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HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF THE ALKALI METAL COMPOUNDS IN THE TEMPERATURE RANGE 300–800 K. I. CESIUM AND RUBIDIUM MOLYBDATES

RAJIV KOHLI*

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and the Department of Nuclear Engineering, University of California Berkeley, Berkeley, CA 94720 (U S A)

WOLFGANG LACOM

Institut für Metallurgie, Österreichisches Forschungszentrum Seibersdorf GmbH, A-1082 Wien (Austria)

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ABSTRACT

The heat capacities of cesium and rubidium molybdates, Cs_2MoO_4 and Rb_2MoO_4, have been measured by differential scanning calorimetry (DSC) in the temperature range 300–800 K. These values have been combined with published low-temperature heat capacity data for Cs_2MoO_4 to obtain thermodynamic functions to 800 K. For Rb_2MoO_4, however, these functions could not be calculated because low-temperature heat capacities are unavailable Instead, only heat capacity data are reported.

INTRODUCTION

Cesium and molybdenum are high yield fission products, and in the oxygen potential range of nuclear fuel they will react to form cesium molybdate, Cs_2MoO_4 [1]. Cs_2MoO_4 is highly volatile and will transport cesium and molybdenum to the cladding. It is also known to play a significant role in the interactions between the cladding and the fuel in nuclear reactors [2]. Although the fission yield of rubidium is considerably less than cesium, it is still a significant fission product. As in the case of Cs_2MoO_4, rubidium and molybdenum are thermodynamically favored to form the molybdate, Rb_2MoO_4, in the in-reactor oxygen potential range of LWRs and LMFBRs and it is not unreasonable to assume that rubidium molybdate could also play a role in reactions at the fuel–cladding interface [1].

* To whom correspondence should be addressed.

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In order to make thermodynamic predictions of the reactions involving cesium and rubidium molybdates in the temperature range (600–900 K) of the fuel–cladding gap in LWRs, high-temperature thermodynamic data are required. Osborne et al. [3] have measured the heat capacity of Cs_2MoO_4 from 5 to 350 K, and Frederickson and Chasanov [4] have obtained the enthalpy increments of Cs_2MoO_4 in the temperature range 550–1190 K by means of drop calorimetry. Except for a standard enthalpy of formation [5], there are no thermodynamic data for Rb_2MoO_4 at high temperatures.

We have measured the heat capacities of cesium and rubidium molybdates in the temperature range 300–800 K by means of differential scanning calorimetry (DSC). These data have been combined with other literature data to obtain thermodynamic functions for these molybdates to 800 K. This paper, which is the first in a series on heat capacity measurements on alkali metal compounds, presents the results for Cs_2MoO_4 and Rb_2MoO_4.

EXPERIMENTAL

Sample preparation and characterization

The salts, whose typical purity was stated to be 99.9 moles %, were purchased from Cerac/Pure, Wisconsin. They were purified by the methods described by O'Hare and Hoekstra for Rb_2MoO_4 [5] and Cs_2MoO_4 [6], and then subjected to X-ray, chemical, and spectrographic analysis. The samples were judged to be better than 99.95% purity.

Calorimetric techniques

The salts were compacted to form small pellets to fit into gas-tight aluminum pans. This was necessary to avoid any reaction between the sample material and the atmosphere and to render a high sample-to-pan mass ratio. The pellets were heated at 673 K for 1 h in order to anneal out stored energy from compaction and, after cooling to room temperature, were hermetically sealed in the pans. The tightness of all filled pans was checked by heating them in a furnace at slightly higher than the maximum temperature used in the DSC instrument. All handling of the samples was carried out in an argon-filled glove box.

The measurements were carried out in a Perkin-Elmer DSC II from 310 K up to 770 K with a heating rate of 40 K min^{-1} and a sensitivity of 5 mcal s^{-1} full-scale defelection. As reference material, ground NBS-sapphire was sealed in a gas-tight pan—its mass was chosen to render a heat capacity similar to those of the samples.

