Thermochimica Acta, 237 (1994) 241–245
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01670-X

Heat capacity and thermodynamic properties of alkali metal compounds. Part 7. Cesium and rubidium dimolybdates

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(Received 4 October 1993; accepted 10 December 1993)

Abstract

The heat capacities of cesium and rubidium dimolybdates have been measured by differential scanning calorimetry (DSC) in the temperature range 310–700 K. These values have been combined with measured and estimated values of the standard entropy and enthalpy of formation for $Cs_2Mo_2O_7$ and $Rb_2Mo_2O_7$ to obtain thermodynamic functions up to 700 K.

INTRODUCTION

Cesium is a high-yield, reactive fission product which forms a number of complex compounds with other fission products during the irradiation of nuclear reactor fuel rods. One of these compounds, cesium orthomolybdate (Cs_2MoO_4), is highly volatile, and at elevated temperatures it tends to disproportionate to form the dimolybdate $Cs_2Mo_2O_7$. Although the fission yield of rubidium is considerably less than that of cesium, rubidium is also highly reactive, and the formation of rubidium dimolybdate ($Rb_2Mo_2O_7$) can be postulated by a similar mechanism.

To define the thermochemical conditions under which these reactions will occur, high temperature thermodynamic data on the alkali metal molybdates are needed. The standard enthalpies of formation of Cs_2MoO_4 [1, 2], Rb_2MoO_4 [3], and $Cs_2Mo_2O_7$ [4] have been published, whereas low temperature heat capacity measurements [5] and enthalpy increments in the temperature range 415–1500 K have been reported [6–8] only for Cs_2MoO_4. For $Rb_2Mo_2O_7$, however, there are no published thermodynamic data at high temperatures. This paper, which is the seventh in a series on the thermodynamic properties of alkali metal compounds, presents the results of heat capacity measurements on $Cs_2Mo_2O_7$ and $Rb_2Mo_2O_7$.

TABLE 1

Molar heat capacity of $Cs_2Mo_2O_7$. Molar mass of $Cs_2Mo_2O_7 = 569.687\ g\ mol^{-1}$

Temperature/K	C_p° /(J K^{-1} mol^{-1})	Temperature/K	C_p° /(J K^{-1} mol^{-1})
310	229.76	530	283.31
350	244.97	550	287.22
370	251.63	580	291.53
380	255.01	600	294.81
400	260.11	630	297.60
430	266.42	650	300.18
450	270.47	680	302.70
480	275.81	700	304.03
500	279.17		

EXPERIMENTAL

Sample preparation and characterization

The compounds were prepared for calorimetry from equimolar quantities of the orthomolybdates and MoO_3 by the method described by O'Hare and Hoekstra [1]. Chemical and spectrographic analyses gave the results shown in the following table.

Compound	Cs content/ mass%	Rb content/ mass%	Mo content/ mass%	Mole ratio
$Cs_2Mo_2O_7$	46.47 ± 0.08	–	33.27 ± 0.09	1.008 ± 0.001
$Rb_2Mo_2O_7$	–	35.87 ± 0.02	40.07 ± 0.08	1.005 ± 0.002

Calorimetric technique

The experimental techniques employed have been described previously [9]. All handling of the samples was carried out in an argon-filled glove box.

The measurements were carried out on a Perkin-Elmer DSC II instrument from 310 to 700 K with a heating rate of 10 K min^{-1} and a sensitivity of 5 mcal s^{-1} full scale deflection. As reference material, ground NBS sapphire was sealed in a gas-tight pan. Its mass was so chosen as to render a heat capacity similar to those of the samples.

The heat capacity was determined in the usual way by measurements on an empty pan (baseline), the samples, and the reference material against an empty pan. The heat capacities were calculated from the expression

$$[C_p^\circ]_{\text{sample}} = [C_p^\circ]_{\text{sapphire}} \times \frac{[m]_{\text{sapphire}} \cdot [d]_{\text{sample}}}{[m]_{\text{sapphire}} \cdot [d]_{\text{sample}}} \quad (1)$$

where $[m]$ = mass, $[d]$ = recorded thermal effect, and $[C_p^\circ]$ = heat capacity.

TABLE 2

Thermodynamic properties of cesium dimolybdate to 700 K

Temperature/ K	C_p° /(J K^{-1} mol^{-1})	$S^\circ(T)$ /(J K^{-1} mol^{-1})	$H^\circ(T) - H^\circ(298)$ /(kJ mol^{-1})	$-[G^\circ(T) - H^\circ(298)]/T$ /(J K^{-1} mol^{-1})	$-\Delta H_f^\circ$ /(kJ mol^{-1})	$-\Delta G_f^\circ$ /(kJ mol^{-1})
298.15	223.70 [a]	339.74	0	228.59	2302.40	2121.951
300	224.631	341.127	0.415	339.744	2302.383	2120.831
350	245.135	377.394	12.192	342.561	2305.634	2089.964
400	259.670	411.125	24.830	349.050	2303.972	2059.260
450	270.735	442.375	38.101	357.706	2301.776	2028.798
500	279.645	471.376	51.868	367.640	2299.166	1998.604
550	287.147	498.390	66.042	378.313	2296.220	1968.688
600	293.690	523.661	80.567	389.384	2292.993	1939.053
650	299.558	547.405	95.400	400.635	2289.523	1909.697
700	304.936	569.804	110.514	411.926	2285.837	1880.617

[a] Estimated value.

