



A calorimetric and thermodynamic investigation of zinc and cadmium hydrous selenites



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ABSTRACT

A calorimetric and thermodynamic investigation of three hydrous selenites, $\text{ZnSeO}_3 \cdot 2\text{H}_2\text{O}$, $\text{ZnSeO}_3 \cdot \text{H}_2\text{O}$ and $\text{CdSeO}_3 \cdot \text{H}_2\text{O}$, was undertaken. All three phases were synthesized by mixing of aqueous solutions of zinc and cadmium nitrates, accordingly, and sodium selenite and characterized by XRD powder diffraction, energy dispersive X-ray microanalysis, inductively coupled plasma mass spectrometry and thermal analysis methods. The low-temperature heat capacity of $\text{ZnSeO}_3 \cdot 2\text{H}_2\text{O}$, $\text{ZnSeO}_3 \cdot \text{H}_2\text{O}$ and $\text{CdSeO}_3 \cdot \text{H}_2\text{O}$ were measured using adiabatic calorimetry between 5 and 324 K, and the third-law entropies were determined. Values of molar third law entropy $S_m^\circ(298 \text{ K}, \text{ZnSeO}_3 \cdot 2\text{H}_2\text{O}, \text{cr.}) = 179 \pm 1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $S_m^\circ(298 \text{ K}, \text{ZnSeO}_3 \cdot \text{H}_2\text{O}, \text{cr.}) = 150 \pm 1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $S_m^\circ(298 \text{ K}, \text{CdSeO}_3 \cdot \text{H}_2\text{O}, \text{cr.}) = 171 \pm 1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ were calculated. The expanded uncertainties for S_m° are given at the 0.95 confidence level ($k \approx 2$). The enthalpies of formation for $\text{ZnSeO}_3 \cdot \text{H}_2\text{O}$, $\text{ZnSeO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{CdSeO}_3 \cdot \text{H}_2\text{O}$ were determined using H_2SO_4 -solution calorimetry giving $\Delta_f H_m^\circ(298 \text{ K}, \text{ZnSeO}_3 \cdot 2\text{H}_2\text{O}, \text{cr.}) = -1238 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^\circ(298 \text{ K}, \text{ZnSeO}_3 \cdot \text{H}_2\text{O}, \text{cr.}) = -931 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^\circ(298 \text{ K}, \text{CdSeO}_3 \cdot \text{H}_2\text{O}, \text{cr.}) = -906 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$. The expanded uncertainties for $\Delta_f H_m^\circ$ are given at the 0.95 confidence level ($k \approx 2$). The Gibbs energy of formation for $\text{ZnSeO}_3 \cdot 2\text{H}_2\text{O}$, $\text{ZnSeO}_3 \cdot \text{H}_2\text{O}$ and $\text{CdSeO}_3 \cdot \text{H}_2\text{O}$ at $T = 298 \text{ K}$, 1 atm have been calculated on the basis on $\Delta_f H_m^\circ$ and $\Delta_f S_m^\circ$: $\Delta_f G_m^\circ(298 \text{ K}, \text{ZnSeO}_3 \cdot 2\text{H}_2\text{O}, \text{cr.}) = -1035 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f G_m^\circ(298 \text{ K}, \text{ZnSeO}_3 \cdot \text{H}_2\text{O}, \text{cr.}) = -790 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f G_m^\circ(298 \text{ K}, \text{CdSeO}_3 \cdot \text{H}_2\text{O}, \text{cr.}) = -768 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$. The expanded uncertainties for $\Delta_f G_m^\circ$ are given at the 0.95 confidence level ($k \approx 2$). Smoothed $C_{p,m}^\circ(T)$ values between $T = 0 \text{ K}$ and $T = 320 \text{ K}$ for $\text{ZnSeO}_3 \cdot 2\text{H}_2\text{O}(\text{cr.})$, $\text{ZnSeO}_3 \cdot \text{H}_2\text{O}(\text{cr.})$ and $\text{CdSeO}_3 \cdot \text{H}_2\text{O}(\text{cr.})$ are presented along with values for S_m° and the functions $[H_m^\circ(T) - H_m^\circ(0)]$ and $[G_m^\circ(T) - H_m^\circ(0)]$. These results motivate a re-evaluation of the natural conditions under which selenites, and selenates replace selenides, and sulfides in the oxidation zones of sulfide ore deposits or upon weathering of technologic waste. The values of $\Delta_f G^\circ$ for $\text{ZnSeO}_3 \cdot 2\text{H}_2\text{O}$, $\text{ZnSeO}_3 \cdot \text{H}_2\text{O}$ and $\text{CdSeO}_3 \cdot \text{H}_2\text{O}$ were used to calculate the Eh–pH diagrams of the Zn–Se– H_2O and Cd–Se– H_2O , systems. These diagrams have been constructed for the average contents of these elements in acidic waters of the oxidation zones of sulfide deposits. The behavior of selenium, zinc, and cadmium in the surface environment have been quantitatively explained by variations of the redox potential and the acidity–basicity of the mineral-forming medium. Precisely these parameters determine the migration ability of selenium compounds and its precipitation in the form of various solid phases.

