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THE THERMOCHEMICAL PROPERTIES OF CESIUM MOLYBDATE, Cs_2MoO_4, FROM 298.15 TO 1500 K

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ABSTRACT

The enthalpy increments of Cs_2MoO_4 have been measured from 415 to 700 K in a drop calorimeter. The temperature and the enthalpy of transition as well as the melting point have been determined by DSC. By combining these results with data from the literature, smoothed thermodynamic functions have been calculated for Cs_2MoO_4.

INTRODUCTION

The thermochemistry of cesium molybdate is of great importance for the evaluation of fuel–fission product interaction in nuclear reactors. Large amounts of both cesium and molybdenum are produced during the fission of uranium and it has been suggested that Cs_2MoO_4 can be formed in fuel pins under the conditions of temperature and oxygen potential during normal operation [1].

In a series of papers from Argonne National Laboratory most aspects of the thermochemistry of cesium molybdate were reported. O'Hare and Hoekstra [1] determined the enthalpy of formation at 298.15 K, Osborne et al. [2] measured the heat capacities from 5 to 350 K, Fredrickson and Chasanov [3] measured the enthalpy from 556 to 1191 K, and Johnson [4] measured the vapor pressure. Shortly afterwards Denielou et al. [5] reported enthalpy increments of liquid Cs_2MoO_4. As we will discuss later, the enthalpy data reported by Frederickson and Chasanov [3] for the orthorhombic Cs_2MoO_4 do not fit the low-temperature data of Osborne et al. [2]. For this reason we decided to remeasure the enthalpy of Cs_2MoO_4.

In the present study we report enthalpy increment measurements of Cs_2MoO_4 from 415 to 700 K by drop calorimetry. Additionally, we performed differential scanning calorimetry (DSC) to obtain information about the transition and melting data of solid Cs_2MoO_4. These data enable us to evaluate the thermodynamic properties of Cs_2MoO_4 up to 1500 K.

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EXPERIMENTAL

The Cs_2MoO_4 sample was purchased from Cerac-Pure Inc. The purity of the material was specified as 99.9 mol%. Before use the sample was heated at 400 °C in an O_2 atmosphere. The cesium content, determined gravimetrically with kalignost in our laboratory, was (62.53 ± 0.04) mass% (calc. 62.43). The molybdenum content, as specified in the Cerac certificate of analysis, was 22.56 mass% (calc. 22.53). X-ray diffraction analysis (Guinier-De Wolff camera, Cu K_α radiation) showed no other phases to be present.

The isothermal diphenyl ether drop calorimeter, in which the enthalpy increments were measured, was previously described by Cordfunke et al. [6]. Briefly, the sample is enclosed in a spherical vitreous silica ampoule which has a volume of 4.2 cm^3. The ampoule is heated in a furnace whose temperature is measured to ±0.1 K with a Pt to Pt + 10 mass% Rh thermocouple. After a reasonable equilibration time, the ampoule is dropped into the calorimeter. The energy of the ampoule plus the sample now melts solid diphenyl ether in equilibrium with its liquid in a closed system. The resulting volume increase of the ether is determined by weighing the displaced mercury. The ratio of heat input to mass of mercury making up the volume change is a constant for the apparatus (79.977 ± 0.063 J g^{-1}), and is obtained by calibration with α-SiO_2 and compared with the National Bureau of Standards (NBS) standard reference material (No. 720) synthetic sapphire, Al_2O_3. Our results with sapphire all agree within 0.2% with the data given by NBS. The enthalpy contributions of the vitreous silica were determined separately.

For the present study 7.39368 g of Cs_2MoO_4 was sealed in the ampoule which had an empty weight of 1.23915 g. A correction on the measurements was made for the difference in enthalpy between the final calorimeter temperature and the standard reference temperature, 298.15 K, using C_p^0 (298.15 K) [2].

The data for the transition and melting points were measured in a Mettler TA-13 DSC apparatus. The sample was heated in an O_2 atmosphere at 10 deg min^{-1}, in Pt or Au crucibles, with reference materials Ag and Sb, respectively.

