Thermodynamic properties of $ZnSO_4$(aq) and phase equilibria in the $ZnSO_4$–H_2O system from 268 K to 373 K

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ABSTRACT

This paper reports a comprehensive thermodynamic treatment of the binary system $ZnSO_4$–H_2O including solution properties and phase equilibria involving various hydrates of zinc sulfate. Published thermodynamic data of $ZnSO_4$(aq), solubilities of the hydrates of zinc sulfate and equilibrium data of the hydration–dehydration reactions have been collected and critically assessed. The more reliable solution properties were used to evaluate the parameters of an extended form of Pitzer's ion interaction model. With this model the activity coefficients and water activities of saturated $ZnSO_4$ solutions have been calculated yielding, together with equilibrium data of hydration–dehydration reactions, the thermodynamic solubility products of the three stable phases, $ZnSO_4·7H_2O$ (goslarite), $ZnSO_4·6H_2O$ (bianchite), $ZnSO_4·H_2O$ (gunningite), and the metastable, monoclinic $ZnSO_4·7H_2O$. Using these solubility products together with the ion interaction model, the predicted solubilities are in excellent agreement with the experimental data. The complete phase diagram of the system has been established in the temperature range (266–378) K.

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1. Introduction

Zinc sulfate is the zinc compound that is most frequently used and there is a variety of applications. For example, zinc sulfate is used in the viscose production process, in galvanizing baths, as an additive in fertilizers and animal feeds, as wood preservative and in medicine as an emetic, astringent or disinfectant [1,2]. The production of metallic zinc via the hydrometallurgical process is based on acidic zinc sulfate solutions [3,4]. The optimization of these processes requires precise knowledge of the binary phase diagram $ZnSO_4$–H_2O as well as the ternary systems with sulfuric acid and impurities, such as calcium and magnesium [5].

Zinc sulfate forms a number of hydrates in the series $ZnSO_4·nH_2O$ several of which are known minerals, i.e. $ZnSO_4·7H_2O$ (goslarite), $ZnSO_4·6H_2O$ (bianchite), $ZnSO_4·4H_2O$ (boyleite) and $ZnSO_4·H_2O$ (gunningite). Usually, these minerals occur as alteration products of sphalerite (ZnS) oxidation and are frequently observed as post-mining efflorescences on rocks [6]. Knowledge of dehydration equilibria of these salts is important to understand their formation under natural conditions. $ZnSO_4·7H_2O$ was also considered as a potential material for heat storage purposes either as a phase change material (PCM) [7] or, more recently, as a

thermochemical storage material [8] utilizing cycles of dehydration and rehydration.

There is a rich literature with experimental solubilities and equilibrium data for the various hydration–dehydration equilibria that were used by different authors to construct the binary phase diagram of the system $ZnSO_4$–H_2O [9–11]. However, the experimental data are significantly scattered and there is no agreement among different authors regarding the invariant points of the binary system. Moreover, compilations of critically evaluated thermodynamic data [12,13] are not consistent with each other and with existing experimental data reported for the equilibrium $ZnSO_4·7H_2O$ + $ZnSO_4·6H_2O$ + vapor [11]. Recently, using the experimental data of Chou and Seal [11], Grevel and Majzlan derived adjusted values of the standard entropies and enthalpies of formation of goslarite and bianchite at 298.15 K [14].

Experimental data of the water activities of the saturated solutions, i.e. the deliquescence humidities (DRH) of the hydrates, are even more scattered and it is nearly impossible to constrain the phase boundaries $ZnSO_4·nH_2O$ + saturated solution in a p/p_0–T phase diagram of the binary system. Since there is a reasonable solubility database, it appears to be more promising to calculate the water activities of the saturated solutions using an electrolyte solution model such as the Pitzer ion interaction model [15]. Such models require thermodynamic data of electrolyte solutions at different temperatures. In the case of $ZnSO_4$(aq), while there is a

reasonable database at 298.15 K [16], there is a lack of data at other temperatures. Where thermal data (heat capacities, heats of dilution) and activity data are available at a reference temperature (usually 298.15 K), activity data can be calculated at other temperatures, not too far away from the reference temperature. This approach was used by Königsberger and Erickson [17] to estimate Pitzer model parameters for ZnSO₄(aq) at high temperatures from available parameters at 298.15 K. The same approach was also used recently by Wang et al. [18].

The major objectives of the present work were to determine the model parameters of an extended Pitzer ion interaction model for ZnSO₄(aq) and to construct an updated phase diagram of the binary system ZnSO₄–H₂O. For that purpose, we have tested the suitability of an automated gravimetric water vapor sorption analyzer for the collection of new isopiestic data. In addition, existing thermodynamic data of ZnSO₄(aq) were carefully reviewed and used together with the new data to determine the model parameters of an extended Pitzer ion interaction model valid from the temperature of freezing to 373 K. This model was used together with available solubility and hydration–dehydration equilibrium data to determine the phase boundaries in the binary system including the stable phases gunningite, bianchite, goslarite and the metastable monoclinic zinc sulfate heptahydrate.

2. Experimental

Osmotic coefficients of ZnSO₄(aq) were determined with a water vapor sorption analyzer SPSx-1μ (ProUmid, Germany) using NaCl(aq) as the isopiestic reference. In the vapor sorption analyzer, solutions are placed in dishes positioned in a plate like sample holder for up to 23 samples. The sample tray is placed inside a temperature-controlled chamber connected to a humidity generator providing the desired constant water vapor pressure during equilibration of the samples. The atmosphere circulates within the chamber providing uniform temperature and vapor pressure. Each sample can be automatically positioned on the load cell of a microbalance by turning and lowering the sample tray. All samples are weighed at predefined time intervals (10 min in this study) with a reading precision of 10^{-6} g. The analyzer can be operated at temperatures from 278.15 K to 313.15 K and relative pressures 0–0.95. With increasing temperature difference between the inside air and the ambient air the maximum relative pressure declines due to condensation at cold spots.