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1. Introduction

Hydrous selenites minerals are found, as a rule, in the oxidation zone of sulfide and selenide ores. Cu, Co, Ni, and Fe are species-

defining cations of these minerals: ahlfeldite ($\text{NiSeO}_3 \cdot 2\text{H}_2\text{O}$), chalcocomenite ($\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$), cobaltocomenite ($\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$), mandarinite ($\text{Fe}_2(\text{SeO}_3)_3 \cdot 6\text{H}_2\text{O}$) [1]. Similar zinc and cadmium minerals (hydrous selenites) have not yet been found in such settings. Chlorine bearing zinc selenite sophiite ($\text{Zn}_2(\text{SeO}_3)\text{Cl}_2$), identified as an exhalative product (Tolbachik eruption, Kamchatka) belongs among anhydrous selenites with additional cations, whose

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formation conditions are very specific: these minerals are formed from the gaseous phase at elevated temperatures (300–400 °C), atmospheric pressure, and apparently at a low partial pressure of water [2]. The second anhydrous Zn selenite mineral (zincomenite, ZnSeO_3) have recently found in fumarole products in the Tolbachik volcano [3]. At the same time, in terms of geochemistry, hydrous selenites of zinc were able to be formed in the oxidation zone of selenium bearing sulfide ores, where zinc is released from Se-bearing sphalerite (ZnS) or stilleite (ZnSe). The geochemistry of cadmium is determined by the behavior of zinc, which is caused by the similar valence shell and close ion radii of these elements. The global mean content of cadmium in the Earth's crust is substantially lower than that of zinc (70 and 0.15 ppm, respectively [4], therefore cadmium, as rule, is incorporated as an admixture into the crystal structures of zinc minerals, and the number of proper cadmium minerals in which this element is species-defining is comparatively small (26 minerals in total) [4,5]. The highest cadmium content was measured in sphalerite (up to a few wt%). The formation of cadmium selenites seems quite possible in the oxidation zone of Se-bearing sulfide ores, where Cd-bearing sulfide and selenides (greenockite, CdS , cadmoselite, CdSe) could be a source of cadmium. Rarity, low abundance and difficulty of the diagnostics are the reasons why zinc and cadmium selenites have not yet been found in this setting [1].

The mineral equilibria in the $\text{Zn-Se-CO}_2\text{-H}_2\text{O}$ and $\text{Cd-Se-CO}_2\text{-H}_2\text{O}$ systems at 25 °C and 1 atm corresponding to the formation conditions of selenium and zinc or cadmium minerals were calculated for the first time by Bur'yanova [6]. These diagrams make it possible to consider the physicochemical formation conditions of selenides and their oxidation to native selenium. As for more oxidative conditions, the author reported the probable formation of selenites of corresponding metals, but did not calculate their stability fields due to absence of required thermodynamic data or information about identification of these minerals in nature in the late 1960s.

Zinc selenite occurs as $\text{ZnSeO}_3\cdot 2\text{H}_2\text{O}$ and $\text{ZnSeO}_3\cdot \text{H}_2\text{O}$ crystal hydrates and anhydrous ZnSeO_3 species. This fact has been known since the 19th century. However, only Markovsky and Sapozhnikov [7] have described the methods to produce these compounds. The overview of the thermodynamic literature on Se and Zn compounds [8–13] appears to indicate that $\text{ZnSeO}_3\cdot \text{H}_2\text{O}$ is better investigated than $\text{ZnSeO}_3\cdot 2\text{H}_2\text{O}$ —the solubility data [8,10,11] are given in the reference book [9], but the authors of point out insufficient validity of the data published by the above researchers. We managed to find only one value of $\log SP$ for $\text{ZnSeO}_3\cdot 2\text{H}_2\text{O}$ in [12]. This value however, was calculated from standard thermodynamic formation functions from the reference book [13], rather than being obtained on the basis of direct experimental measurements. Therefore, the real composition of the solid phase also remained an open question. The overview of the thermodynamic literature on Se and Zn compounds appears to indicate that $\text{ZnSeO}_3\cdot \text{H}_2\text{O}$ is better investigated than $\text{ZnSeO}_3\cdot 2\text{H}_2\text{O}$ [8–13].

