J. Chem. Thermodynamics 120 (2018) 205–216

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Thermodynamic study of $Cs_3Na(MoO_4)_2$: Determination of the standard enthalpy of formation and standard entropy at 298.15 K

A.L. Smith [a,*], M.-C. Pignié [b], L. van Eijck [a], J.-C. Griveau [c], E. Colineau [c], R.J.M. Konings [c]

[a] *Delft University of Technology, Faculty of Applied Sciences, Radiation Science & Technology Department, Mekelweg 15, 2629 JB Delft, The Netherlands*
[b] *PSL Research University, Chimie ParisTech-CNRS, Institut de Recherche de Chimie Paris, 75005 Paris, France*
[c] *European Commission, Joint Research Centre (JRC), Directorate for Nuclear Safety and Security, Postfach 2340, D-76125 Karlsruhe, Germany*

ARTICLE INFO

Article history:
Received 19 September 2017
Received in revised form 17 January 2018
Accepted 18 January 2018

Keyword:
Solution calorimetry
Thermal-relaxation calorimetry
Double molybdates
Cesium molybdate
Sodium molybdate

ABSTRACT

The enthalpy of formation at 298.15 K and low temperature heat capacity of $Cs_3Na(MoO_4)_2$ have been measured for the first time in this work using solution calorimetry and thermal-relaxation calorimetry in the temperature range $T = (1.9–299.6)$ K, respectively. The solution calorimetry measurements, performed in 2 M HNO_3 solution, have yielded an enthalpy equal to $\Delta_r H_m(298.15\ \mathrm{K}) = (6.79 \pm 1.72)$ $\mathrm{kJ{\cdot}mol^{-1}}$ for the reaction:

$$3/2Cs_2MoO_4(cr) + 1/2Na_2MoO_4(cr) = Cs_3Na(MoO_4)_2(cr)$$

Combining with the enthalpies of formation of Cs_2MoO_4(cr) and Na_2MoO_4(cr), also determined in this work in 0.1 M CsOH and 0.1 M NaOH solutions, respectively, the standard enthalpy of formation of $Cs_3Na(MoO_4)_2$ at 298.15 K has been determined as $\boldsymbol{\Delta_f H^o_m}(Cs_3Na(MoO_4)_2, \mathrm{cr}, 298.15\ \mathrm{K}) = -(2998.5 \pm 3.0)$ $\mathrm{kJ{\cdot}mol^{-1}}$. The heat capacity and entropy values of $Cs_3Na(MoO_4)_2$ at 298.15 K have been derived as $C^o_{p,m}(Cs_3Na(MoO_4)_2, cr, 298.15\ \mathrm{K}) = (296.3 \pm 3.3)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ and $S^o_m(Cs_3Na(MoO_4)_2, cr, 298.15\ \mathrm{K}) = (467.2 \pm 6.8)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. Combining the newly determined thermodynamic functions, the Gibbs energy of formation of $Cs_3Na(MoO_4)_2$ at 298.15 K has been derived as $\Delta_f G^o_m(Cs_3Na(MoO_4)_2, cr, 298.15K) = -(2784.6 \pm 3.4)\ \mathrm{kJ{\cdot}mol^{-1}}$. Finally, the enthalpies, entropies and Gibbs energies of formation of $Cs_3Na(MoO_4)_2$ from its constituting binary and ternary oxides have been calculated.

© 2018 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

A recent re-investigation of the Na_2MoO_4-Cs_2MoO_4 system has revealed the existence of the double molybdate phase $Cs_3Na(MoO_4)_2$ [1]. Although the Na_2MoO_4-Cs_2MoO_4 pseudo-binary phase diagram has been investigated as early as 1964 [2] by thermal analysis and X-ray diffraction, the presence of this intermediate compound had not been identified to this date. The newly synthesized compound belongs to the class of double molybdate materials $A_nR_m(MoO_4)_2$ (A = alkalis, alkaline-earths, Cu, Tl; R = rare earth elements, Bi, Pb, Zn), which have attracted much interest in recent years because of their interesting properties as phosphor luminescent materials [3,4], solid state lasers [5,6], ferroelastics and ferroelectrics [7–9]. The existence of the $Cs_3Na(MoO_4)_2$ phase is also of relevance for the safety assessment of next generation Sodium cooled Fast Reactors [10]. During irradiation of the $(U_{1-y}Pu_y)O_{2-x}$ nuclear fuel in such reactors, cesium and molybdenum are generated with a high fission yield [11], and subsequently migrate from the centre of the fuel pin towards the pellet rim due to the strong axial temperature gradient (~450 $\mathrm{K{\cdot}mm^{-1}}$). They accumulate in the space between the fuel and cladding in the form of a 150–300 μm layer of cesium orthomolybdate Cs_2MoO_4 [11]. In case of a breach of the stainless steel cladding, although extremely rare under normal operating conditions, the liquid sodium coolant in these reactors would come into contact with the cesium orthomolybdate layer. The aftermath of this reaction is still subject of controversy. Past studies have suggested a substitution of the cesium by sodium to form sodium molybdate and cesium metal which would dissolve in the liquid sodium [12,13]. But the later work by [14] has contradicted this hypothesis, and rather suggested the formation of cesium, sodium and molybdenum oxides. In light of the evidence for the possible formation of the $Cs_3Na(MoO_4)_2$ quaternary phase [1], the mechanism of the interaction between liquid sodium and cesium orthomolybdate needs to be re-visited [10]. To this end, the determination of the thermodynamic properties of $Cs_3Na(MoO_4)_2$ is a necessity.

