



Thermodynamic properties for calcium molybdate, molybdenum tri-oxide and aqueous molybdate ion



Masao Morishita^{a,*}, Yoshiki Kinoshita^b, Hiroki Houshiyama^b, Ai Nozaki^a, Hiroaki Yamamoto^a

^a Department of Chemical Engineering and Materials Science, University of Hyogo, Japan

^b Graduate Student of University of Hyogo, Japan

ARTICLE INFO

Article history:

Received 28 December 2016

Received in revised form 10 May 2017

Accepted 13 May 2017

Available online 24 June 2017

Keywords:

Heat capacity

Standard molar entropy

Standard Gibbs energy function

Nuclear fuel waste glass

Fission product

Yellow phase

ABSTRACT

The thermodynamic properties for $\text{CaMoO}_4(\text{cr})$, $\text{MoO}_3(\text{cr})$ and $\text{MoO}_4^{2-}(\text{aq})$ were investigated. $\text{CaMoO}_4(\text{cr})$ is the one of the host crystals of the yellow phases which are known as hygroscopic harmful phases in the nuclear fuel glasses. $\text{MoO}_3(\text{cr})$ is the main component of the host crystals. $\text{MoO}_4^{2-}(\text{aq})$ is the aqueous ion present in underground water after dissolution of the yellow phases. The standard molar entropies, $\Delta_0^T S_m^\circ$, at 298.15 K for $\text{CaMoO}_4(\text{cr})$ and $\text{MoO}_3(\text{cr})$ were determined by measuring their isobaric heat capacities, $C_{p,m}^\circ$, from 2 K. Their standard Gibbs energies of formation, $\Delta_f G_m^\circ$, were determined by combining the $\Delta_0^T S_m^\circ$ data with the reference data of the standard enthalpies of formation, $\Delta_f H_m^\circ$. The standard electrochemical potential, E° , of $\text{MoO}_4^{2-}(\text{aq})$ was determined from the thermodynamic cycle on the basis of thermodynamic properties obtained for $\text{CaMoO}_4(\text{cr})$ and $\text{MoO}_3(\text{cr})$. The unknown standard Gibbs energies of solution, $\Delta_{\text{sin}} G_m^\circ$, at 298.15 K for the actinide molybdates $\text{ThMo}_2\text{O}_8(\text{cr})$ and $\text{UMoO}_6(\text{cr})$ were predicted from the presently obtained thermodynamic data for $\text{CaMoO}_4(\text{cr})$, $\text{MoO}_3(\text{cr})$ and $\text{MoO}_4^{2-}(\text{aq})$. The obtained thermodynamic values are as follows:

$$\Delta_0^T S_m^\circ(\text{CaMoO}_4(\text{cr}), 298.15 \text{ K})/(\text{J K}^{-1} \text{ mol}^{-1}) = 122.23 \pm 1.22.$$

$$\Delta_0^T S_m^\circ(\text{MoO}_3(\text{cr}), 298.15 \text{ K})/(\text{J K}^{-1} \text{ mol}^{-1}) = 75.43 \pm 0.75.$$

$$\Delta_0^T S_m^\circ(\text{MoO}_4^{2-}(\text{aq}), 298.15 \text{ K})/(\text{J K}^{-1} \text{ mol}^{-1}) = 32.25 \pm 4.41.$$

$$\Delta_f G_m^\circ(\text{CaMoO}_4(\text{cr}), 298.15 \text{ K})/(\text{kJ mol}^{-1}) = -1437.78 \pm 1.11.$$

$$\Delta_f G_m^\circ(\text{MoO}_3(\text{cr}), 298.15 \text{ K})/(\text{kJ mol}^{-1}) = -667.20 \pm 0.63.$$

$$\Delta_f G_m^\circ(\text{MoO}_4^{2-}(\text{aq}), 298.15 \text{ K})/(\text{kJ mol}^{-1}) = -836.61 \pm 1.02.$$

$$E^\circ(\text{MoO}_4^{2-}(\text{aq}), 298.15 \text{ K})/V = 4.34 \pm 0.01.$$

$$\Delta_{\text{sin}} G_m^\circ(\text{ThMo}_2\text{O}_8(\text{cr}), 298.15 \text{ K})/(\text{kJ mol}^{-1}) = 184.84 \pm 42.48.$$

$$\Delta_{\text{sin}} G_m^\circ(\text{UMoO}_6(\text{cr}), 298.15 \text{ K})/(\text{kJ mol}^{-1}) = 68.33 \pm 34.47.$$

The present obtained data are expected to be useful for geo-chemical simulation of diffusion of radioactive elements through underground water.