According to literature data, in environment cadmium selenite occurs as anhydrous salt CdSeO_3 or crystalline hydrate ($\text{CdSeO}_3\cdot n\text{H}_2\text{O}$). The formation of the other cadmium selenites (for example $3\text{CdSeO}_3\cdot \text{H}_2\text{SeO}_3$ and $\text{CdSeO}_3\cdot \text{SeO}_2$ [14,15] require excess selenious acid; therefore, it is hardly possible in nature. The first references to the synthesis of these compounds are from the 19th century: Nilson [16] and Boutzoureano [17] synthesized CdSeO_3 and $\text{CdSeO}_2\cdot 1.5\text{H}_2\text{O}$. Markovsky and Sapozhnikov [18] described synthesis of only anhydrous CdSeO_3 ; however, later, these authors [19] reported the formation enthalpies and thermal properties of crystal hydrates $\text{CdSeO}_3\cdot 0.5\text{H}_2\text{O}$ and $\text{CdSeO}_3\cdot 2/3\text{H}_2\text{O}$. Micka et al. [14] established two modifications of CdSeO_3 along with cadmium acidic salts and diselenide in a study of the solubility diagrams of the $\text{CdSeO}_3\text{-SeO}_2\text{-H}_2\text{O}$ system at 25 °C. Gospodinov and Barkov

[15] found only one modification of CdSeO_3 in an experimental study of the solubility in the $\text{CdSeO}_3\text{-SeO}_2\text{-H}_2\text{O}$ system at 25 °C, but that paper also mentions literature information on $\text{CdSeO}_3\cdot 2.5\text{H}_2\text{O}$ and $\text{CdSeO}_3\cdot 3\text{H}_2\text{O}$ crystal hydrates. Lastly, the crystal structure of $\text{CdSeO}_3\cdot \text{H}_2\text{O}$ was reported [20,21]. Thus, crystal hydrates of cadmium selenite containing 0.5, 2/3, 1, 1.5, 2.5, or 3 water molecules are mentioned in the literature with the structural characteristics being determined only for anhydrous CdSeO_3 and $\text{CdSeO}_3\cdot \text{H}_2\text{O}$. Olin et al. [9] recommended the $\log SP$ value for CdSeO_3 due to revision of experimental data of [8,22]. For crystal hydrates of cadmium selenite, we found only the data for $\log SP$ of compounds $\text{CdSeO}_3\cdot 0.5\text{H}_2\text{O}$ or $\text{CdSeO}_3\cdot x\text{H}_2\text{O}$ in the reference book [12]. Thus, these data do not clarify the formula (or formulas) of crystal hydrate and cannot be used to calculate mineral equilibria. The thermodynamic properties of $\text{CdSeO}_3\cdot x\text{H}_2\text{O}$ have not been investigated in a full and systematic manner.

Any progresses in our understanding of low-temperature mineral assemblages strongly depend on our knowledge of the thermodynamic stability of the constituting mineral phases. Experimental and thermodynamic modeling is quite essential to analyze the conditions under which selenites and selenates replace selenides, and selenium-bearing sulfides in the oxidation zones of sulfide ore deposits or upon weathering of technologic waste. The physicochemical modeling is based on the thermodynamic constants of minerals. Reliable solubility product or Gibbs energy of formation values of the phases crystallized in the system are necessary for calculation of mineral equilibria.

Thus, in this study, we continue our systematic investigation of the thermodynamic properties of hydrous selenites [23,24] by performing a calorimetric and thermodynamic study of three zinc and cadmium hydrous selenites: $\text{ZnSeO}_3\cdot \text{H}_2\text{O}$, $\text{ZnSeO}_3\cdot 2\text{H}_2\text{O}$ and $\text{CdSeO}_3\cdot 2\text{H}_2\text{O}$.

2. Experimental methods

2.1. Sample preparation

Both species of zinc selenite were synthesized using the techniques elaborated by [7]. $\text{ZnSeO}_3\cdot 2\text{H}_2\text{O}$ was produced by slowly mixing concentrated (1 M) aqueous solutions of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (pH 6) and Na_2SeO_3 (pH 6.2). The reaction was conducted at room temperature. Then the solution with the obtained compound was cooled to below room temperature. The precipitate of Zn selenite dihydrate was decanted from the solution and washed with distilled water; then it was dried over three weeks at below room temperature (10–15 °C). Zinc selenite monohydrate was synthesized by means of slow stirring diluted (0.1 M) aqueous solutions of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (pH 6) and Na_2SeO_3 (pH 6.2) in stoichiometric proportions at 50 °C. Then the solution with the obtained compound was cooled to room temperature. The precipitate was decanted from the solution, washed with distilled water, and was being dried for two weeks at 40 °C. A white powder was obtained. Transparent rhombic $\text{ZnSeO}_3\cdot 2\text{H}_2\text{O}$ or acicular $\text{ZnSeO}_3\cdot \text{H}_2\text{O}$ crystals are visible under a microscope (Supplementary Figs. S1, S2).

$\text{CdSeO}_3\cdot \text{H}_2\text{O}$ was synthesized from the cadmium nitrate and sodium selenite solutions. A 0.025 M solution of Na_2SeO_3 (pH 6.0) was slowly added at a rate of 5 mL/min to a 0.025 M solution of $\text{Cd}(\text{NO}_3)_2$ (pH 6). The reaction was conducted at room temperature; then the solution with the residue have been left to ripen at room temperature for two weeks, after which the formed precipitate was separated by decantation, washed with distilled water and dried during 6 h at room temperature. A white powder was obtained. Transparent plate crystals are visible under a microscope (Supplementary Fig. S3).

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