Zinc sulfate solutions were prepared from ZnSO₄·7H₂O (Emsure, Merck, Germany) dehydrated at 723.15 K for 72 h in a furnace. After the thermal treatment, the anhydrous ZnSO₄ was dissolved without further purification in doubly distilled water. The NaCl (Rectapur, VWR, Germany) used for the preparation of the reference solutions was treated in the same way. The major difference to the usual isopiestic technique is that in this setup the water activities of all solutions are determined by the relative humidity in the sorption analyzer as controlled by the humidity generator. Depending on their initial water activities, the solutions equilibrate with the surrounding atmosphere by release or uptake of water vapor resulting in a change in solution molalities. Equilibrations at constant temperature and pressure were continued until the rate of weight change was <0.05% during a period of 2 h for all solutions. In this case, isopiestic equilibrium was assumed and the next series of measurements at a different predefined relative pressure was initiated automatically. Total equilibration times were typically in the order of 35–50 h. Values of the osmotic coefficients ϕ^* of the NaCl(aq) reference solutions were calculated with the equation of Archer [19] and those of ZnSO₄(aq) were calculated using the equation for isopiestic equilibrium

$$\phi = v^* m^* \phi^* / v m \qquad (1)$$

where m^* and ϕ^* are the molality and the osmotic coefficient of NaCl(aq), m is the molality of ZnSO₄(aq) and v^* and v are the total number of ions formed upon complete dissociation. In this study, $v^* = v = 2$.

Three solutions of both electrolytes were simultaneously exposed at constant temperature and vapor pressure. Measurements were first carried out at 298.15 K and the osmotic coefficients determined in this series were compared to the values recommended by Albright et al. [16]. Once the results were in satisfactory agreement, the temperature was changed to 288.15 K, 308.15 K and 313.15 K. Due to the problems with condensation mentioned before, measurements were only possible in a very narrow range of ZnSO₄ molalities with water activities from about 0.82–0.90 which is very close to the saturation water activities of ZnSO₄(aq) in this temperature range. Therefore, many of the values obtained represent supersaturated solutions.

3. Theory and equations

3.1. Phase equilibria

The thermodynamic solubility product of a hydrate of composition ZnSO₄·nH₂O is given by

$$\ln K_n = \ln(m_{\mathrm{Zn}}/m^\circ) + \ln(m_{\mathrm{SO4}}/m^\circ) + \ln \gamma_{\mathrm{Zn}} + \ln \gamma_{\mathrm{SO4}} + n \ln a_{\mathrm{w}} \qquad (2)$$

where m and γ are the molalities and activity coefficients of the zinc and sulfate ions at saturation, a_{w} is the water activity of the saturated solution and $m^\circ = 1$ mol kg⁻¹. Neglecting the minor influence of the non-ideal behavior of water vapor, at equilibrium, the water activity of a solution is given by

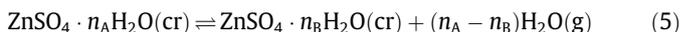$$a_{\mathrm{w}} = p_{\mathrm{w}}/p_{\mathrm{w}}^{\mathrm{o}} = \varphi \qquad (3)$$

where p_{w} and $p_{\mathrm{w}}^{\mathrm{o}}$ represent the water vapor pressure above the solution and the saturation vapor pressure of pure water at the given temperature and φ is the relative humidity (RH). The water activity is related to the osmotic coefficient ϕ. For a binary ZnSO₄ solution of molality m, this yields:

$$\ln a_{\mathrm{w}} = -2m\phi/m_{\mathrm{w}} \qquad (4)$$

Here, $m_{\mathrm{w}} = 55.50844$ mol kg⁻¹ is the molality of water.

Decomposition equilibria between different ZnSO₄ hydrates are given by

$$\mathrm{ZnSO_4 \cdot} n_{\mathrm{A}}\mathrm{H_2O(cr)} \rightleftharpoons \mathrm{ZnSO_4 \cdot} n_{\mathrm{B}}\mathrm{H_2O(cr)} + (n_{\mathrm{A}} - n_{\mathrm{B}})\mathrm{H_2O(g)} \qquad (5)$$

where subscripts A and B refer to two different hydrates containing n_{A} and n_{B} mol of water, respectively. The equilibrium constant of the decomposition reaction is given by

$$K_{\mathrm{AB}} = p_{\mathrm{w,AB}}/p_{\mathrm{w}}^{\mathrm{o}} = \varphi_{\mathrm{AB}} \qquad (6)$$

where $p_{\mathrm{w,AB}}$ and φ_{AB} refer to the equilibrium water vapor partial pressure and the equilibrium relative humidity for the hydration–dehydration equilibrium, i.e. the decomposition humidity of a hydrate. Therefore, values of K_{AB} can be obtained directly from experimental determinations of φ_{AB}. The equilibrium humidity, i.e. the equilibrium constant K_{AB}, is also related to the thermodynamic solubility products of the respective hydrates by

$$\ln K_{\mathrm{B}} = \ln K_{\mathrm{A}} - (n_{\mathrm{A}} - n_{\mathrm{B}}) \ln K_{\mathrm{AB}} \qquad (7)$$

3.2. Ion interaction model

In order to represent the available thermodynamic data for aqueous zinc sulfate the ion interaction approach of Pitzer [15] was used. The Pitzer equations incorporate an extended Debye–Hückel limiting law and a virial expansion representing short