RESULTS AND DISCUSSION

The results of the fifteen drop calorimetric measurements are listed in Table 1. The experimental enthalpy increments can be represented by the polynomial equation

$$\begin{aligned}&[H^0(T) - H^0(298.15\ \mathrm{K})] \quad (\mathrm{J\ mol^{-1}})\\ &\quad = 116.404(T/\mathrm{K}) + 54.1106 \times 10^{-3}(T/\mathrm{K})^2 - 39515.9 \qquad (1)\end{aligned}$$

TABLE 1

Calorimetric enthalpy increment measurements for Cs_2MoO_4

T(K)	$[H^0(T) - H^0(298.15\ K)]$ (J mol^{-1})		δ (%)
	Exp.	Calc.	
415.1	18155	18104	0.28
440.0	22165	22149	0.07
449.8	23860	23761	0.42
459.2	25330	25316	0.06
478.9	28638	28608	0.10
508.6	33562	33652	−0.27
528.4	37119	37071	0.13
558.0	42147	42263	−0.27
578.1	45901	45846	0.12
598.1	49457	49456	0.00
618.1	52998	53112	−0.21
638.0	56889	56795	0.17
657.9	60448	60523	−0.12
678.2	64428	64372	0.09
698.1	68208	68191	0.02

for the interval 298.15–700 K, applying $C_p^0(298.15\ K) = 148.67$ J K^{-1} mol^{-1} [2] and $[H^0(T) - H^0(298.15\ K)] = 0$ as boundary conditions. The standard deviation is 80 J mol^{-1} or 0.19%.

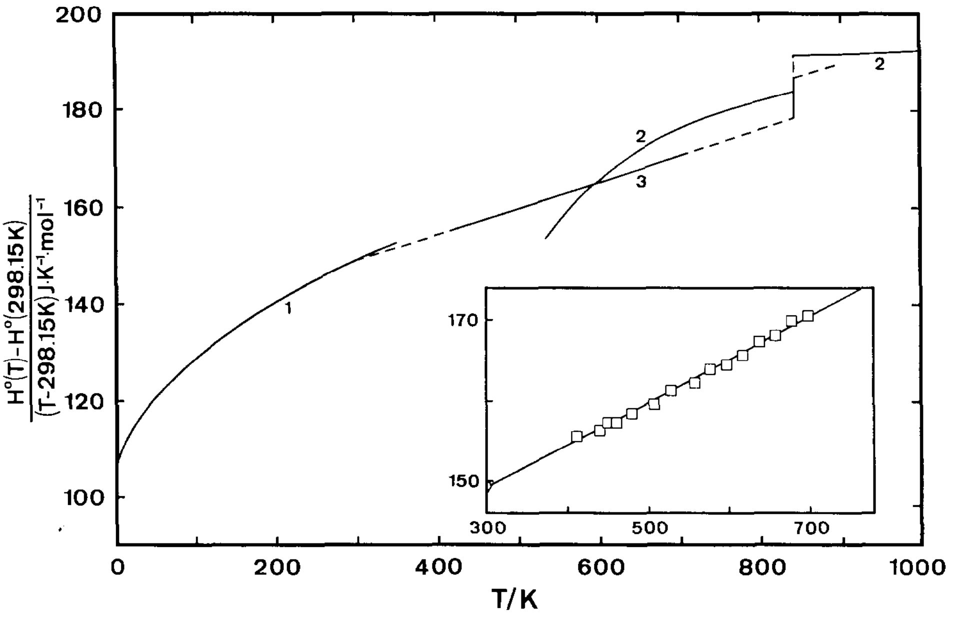

Fig. 1. The reduced enthalpy increments of Cs_2MoO_4. 1, Osborne et al.; 2, Fredrickson and Chasanov; 3, present work.

The results are plotted in Fig. 1 in a $[H^0(T) - H^0(298.15\ \mathrm{K})]/(T - 298.15)$ vs. T plot, together with the results of Osborne et al. [2], and Fredrickson and Chasanov [3]. Our measurements smoothly join the low-temperature measurements of Osborne et al. [2] at 298.15 K. On the contrary, a serious disagreement exists between our measurements and the data of Fredrickson and Chasanov [3], which are evidently in error.

The linear relationship which is found here (Fig. 1) permits an extrapolation of our results to the temperature of transition. The transition from an orthorhombic to a hexagonal structure is found at 841.3 ± 0.4 K in the DSC runs. The enthalpy of transition, determined in the same runs, is 4.6 ± 0.1 kJ mol^{-1}. These values are in good agreement with previous data; Hoekstra [7] reported a transition temperature of 845 K and Fredrickson and Chasanov [3] an enthalpy of transition of 4.2 kJ mol^{-1}. The enthalpy of solid Cs_2MoO_4 above the transition point has been measured by Fredrickson and Chasanov [3], but in view of their erroneous results for the enthalpy below the transition point we reject these measurements.