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1. Introduction

The Organization for Economic Co-operation and Development (OECD) Nuclear Energy Agency (NEA) Thermochemical Database (TDB) project provides a database of chemical thermodynamic values treating the most significant elements related to nuclear waste management [1]. The thermodynamic properties for alkaline earth molybdates SrMoO_4 [2] and BaMoO_4 [3] were measured as a part of the OECD/NEA TDB Mo project in our previous studies [2–5]. Molybdenum is generated as a fission product from uranium in the operating nuclear reactor [6–12]. It is a harmful element as it

forms hygroscopic crystals called yellow phase in the borosilicate nuclear waste glass. $\text{CaMoO}_4(\text{cr})$ is one of the host crystal of the yellow phase, depending on composition [10–12]. There is immiscibility in alkali silicate [13] and alkali borosilicate glasses [6]. MoO_3 component in the borosilicate glass expands the compositional range and elevates the temperature of immiscibility [6,7,9], this means that it precipitates in the sodium- and boron-rich region of the glass matrix [8]. Hyatt et al. [8] clarified that MoO_3 component in the glass, which is not immobilized within the polymeric borosilicate network, instead is likely to be located in extra-framework cavities, together with network modifier CaO component. Therefore, the yellow phase appears to be crystallized as the equilibrium phase resulting from the reaction between MoO_3 and CaO components [8–11]. To understand the phase

* Corresponding author.

E-mail address: morisita@eng.u-hyogo.ac.jp (M. Morishita).

stability of $\text{CaMoO}_4(\text{cr})$, not only its thermodynamic properties but also ones for $\text{MoO}_3(\text{cr})$ are inevitably necessary. In the present study, the standard molar entropies, $\Delta_0^T S_m^\circ$, of $\text{CaMoO}_4(\text{cr})$ and $\text{MoO}_3(\text{cr})$ were determined by measuring the $C_{p,m}^\circ$ data from 2 K by the relaxation method [2,3,14–22] for determining their Gibbs energies of formation, $\Delta_f G_m^\circ$. Thermodynamic properties for the aqueous molybdate ion $\text{MoO}_4^{2-}(\text{aq})$ were determined from the data obtained for $\text{CaMoO}_4(\text{cr})$ and $\text{MoO}_3(\text{cr})$. Unknown solubility products, K_s , and standard Gibbs energies for solution into water, $\Delta_{\text{sln}} G_m^\circ$, for strong radioactive molybdates $\text{ThMo}_2\text{O}_8(\text{cr})$ and $\text{UMoO}_6(\text{cr})$ were predicted on the basis of the thermodynamic properties for $\text{MoO}_4^{2-}(\text{aq})$ obtained in the present study.

Muldrow and Hepler [23] and Barany [24] investigated the standard enthalpy of formation, $\Delta_f H_m^\circ$, of $\text{CaMoO}_4(\text{cr})$ at 298.15 K by solution calorimetry. Gamsjäger and Morishita [4] re-evaluated their thermodynamic cycles [23,24]. Weller and King [25] measured the low temperature $C_{p,m}^\circ$ of $\text{CaMoO}_4(\text{cr})$ at 50–300 K by the adiabatic method. Saha et al. [26] measured the change in enthalpy of as a function of temperature, $\Delta_{298.15}^T H_m^\circ$, by the drop calorimetry up to 1637 K and evaluated $C_{p,m}^\circ$ from the derivative of $\Delta_{298.15}^T H_m^\circ$ with respect to temperature. Zhidikova and Malinin [27], Essinton [28], Grambow and Müller [29], and Felmy et al. [30], investigated the solid products, K_s and the standard Gibbs energy of solution, $\Delta_{\text{sln}} G_m^\circ$. Gamsjäger [31] reevaluated the reliable data for its K_s and $\Delta_{\text{sln}} G_m^\circ$. Gürmen et al. [32] determined the crystal structure of $\text{CaMoO}_4(\text{cr})$.