The heat capacity was determined in the usual way by measuring an empty pan (baseline), the samples, and the reference material against an

empty pan. The heat capacities were calculated from the expression

$$C^0_{p,\,sample} = C^0_{p,\,sapphire} \frac{m_{sapphire}\, d_{sample}}{m_{sample}\, d_{sapphire}} \quad (1)$$

where m is the mass, d is the recorded thermal effect and C^0_p is the heat capacity.

RESULTS AND DISCUSSION

Cesium molybdate

The experimental values of the heat capacity are listed in Table 1. These values were fitted to a polynomial by a least squares method to obtain the following expression for the heat capacity in the temperature range 350–800 K

$$C^0_p\ (\mathrm{JK^{-1}\ mole^{-1}}) = 154.50 + 5.8562 \times 10^{-2} T - 1.9832 \times 10^{6} T^{-2} \quad (2)$$

A plot of C^0_p vs. T for Cs_2MoO_4 (Fig. 1) shows that our high-temperature data merge smoothly with the data of Osborne et al. [3] at low temperatures. Equation (2) was combined with the low-temperature data of Osborne et al. to determine C^0_p values in the temperature range 298–800 K. These values

TABLE 1

Molar heat capacity of Cs_2MoO_4 (molar Mass of Cs_2MoO_4 = 425.75 g mole^{-1})

Temp. (K)	C^0_p (J K^{-1} mole^{-1})
350	157.21
380	163 11
410	168.35
440	171.42
470	174 39
490	175.84
520	177.74
550	178.38
580	179.88
600	182 48
630	185.77
660	189 34
690	191.10
710	191.87
740	193.92
770	198 39

TABLE 2

Thermodynamic properties of cesium molybdate to 800 K

T (K)	C_p^0 (J K^{-1} $mole^{-1}$)	$S^0(T)$ (J K^{-1} $mole^{-1}$)	$H^0(T)-H^0(298)$ (kJ $mole^{-1}$	$-\{G^0(T)-H^0(298)\}/T$ (J K^{-1} $mole^{-1}$)	$-\Delta H_f^0$ (kJ $mole^{-1}$)	$-\Delta G_f^0$ (kJ $mole^{-1}$)
298.15	148 67	248.35	0	248 35	1514.6	1407.1
300	148.95	249 27	0.27	248.37	1514.6	1406.4
350	158.81	273.10	7 73	251.10	1514.4	1389.1
400	165.53	294.76	15.85	255.14	1514.4	1370.5
450	171.06	314.58	24 27	260 66	1513.9	1352.6
500	175.85	332.91	32.94	267 03	1513.3	1333.6
550	180.15	349.83	41.84	273 75	1512.6	1315.5
600	184.13	365.67	50.95	280.76	1511.8	1296.5
650	187.87	380.56	60 25	287.87	1510.8	1278.2
700	191.45	394.62	69.74	294.99	1509.7	1259.2
750	194.90	407.94	79.39	302 08	1508.5	1240.8
800	198.25	420.63	89.22	309.10	1507.1	1221.7