We have also determined the melting point of Cs_2MoO_4 in the DSC, which was found to be 1229.5 ± 0.2 K. Unfortunately, we could not determine the enthalpy of fusion of Cs_2MoO_4 since the melting of the samples was associated with a mechanical deformation of the platinum or gold crucibles of which the origin is yet unknown. The melting point found in this work is in fair agreement with the value reported by Denielou et al. [5] (1220 ± 5 K) measured by drop calorimetry. Schmutz-Dumont [8] reported a value of 1209 K, which was 20 degrees lower than ours. Denielou et al. [5] reported a value of $\Delta H_\mathrm{m}^0 = 31.8 \pm 0.8$ kJ mol^{-1} by calculating the difference between the enthalpy of liquid Cs_2MoO_4 (eleven determinations) and solid Cs_2MoO_4 (five or six determinations). However, they did not report any numerical results. Johnson [4] calculated the enthalpy of melting from the change in the slope of the vapor pressure of Cs_2MoO_4 at the melting point, and obtained $\Delta H_\mathrm{m}^0 = 43.1 \pm 26.8$ kJ mol^{-1}. He also quoted a personal communication of Fredrickson who obtained 43.9 kJ mol^{-1} by means of drop calorimetry. Since no further information on the work of Fredrickson is available, the value of Denielou et al. [5] is adopted here.

The drop calorimetric results [5] for liquid Cs_2MoO_4 can be represented by the equation

$$[H^0(T) - H^0(298.15\ \mathrm{K})] \quad (\mathrm{J\ mol^{-1}}) = 210.154(T/\mathrm{K}) - 38787.5 \qquad (2)$$

using $[H^0(298.15\ \mathrm{K}) - H^0(273.15\ \mathrm{K})] = 3667$ J mol^{-1} [2] to convert their function to 298.15 K as the reference temperature. The enthalpy of hexagonal Cs_2MoO_4 at the melting point follows from eqn. (2) and the enthalpy of melting. The enthalpy of hexagonal Cs_2MoO_4 at the transition point is calculated from eqn. (1) and the enthalpy of transition. Using these values we obtain for the enthalpy of hexagonal Cs_2MoO_4

TABLE 2

Thermodynamic functions of solid Cs_2MoO_4

T (K)	C_p^0 ($J\ K^{-1}\ mol^{-1}$)	S^0 ($J\ K^{-1}\ mol^{-1}$)	$-[G^0(T)-H^0(298)]/T$ ($J\ K^{-1}\ mol^{-1}$)	$H^0(T)-H^0(298)$ ($J\ mol^{-1}$)	$\Delta H_f^0(T)$ ($J\ mol^{-1}$)	$\Delta G_f^0(T)$ ($J\ mol^{-1}$)
298	148.670	248.350	248.350	0	−1514600	−1407042
300	148.870	249.270	248.354	275	−1514599	−1406376
400	159.692	293.580	254.322	15703	−1518261	−1368988
500	170.515	330.377	265.951	32213	−1516735	−1331824
600	181.337	362.422	279.412	49806	−1514180	−1295066
700	192.159	391.188	293.358	68481	−1510613	−1258815
800	202.981	417.553	307.256	88238	−1506079	−1223140
841.3	–	427.882	312.926	96713	−1503961	−1208805
841.3	–	433.350	312.926	101313	−1499361	−1208805
900	209.639	447.295	321.238	113451	−1496264	−1188406
1000	219.344	469.885	334.985	134900	−1625925	−1147329
1100	229.049	491.246	348.228	157320	−1617530	−1099868
1200	238.754	511.592	361.000	180710	−1608298	−1053213
1229.5	–	517.425	364.683	187796	−1605425	−1039717
1229.5	–	543.289	364.683	219596	−1573625	−1039716
1300	210.154	555.007	374.690	234412	−1568884	−1009108
1400	210.154	570.581	388.132	255428	−1562289	−966297
1500	210.154	585.080	400.785	276443	−1555829	−923955

$$[H^0(T) - H^0(298.15\ \mathrm{K})] \quad (\mathrm{J\ mol^{-1}})$$
$$= 122.295(T/\mathrm{K}) + 48.5245 \times 10^{-3}(T/\mathrm{K})^2 - 35918.7 \qquad (3)$$

The thermodynamic quantities for Cs_2MoO_4 from 298.15 to 1500 K are given in Table 2. Since no meaning can be assigned to $C_p^0(T)$ values, calculated from enthalpy increment measurements at transition points, these values have been omitted. $\Delta H_f^0(298.15\ \mathrm{K})$ was taken from O'Hare and Hoekstra [1], and $S^0(298.15\ \mathrm{K})$ from Osborne et al. [2]. For the calculation of $\Delta H_f^0(T)$ and $\Delta G_f^0(T)$ the enthalpy increments and standard entropies of Cs, Mo and O_2 were taken from the tables by Glushko et al. [9].

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