Moose and Parr [33], Nueman et al. [34], Staskiewicz et al. [35] and Mah [36] measured $\Delta_f H_m^\circ$ at 298.15 of $\text{MoO}_3(\text{cr})$ by the combustion calorimetry. Seltz et al. [37] and Smith et al. [38] measured $C_{p,m}^\circ$ by the adiabatic method in the ranges of 70–299 K and 18–300 K, respectively. Cosgrove and Snyder [39] measured $\Delta_{298.15}^T H_m^\circ$ to 1068 K by the ice calorimetry [40] and evaluated $C_{p,m}^\circ$. King and Weller [41] measured $\Delta_{298.15}^T H_m^\circ$ to 1400 K by the drop calorimetry and evaluated $C_{p,m}^\circ$ for the solid and liquid sates, determining the melting point as 1074 K, and the enthalpy of fusion. Feiser [42] and Zelikman et al. [43] measured vapor pressures of gaseous species, $p((\text{MoO}_3)_n)$, by the boiling method. Ueno [44], Blackburn et al. [45], Gulbransen [46] and Kazena et al. [47] measured $p((\text{MoO}_3)_n)$ by the Knudsen effusion method. Ackerman et al. [48] measured $p((\text{MoO}_3)_n)$ by the transpiration method. Charlu and Kleppa [49] measured the enthalpy of vaporization, $\Delta_{\text{vap}} H_m^\circ$, by the drop calorimetry. Anderson and Magneli [50], and Chang and Philip [51] investigated the crystal structure of $\text{MoO}_3(\text{cr})$. Their structure was adopted in the data book edited by Villars and Calvert [52]. Brewer and Lamoreaux [53] reviewed these studies before 1980 [80BRE/LAM]. The 3rd [54] and 4th [55] editions of NIST-JANAF data books were edited on the basis of the review by Brewer and Lamoreaux [53].

Thermodynamic properties for $\text{MoO}_4^{2-}(\text{aq})$ were investigated by Graham and Hepler [56], O'Hare and Hoekstra [57,58], O'Hare [59], O'Hare et al. [60], Crouch-Baker and Dickens [61], and Shukla et al. [62]. $\Delta_f H_m^\circ$ at 298.15 K of $\text{MoO}_4^{2-}(\text{aq})$ was determined by measuring the enthalpies of reactions, $\Delta_r H_m^\circ$ of: (1) $\text{MoO}_3(\text{cr})$ solvled into $\text{MOH}(\text{aq})$ (M: Li [60,62]; Na [56,61]; Rb [58]; Cs [57]) to precipitate $\text{M}_2\text{MoO}_4(\text{cr})$; (2) $\text{Cs}_2\text{MoO}_4(\text{cr})$ solvled into $\text{BaCl}_2(\text{aq})$ to precipitate $\text{BaMoO}_4(\text{cr})$ [59]. Gamsjäger and M. Morishita [4] suggested the recommended datum from evaluating the weighed mean of their data [56–61].

Although a large body of literatures has been published for $\text{CaMoO}_4(\text{cr})$ and $\text{MoO}_3(\text{cr})$, their $C_{p,m}^\circ$ from a very low temperature have not been measured. Therefore, the present measurements from 2 K are useful in determining the $\Delta_0^T S_m^\circ$ data for $\text{CaMoO}_4(\text{cr})$ and $\text{MoO}_3(\text{cr})$. The $\Delta_f G_m^\circ$ data for $\text{CaMoO}_4(\text{cr})$ and $\text{MoO}_3(\text{cr})$ were

determined by combining the obtained S_m° data with the $\Delta_f H_m^\circ$ data [4,23,24,33–36]. The hierarchy of phase stabilities in the nuclear waste glasses for $\text{CaMoO}_4(\text{cr})$ was investigated from the presently obtained $\Delta_f G_m^\circ$, compared with ones of the end members of the yellow phase $\text{SrMoO}_4(\text{cr})$ [2], $\text{BaMoO}_4(\text{cr})$ [3], and the transition metal molybdates $\text{NiMoO}_4(\text{cr})$ [16] determined in our previous studies [2,3,16]. At the same time, the phase stabilities for the related transition metal molybdates $\text{MnMoO}_4(\text{cr})$ [63,64], $\text{FeMoO}_4(\text{cr})$ [65–69], $\text{CoMoO}_4(\text{cr})$ [70–72], $\text{ZrMo}_2\text{O}_8(\text{cr})$ [73–75], $\text{Ag}_2\text{MoO}_4(\text{cr})$ [76–86], as well as the actinide molybdates $\text{ThMo}_2\text{O}_8(\text{cr})$ [87,88] and $\text{UMoO}_6(\text{cr})$ [89–91] were evaluated on the basis of the presently obtained thermodynamic data.