---

* Corresponding author.
E-mail address: a.l.smith@tudelft.nl (A.L. Smith).

https://doi.org/10.1016/j.jct.2018.01.016
0021-9614/© 2018 The Author(s). Published by Elsevier Ltd.
This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

In this work we report for the first time the determination of the standard enthalpy of formation and standard entropy of $Cs_3Na(MoO_4)_2$ at 298.15 K using solution calorimetry and low temperature thermal-relaxation calorimetry. The standard enthalpies of formation of Cs_2MoO_4 and Na_2MoO_4 were moreover measured with the same solution calorimeter, and compared to literature data to serve as a benchmark for the present studies. Combining the newly determined thermodynamic functions, the Gibbs energy of formation of $Cs_3Na(MoO_4)_2$ at 298.15 K was derived, as well as the Gibbs energies of formation from the constituting oxides (Table 10).

2. Experimental methods

2.1. Sample preparation

$Cs_3Na(MoO_4)_2$ was synthesized by reaction between accurately weighted quantities of cesium orthomolybdate Cs_2MoO_4 and sodium orthomolybdate (Na_2MoO_4 anhydrous, 99.9% trace metal basis, Sigma–Aldrich). The cesium orthomolybdate starting material was synthesized as described in [15]. The stoichiometric mixture was heated under argon inside a tightly closed stainless steel container at 723 K for 200 h, with intermediate regrinding steps. Because of the molybdates' hygroscopic nature, handling was done exclusively inside the dry atmosphere of an argon-filled glove box. The purity of the sample was examined by X-ray and neutron diffraction [10] at room temperature, Differential Scanning Calorimetry [10], and ICP-MS analysis. No secondary phases were detected by XRD and neutron diffraction. The ICP-MS analysis yielded a cesium to molybdenum ratio of (1.44 ± 0.07[1]) at/at and a sodium to molybdenum ratio of (0.51 ± 0.03[2]), which corresponds to the global composition $Cs_{2.88(\pm 0.14)}Na_{1.02(\pm 0.06)}(MoO_4)_2$, hence within uncertainties, in good agreement with the stoichiometric formula. In addition, the Differential Scanning Calorimetry measurements performed on this compound, and reported in detail in [10], showed a single peak in the heat flow signal as a function of temperature, corresponding to the melting event. No additional peaks could be assigned to impurities, in good agreement with the X-ray and neutron diffraction data. The sample purity is expected to be better than 99 wt% (Table 1).

2.2. Powder X-ray and neutron diffraction

The X-ray diffraction measurements were carried out at room temperature (295 ± 3[3] K) using a PANalytical X'Pert PRO X-ray diffractometer mounted in the Bragg–Brentano configuration with a Cu anode (0.4 mm × 12 mm line focus, 45 kV, 40 mA). The X-ray scattered intensities were measured with a real time multi strip (RTMS) detector (X'Celerator). The data were collected by step scanning in the angle range $10° \leqslant 2\theta \leqslant 120°$ with a step size of 0.008° (2θ); total measuring time was about 8 h.

Neutron diffraction data were recorded on the beamline PEARL at the Hoger Onderwijs Reactor at TU Delft [16]. The sample was encapsulated in a vanadium container hermetically closed with a rubber o-ring. The data were collected at room temperature (295 ± 3[4] K), at a fixed wavelength ($\lambda = 0.1667$ nm) for 43 h over the range $11° \leqslant 2\theta \leqslant 158°$. Structural analysis was performed by the Rietveld method with the Fullprof2k suite [17].

