



Thermodynamic modelling of aqueous Mn(II) sulfate solutions

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ABSTRACT

The H₂O–MnSO₄ system has been modelled using the Pitzer activity coefficient approach over a temperature interval of –11–175 °C and in concentrations from pure water to the solubility limit of manganese sulfate hydrates, the maximum MnSO₄ molality being 4.26 mol/kg at the MnSO₄·5H₂O(s) to MnSO₄·H₂O(s) transition temperature of 23.9 °C. The thermodynamic properties of MnSO₄ hydrates were refined. The model in this work presents all the experimental data available, including the solubilities, mean activity coefficients, activities of water, enthalpy and heat capacity of solution and hydrate dissociation pressure, with good accuracy and consistently up to 175 °C, but the model has limitations at higher than 100 °C due to lack of experimental data.

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1. Introduction

The water–manganese sulfate system has been studied due to its key importance in many hydrometallurgical applications, which operate typically at temperatures between 50 and 300 °C. Hydrometallurgical processes such as stainless steel pickling acid regeneration and manganese ore leaching need internally consistent thermodynamic databases to improve, develop, and better understand systems and phenomena in the aqueous process solutions and environments.

Manganese has oxidation states of +2, +3, +4, +6 and +7 but in this work only the most stable +2 state was considered [1]. In aqueous solutions, manganese sulfate forms hydrates with 1, 2, 4, 5 and 7 molecules of crystalline water [2,3]. The aim of this study was to compile and reassess the experimental observations of the system and extend the thermodynamic description for the MnSO₄–H₂O system up to 175 °C. The assessment procedure was similar as used earlier for FeSO₄–H₂O [4] and NiSO₄–H₂O [5] systems.

Thermodynamics of the H₂O–MnSO₄ system has been modelled in many papers [6–22]. Przepiera [14] has modelled this system as part of his H₂O–MnSO₄–H₂SO₄ assessment using Pitzer model from 0 to 100 °C. Unfortunately, Przepiera [14] paper do not include thermodynamic data of the species and that is why it is not possible to recalculate his results. Przepiera and Kalbarczyk [16] derived

temperature dependent Pitzer parameters from their enthalpy of solution measurements at 25, 45 and 55 °C but their reported temperature dependent Pitzer parameters are not consistent. Guendouzi et al. [9] optimised Pitzer parameters to fit their experimental water activity data at 25 °C. Also Malatesta et al. [11] has modelled the system with Pitzer model but using different internal constants ($\alpha_1=1.14$ and $\alpha_2=18.34$) than in the original work of Pitzer [6,23,24]. Schreiber et al. [17] have assessed temperature derivatives of the Pitzer parameters from their enthalpy of dilution measurements. We found errors in the Pitzer model equations of Schreiber et al. for apparent enthalpy of solution ($^{\phi}L$); see Pitzer [25]. Azimi et al. [19,20] modelled the system using Mixed Solvent Electrolyte (MSE) model from 0 to 170 °C with following experimental data from the literature: solubility of MnSO₄, activity of water, mean activity coefficient and heat capacity of solution data. Iliuta et al. [8] modelled the system using extended UNiVersal QUAsiChemical (UNIQUAC) model at –11.4–100 °C using solubility and osmotic coefficient data. Safaeefar et al. [21] modelled the system with modified extended Non-Random Two-Liquid (NRTL) model at 18–28 °C as a part of the quaternary system MnSO₄·4H₂O(s)+MgSO₄·7H₂O(s)+CH₃OH(l)+H₂O(aq). Maeda et al. [7] modelled the system and magnesium sulfate with NRTL model at 0–80 °C using their own solubility measurements.

All the experimental data used in the modelling were taken from the literature and reviewed critically. The resulting thermodynamic model was obtained using the thermodynamic equilibrium calculation program MTDATA[®] (www.mtdata-software.com), which uses global Gibbs energy minimisation routine and includes the Pitzer activity coefficient model for the excess Gibbs energy of the aqueous solutions. The CALculation of PHase Diagrams (CALPHAD) method

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was used in modelling, to ensure internal consistency of the thermodynamic database [26].