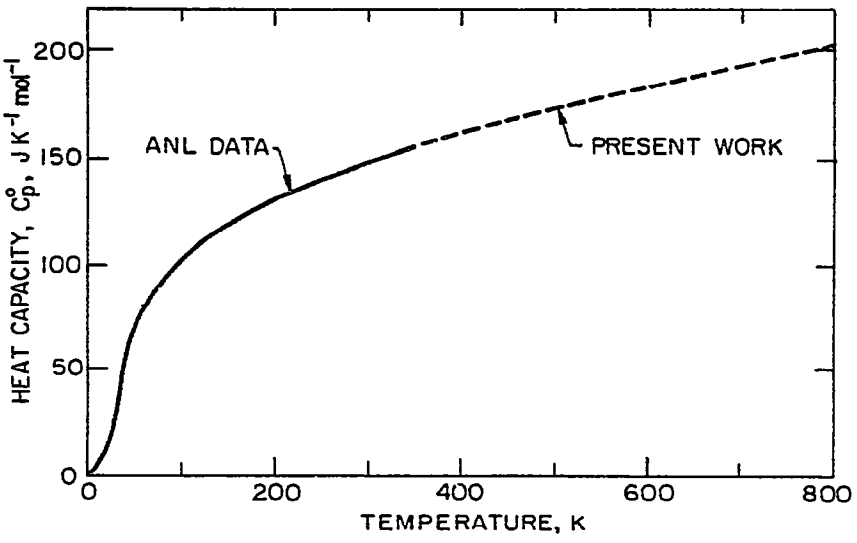

Fig. 1. Molar heat capacity of cesium molybdate, Cs_2MoO_4, at constant pressure. ANL data are the low-temperature data of Osborne et al. [3]

are listed in Table 2 at selected temperatures. Table 2 also lists entropy and enthalpy values which were derived from appropriate integrations of eqn. (2). The free energy function

$$\frac{G^0(T) - H^0(298)}{T} = \frac{H^0(T) - H^0(298)}{T} - S^0(T) \tag{3}$$

was also calculated. Finally. the standard enthalpy, ΔH_f^0, and the standard Gibbs energy of formation, ΔG_f^0, were obtained for each temperature and are listed in Table 2. The thermodynamic properties of cesium and oxygen used in the calculation of these functions were taken from the JANAF Tables [7], while those for molybdenum were taken from the recent IAEA monograph [8].

Rubidium molybdate

Table 3 lists the experimental values of the heat capacity for Rb_2MoO_4 from 350 to 750 K. The results can be represented by the following polynomial expression for the heat capacity, which was obtained by least squares fitting of the data

$$C_p^0(\mathrm{JK^{-1}mole^{-1}}) = 105.76 + 12.914 \times 10^{-2}T + 8.8891 \times 10^5 T^{-2} \tag{4}$$

Except for a value for the standard enthalpy of formation at 298 K [5], there are no thermodynamic data for Rb_2MoO_4. In the absence of low-temperature heat capacities for Rb_2MoO_4, no attempt has been made to derive thermodynamic functions for this compound.

We hope to be able to extend the temperature range of our measurements

TABLE 3

Molar heat capacity of Rb_2MoO_4 (molar mass of $Rb_2MoO_4 = 330.91$ g mole^{-1})

Temp. (K)	C_p^o (J K^{-1} mole^{-1})
350	156.45
380	160.28
400	163.097
420	166.29
450	170.30
480	173.92
500	174 87
520	176.44
550	178.88
580	181.46
600	183.60
620	186.69
650	189.68
680	193.92
700	196 88
720	200 98
750	210.17

to 1000 K in the near future by making certain modifications to our DSC instrument, and to 1500 K by using a high-temperature drop calorimeter.

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REFERENCES

1 R. Kohli, in N.A. Gokcen (Ed.), Chemical Metallurgy—A Tribute to Carl Wagner, Publ. Met. Soc AIME, Pennsylvania, June 1981, p. 309.
2 R. Kohli, Ein thermodynamischer Beitrag zum Verstandnis des Vielstoffsystems Urandioxid–Spaltprodukte–Zircaloy, Aus. Res. Center Rep. No. SGAE-3014, December 1978.
3 D.W. Osborne, H.E. Flotow and H R. Hoekstra, J. Chem. Thermodyn., 6(1974)179.
4 D.R. Frederickson and M.G. Chasanov, in S R Porter and J.F. Johnson (Eds.), Analytical Chemistry, Vol. 3, Plenum Press, New York, 1974, p. 723.
5 P.A.G O'Hare and H R. Hoekstra, J. Chem. Thermodyn., 6(1974)117.
6 P.A.G O'Hare and H.R. Hoekstra, J. Chem. Thermodyn., 5(1973)851.
7 JANAF Thermochemical Tables, 2nd edn , Natl. Bur. Stand. Rep. No. NSRDS-NBS 37, June 1971.
8 L. Brewer, in Molybdenum: Physico-Chemical Properties of its Compounds and Alloys, At. Energy Rev. Spec. Issue No. 7, IAEA, Vienna, 1980.