$Cs_3Na(MoO_4)_2$ crystallizes with a hexagonal structure, in space group $P\overline{3}m1$ ($Z = 1$), belonging to the glaserite type. The refined cell parameters by XRD ($a = 0.634381$[5] and $c = 0.821888$[6] nm (note that the statistically derived s.u:s are underestimated by about one order of magnitude); $\rho = 4.2991$[7] g·cm^{-3}) and neutron diffraction ($a = 0.63352$[8] and $c = 0.82068$[9] nm (note that the statistically derived s.u:s are underestimated by about one order of magnitude); $\rho = 4.317$[10] g·cm^{-3}) were found in good agreement with the single crystal data of Zolotova et al. ($a = 0.63461$[11] and $c = 0.82209$[12] nm) [1]. The refined lattice parameters using XRD are considered more precise than those derived from the neutron diffraction data. A detailed structural study of this compound can be found in [10] (Fig. 1).

2.3. Solution calorimetry

The enthalpy of dissolution of $Cs_3Na(MoO_4)_2$, Cs_2MoO_4 and Na_2MoO_4 materials were measured using a TA Instruments Precision Solution Calorimeter (semi-adiabatic or isoperibolic calorimeter) and TAM IV thermostat. The calorimetric unit consists of a reaction vessel and stirrer system (motor and gold stirrer holding a glass ampoule). The experiments were performed in a thin-walled 25 mL Pyrex-glass reaction vessel equipped with a thermistor for measuring the temperature rise and a heater for calibration during the measurement and equilibration of the initial baseline in the optimal operating range of the calorimeter before starting the experiment. The samples to be studied were placed inside a 1 mL glass ampoule, which was subsequently sealed using bee wax. The latter operation was performed in the dry atmosphere of the glove box because of the sensitivity of the samples to air and moisture. The solid samples were dissolved into solution (cesium hydroxyde CsOH, sodium hydroxyde NaOH, or nitric acide HNO_3 solutions) by breaking the bottom of the glass ampoule on the sapphire breaking tip mounted at the bottom of the reaction vessel. The heat of breaking is exothermic, with a value below 10 mJ, and can thus be neglected. The temperature during the measurements was maintained in the oil bath with an accuracy of $\pm 1{\cdot}10^{-4}$ K. Electrical calibrations were performed immediately before and after each enthalpy of reaction measurement so as to determine the energy equivalent of the system.

The accuracy of the measurements was verified by measuring the enthalpy of dissolution of potassium chloride (KCl, Sigma–Aldrich, 99.7%) in distilled water. The experimentally determined dissolution enthalpy of KCl(cr) into 1000 H_2O (molality m = 0.05551 mol·kg^{-1}), i.e. $\Delta_{diss}H^{o}_{m}(1000H_2O, 298.15\ K) = (17.510 \pm 0.024)$ kJ·mol^{-1} corresponding to $\Delta_{diss}H^{o}_{m}(500H_2O, 298.15\ K) = (17.560 \pm 0.024)$ kJ·mol^{-1} after correction[13] to m = 0.111 mol·kg^{-1}, was found in very good agreement with the value recommended by

---

[1] The uncertainty is an expanded uncertainty $U = k{\cdot}u_c$ where u_c is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement. The coverage factor is $k = 2$.

[2] The uncertainty is an expanded uncertainty $U = k{\cdot}u_c$ where u_c is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement. The coverage factor is $k = 2$.

[3] The quoted uncertainty is a standard uncertainty.

[4] The quoted uncertainty is a standard uncertainty.

[5] Standard uncertainties u are $u(a)$ = 0.000002 nm.

[6] Standard uncertainties u are $u(c)$ = 0.000003 nm.

[7] Standard uncertainties u are $u(\rho)$ = 0.0002 g·cm^{-3}.

[8] Standard uncertainties u are $u(a)$ = 0.00003 nm.

[9] Standard uncertainties u are $u(c)$ = 0.00005 nm.

[10] Standard uncertainties u are $u(\rho)$ = 0.004 g·cm^{-3}.

[11] Standard uncertainties u are $u(a)$ = 0.00002 nm.

[12] Standard uncertainties u are $u(c)$ = 0.00003 nm.

[13] The correction mentioned here was performed as recommended by the NBS in [18]: the measured dissolution enthalpy was corrected to the molality of the certified enthalpy value m = 0.111 mol·kg^{-1} using the relationship $\Delta H^{o}(500H_2O, 298.15\ K) = \Delta H(nH_2O, 298.15\ K) - \{\Phi_L(nH_2O) - \Phi_L(500H_2O)\}$, where $\Delta H(nH_2O, 298.15\ K)$ is the measured dissolution enthalpy corrected to the reference temperature, and the term $\{\Phi_L(nH_2O) - \Phi_L(500H_2O)\}$, derived from Parker's tabulation [19] and listed in [18], corrects the molality to the certified value. The uncertainty on the correction was estimated not to exceed 5 J·mol^{-1} [18].

Download English Version:

https://daneshyari.com/en/article/6659783

Download Persian Version:

https://daneshyari.com/article/6659783

Daneshyari.com