TABLE 3

Measured molar heat capacity of $Rb_2Mo_2O_7$. Molar mass of $Rb_2Mo_2O_7 = 474.810$ g mol^{-1}

Temperature/K	C_p°/(J K^{-1} mol^{-1})	Temperature/K	C_p°/(J K^{-1} mol^{-1})
310	215.03	530	271.03
359	231.06	550	272.73
370	235.08	580	227.28
380	238.41	600	280.71
400	244.21	630	284.17
430	251.67	650	287.28
450	254.39	680	291.65
480	262.88	700	293.58
500	264.31		

RESULTS AND DISCUSSION

Cesium dimolybdate

The experimental heat capacity values are given in Table 1 for each temperature. Least squares fitting of the data resulted in the following polynomial for the heat capacity in the range 310–700 K

$$C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = 266.321 + 7.173 \times 10^{-2}T - 5.65075 \times 10^6 \times T^{-2} \quad (2)$$

As mentioned earlier, there are no experimental heat capacity measurements for $Cs_2Mo_2O_7$. The heat capacity at 298.15 K was estimated by addition of the $C_p^\circ(298.15)$ values for Cs_2MoO_4 and MoO_3, taken from Osborne et al. [5] and from the review by Cordfunke and Konings [10]. This

TABLE 4

Thermodynamic properties of rubidium dimolybdate to 700 K

Temperature K	C_p° /(J K^{-1} mol^{-1})	$S^\circ(T)$ /(J K^{-1} mol^{-1})	$H^\circ(T) - H^\circ(298)$ /(kJ mol^{-1})	$-[G^\circ(T) - H^\circ(298)]/T$ /(J K^{-1} mol^{-1})	$-\Delta H_f^\circ$ /(kJ mol^{-1})	$-\Delta G_f^\circ$ /(kJ mol^{-1})
298.15	206.99 [a]	325.54 [a]	0	325.54	2276.10 [a]	2096.402
300	208.610	326.828	0.385	325.544	2276.108	2095.287
350	229.191	360.627	11.361	328.166	2280.345	2064.624
400	244.081	392.250	23.211	334.223	2279.472	2033.859
450	255.662	421.692	35.715	342.326	2278.043	2003.238
500	265.189	449.136	48.743	351.650	2276.171	1972.800
550	273.373	474.804	62.211	361.692	2273.932	1942.569
600	280.643	498.908	76.065	372.133	2271.376	1912.556
650	287.269	521.636	90.265	382.767	2268.539	1882.767
700	293.428	543.153	104.784	393.461	2265.448	1853.207

[a] Estimated value.

value was used in conjunction with eqn. (2) to obtain the thermodynamic properties of $Cs_2Mo_2O_7$ listed in Table 2. The thermodynamic properties of cesium, oxygen, and molybdenum used in the calculations for Table 2 were taken from published sources [10–14].

Rubidium dimolybdate

The experimental values for the heat capacity (listed in Table 3) were fitted by a least squares polynomial to obtain the following expression for the heat capacity of $Rb_2Mo_2O_7$ in the range 310–700 K

$$C_p^\circ/(\text{J K}^{-1}\,\text{mol}^{-1}) = 236.882 + 9.565 \times 10^{-2}T - 4.94945 \times 10^6 \times T^{-2} \quad (3)$$

There is no experimental information on the heat capacity of $Rb_2Mo_2O_7$. The heat capacity and entropy at 298.15 K have been estimated based on the experimental values for MoO_3 and the estimated C_p° value for Rb_2MoO_4. The standard enthalpy of formation was also estimated by analogy with the other alkali dimolybdates. These values were used with appropriate integrals of eqn. (3) to obtain the thermodynamic functions of $Rb_2Mo_2O_7$ up to 700 K (Table 4). The thermodynamic properties of rubidium, oxygen, and molybdenum used in the calculations were obtained from refs. 10–14.

ACKNOWLEDGMENTS

The author is grateful to Paul Tomlin for experimental assistance. He also thanks Karen Rush for assistance in manuscript preparation. Dr. Malcolm Chase at the National Institute of Standards and Technology kindly provided us with the review of the thermodynamic properties of the alkali metals in advance of publication.

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