In a conference review by Gamsjäger and Morishita [4], the thermodynamic properties for $\text{MoO}_4^{2-}(\text{aq})$ were evaluated from the thermodynamic cycle on the basis of the values for $\text{CaMoO}_4(\text{cr})$, $\text{SrMoO}_4(\text{cr})$, $\text{BaMoO}_4(\text{cr})$, $\text{Ag}_2\text{MoO}_4(\text{cr})$ and $\text{MoO}_3(\text{cr})$. However, the $\Delta_0^T S_m^\circ$ data at 298.15 K for CaMoO_4 and Ag_2MoO_4 adopted in their review [4] were obtained from a private communication, and one for $\text{MoO}_3(\text{cr})$ was based on studies measuring $C_{p,m}^\circ$ over 50 K [37] and 18 K [38]. Therefore, re-evaluation of the thermodynamic properties for $\text{MoO}_4^{2-}(\text{aq})$ is necessary. Recently $\Delta_0^T S_m^\circ$ of $\text{Ag}_2\text{MoO}_4(\text{cr})$ was determined in our previous study [86]. In the present study, $\Delta_f G_m^\circ$ and the standard electrochemical potential, E° , for $\text{MoO}_4^{2-}(\text{aq})$ were determined from the present obtained $\Delta_0^T S_m^\circ$ data for $\text{CaMoO}_4(\text{cr})$ and $\text{MoO}_3(\text{cr})$ and the recently obtained $\Delta_0^T S_m^\circ$ of $\text{Ag}_2\text{MoO}_4(\text{cr})$ [86]. The unknown solubility products, K_s , for $\text{ThMo}_2\text{O}_8(\text{cr})$ and $\text{UMoO}_6(\text{cr})$ were predicted from the presently obtained $\Delta_f G_m^\circ$ of $\text{MoO}_4^{2-}(\text{aq})$.

2. Experimental

2.1. Starting materials

Table 1 shows details of the samples. Commercial powders of $\text{CaMoO}_4(\text{cr})$ and $\text{MoO}_3(\text{cr})$ were used as the starting materials. Each powder was pressed in a steel die at 392 MPa to form a powder compact ($\phi 10 \times 5$ mm). The powder compacts were sintered at 807 K held for 2hr ($\text{CaMoO}_4(\text{cr})$) and at 873 K held for 3hr ($\text{MoO}_3(\text{cr})$) in Ar. The X-ray diffraction (XRD) patterns confirmed that the sintered bodies were composed of the mono-phase. The samples were subjected to the $C_{p,m}^\circ$ measurement. Pure copper (shown in Table 1) was used as the standard material. Commercial copper plate was used as the starting material.

2.2. Low temperature $C_{p,m}^\circ$

The heat capacities, $C_{p,m}^\circ$, for $\text{CaMoO}_4(\text{cr})$ and $\text{MoO}_3(\text{cr})$ were measured from very low temperature (2 K) to room temperature using a relaxation method instrument (model PPMS, Quantum Design, San Diego, CA) [14,15] as in our previous studies [2,3,16–22]. A sample is mounted with grease on a platform (3×3 mm²) attached to a puck with eight fine Au-Pd wire, where a heater to supply the sample Joule's heat pulse and thermometer are attached to its bottom side. Temperature increase supplied by the heat pulse is measured by the thermometer. $C_{p,m}^\circ$ of the sample can be determined: (Step 1) the heat capacity of the platform with grease is measured as the addenda measurement by heat pulse from the heater; (Step 2) the heat capacity of the sample and platform with grease is measured after mounting the sample on the platform. $C_{p,m}^\circ$ of the sample can be calculated using PPMS software which subtracts addenda measurement.

Two samples for each substance were prepared by polishing the sintered bodies with emery paper to a thickness about 0.7–1.0 mm.

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