (cal mol^{-1})	Temp (K)	$H_T^\ominus - H_{298}^\ominus$ (cal mol^{-1})	$C_p^\ominus$ (cal K^{-1} mol^{-1})	$S_T^\ominus$ (cal K^{-1} mol^{-1})	$-(G_T^\ominus - H_{298}^\ominus)/T$ (cal K^{-1} mol^{-1})
1034	32564	32587	298	0	29 6063	28 8904	28 8904
1048	34205	33343	300	55	29 77	29 07	28 89
1097	35958	36026	400	3381	36 15	38 60	30 15
1142	37798	38536	500	7209	40 20	47 13	37 71
1191	41163	41319	600	11392	43 34	54 74	35 74
1233	44106	43745	700	15864	46 05	61 63	38 97
1281	45622	46565	800	20594	48 53	67 79	42 05
1319	48474	48833	900	25566	50 88	73 80	45 39
1367	50746	51740	1000	30767	53 14	79 27	48 50
1405	55314	54077	1100	36192	55 35	84 44	51 54
1439	55184	56194	1200	41836	57 52	89 35	54 49
1492	64109	59542	1300	47695	59 67	94 04	57 35
1528	65440	61857	1400	53768	61 79	98 54	60 13
			1500	60053	63 91	102 88	62 84
			1600	66549	66 01	107 07	65 48

in cal mol^{-1} (298–1735 K) The standard error for the fit was found to be 4 5%

The measured values of $H_T^\ominus - H_{298}^\ominus$ together with the fitted values and the derived thermodynamic properties, $C_{pT}^\ominus$, $S_T^\ominus$ and $-(G_T^\ominus - H_{298}^\ominus)/T$ are given in Table 2 as functions of temperature $C_{p298}^\ominus$ and $S_{298}^\ominus$ were taken from Westrum et al [6]

$CaUO_4$

Measurement on this uranate covered the temperature range 1034–1528 K The smoothed enthalpy values are given by the expression

$$H_T^\ominus - H_{298}^\ominus = 33\ 4876T + (10\ 271 \times 10^{-3})T^2 + (8\ 8946 \times 10^5)T^{-1} - 13\,881$$

in cal mol^{-1} (298–1528 K). The standard error of this fit was computed to be 3 5%

Table 3 gives the thermodynamic functions of this compound derived from the measured enthalpy increments using $C_{p298}^\ominus$ and $S_{298}^\ominus$ from the low temperature data of Westrum et al [6].

DISCUSSION

A high temperature drop calorimetric study of $BaUO_4$ has been described by Leonidov et al [7] They measured enthalpy increments in the range

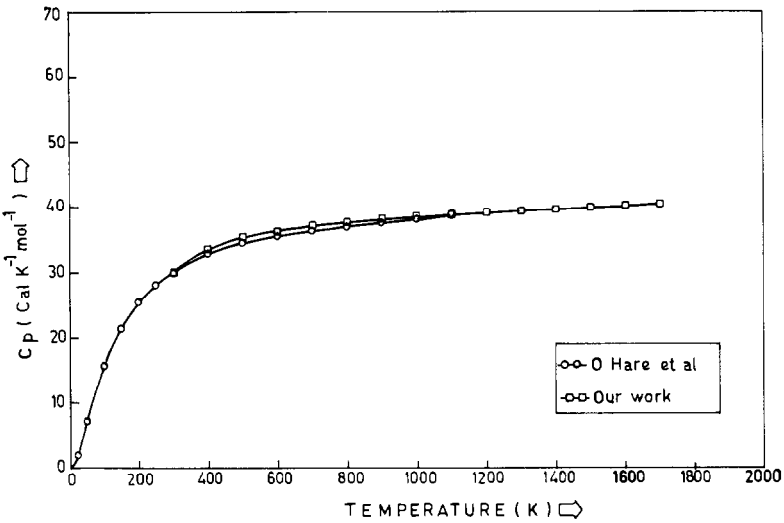

Fig 1 Heat capacity of $BaUO_4$

588–1084 K O'Hare et al [5] interpolated these results to 298 K and combined them with their own low temperature data The high temperature C_p values of Leonidov et al merge smoothly with the low temperature data of O'Hare et al Our measured values extend the existing data up to 1660 K, and the results also merge smoothly with those of O'Hare et al They are in agreement with the combined expression given by O'Hare et al within $\pm 2\%$ (in the temperature range of the latter's applicability) In the temperature range 1000–1660 K our data show that the C_p–T curve flattens out, however, this is not the case with the extrapolated curve of O'Hare et al These results are shown in Fig 1

High temperature heat capacity data on α-$SrUO_4$ are not available in the literature The C_p values obtained in this study do not merge smoothly with the low temperature heat capacity data of Westrum et al [6] It was observed by O'Hare et al , and also by the present authors, that the heat capacity data of $BaUO_4$ did not merge smoothly with Westrum's low temperature heat capacity values O'Hare et al attributed this discrepancy to the impurity of Westrum's sample It is possible that the same argument may also be valid in the case of α-$SrUO_4$, but this could not be checked owing to lack of information

Faustova et al [8] and Leonidov et al [7] have carried out drop calorimetric measurements on $CaUO_4$ However, the values could not be used with this work, since the temperature range of measurement was very narrow, namely 998–1189 K The heat capacity values obtained in this work merge very well with the low temperature values of Westrum et al [6] All the uranates studied in this work were prepared following the procedures used by Cordfunke and Loopstra [9] and O'Hare et al [5] Uranium exists in the

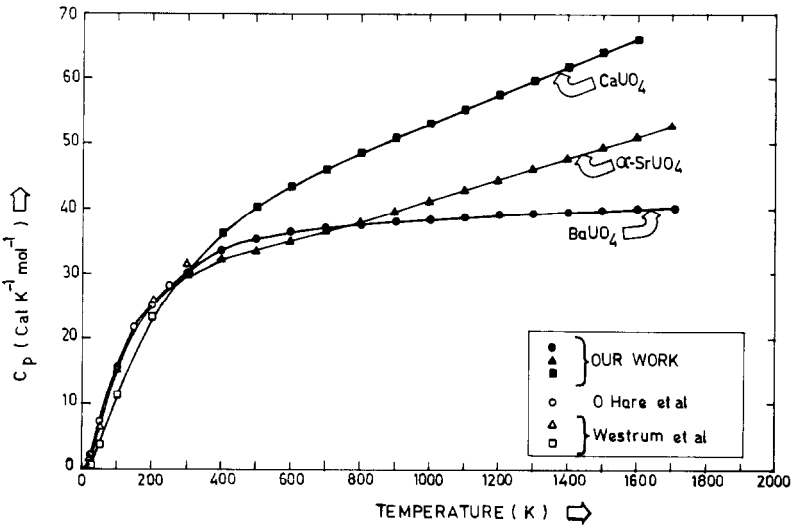

Fig 2 Heat capacities of alkaline earth monouranates

highest oxidation state (VI) in these compounds and, considering the oxidising conditions of the preparation, the compounds are expected to be stoichiometric The above authors also appear to have come to the same conclusion X-ray patterns taken before and after the highest experimental temperatures of the uranates had been reached showed no change in the pattern, thereby suggesting that stoichiometric change, if any, on heating was not significant Figure 2 shows the heat capacity as a function of temperature for $BaUO_4$, α-$SrUO_4$ and $CaUO_4$ At high temperatures $BaUO_4$ has the lowest heat capacity and $CaUO_4$ the highest The C_p–T curve of $BaUO_4$ flattens out relatively early, whereas the other two curves do not show this tendency even at 1600 K

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