2. Modelling the aqueous solutions

The Pitzer model is one of the most used activity coefficient models for aqueous solutions. The original approach assumes that the aqueous solution consists of ions only, and no ion complexes are formed. Details of the Pitzer model used are available in [6,23,24]. Later, Harvie and Weare [27] and Harvie et al. [28] included unsymmetrical electrostatic mixing terms in their modification of the Pitzer model, which has been shown to improve the fit in multicomponent systems. All the necessary Pitzer model equations, variables and parameters have been explained in the following equations; see Appendix 2 for symbols.

$$f^{\gamma} = -A_{\phi} \left[\frac{\sqrt{I}}{(1+b\sqrt{I})} + \left(\frac{2}{b}\right) \ln(1+b\sqrt{I}) \right] \quad (1)$$

$$\ln \gamma_{\pm} = z_M |z_X| f^{\gamma} + 2m \left(\frac{v_M v_X}{v} \right) (B_{MX}^{\phi} + B_{MX}) + 3m^2 \left[\frac{(v_M v_X)^{3/2}}{v} \right] C^{\phi} \quad (2)$$

$$\phi - 1 = -A_{\phi} z_M |z_X| \left[\frac{1^{1/2}}{(1+bI^{1/2})} \right] + 2m \left(\frac{v_M v_X}{v} \right) B_{MX}^{\phi} + 2m^2 \left[\frac{(v_M v_X)^{3/2}}{v} \right] C^{\phi} \quad (3)$$

$$B_{MX}^{\phi} = \beta^{(0)} + \beta^{(1)} \exp(-\alpha_1 I^{1/2}) + \beta^{(2)} \exp(-\alpha_2 I^{1/2}) \quad (4)$$

$$B_{MX} = \beta^{(0)} + \beta^{(1)} g(\alpha_1 I^{1/2}) + \beta^{(2)} g(\alpha_2 I^{1/2}) \quad (5)$$

$$g(x) = \frac{2(1-(1+x)e^{-x})}{x^2} \quad (6)$$

values for internal constant parameters of the Pitzer model used in this work are $b=1.2$, $\alpha_1=1.4$ and $\alpha_2=12$ for the 2–2 electrolyte.

Relations between apparent molal enthalpy ($^{\phi}L$) of solution and measured enthalpy of solution $H_s(T)$ is calculated using Eq. (7). Pitzer model equation for $^{\phi}L$ is in Eq. (8).

$$H_s(T) = H_s^{\circ}(T) + ^{\phi}L \quad (7)$$

$$^{\phi}L = v |z_M z_X| A_L \frac{\ln(1+bI^{1/2})}{2b} - 2v_M v_X RT^2 m \left[\beta^{(0)L} + g(\alpha_1 I^{1/2}) \beta^{(1)L} + g(\alpha_2 I^{1/2}) \beta^{(2)L} + \frac{m v_M z_M}{2 |z_M z_X|^{1/2}} C^{\phi L} \right] \quad (8)$$

where symbols A_L refer to

$$\frac{A_L}{RT} = 4T \left(\frac{dA_{\phi}}{dT} \right)_p \quad (9)$$

and Pitzer parameters are temperature derivatives of the activity coefficient parameters

$$\beta^{(i)L} = \left(\frac{d\beta^{(i)}}{dT} \right)_p, \quad i = 0, 1, 2 \quad (10)$$

$$C^{\phi L} = \left(\frac{dC^{\phi}}{dT} \right)_p \quad (11)$$

Relations between apparent molal heat capacity ($^{\phi}C_p$) of solution and measured heat capacity of solution C_{p2} is calculated using Eq. (12). Pitzer model equation for $^{\phi}C_p$ is in Eq. (13).

$$^{\phi}C_p = \frac{m_{g,sol} C_{p2} - n_1 C_{p1}^{\circ}}{n_2} \quad (12)$$

$$^{\phi}C_p = C_{p2}^{\circ} + v |z_M z_X| A_J \frac{\ln(1+bI^{1/2})}{2b} - 2v_M v_X RT^2 m \left[\beta^{(0)J} + g(\alpha_1 I^{1/2}) \beta^{(1)J} + g(\alpha_2 I^{1/2}) \beta^{(2)J} + \frac{m v_M z_M}{2 |z_M z_X|^{1/2}} C^{\phi J} \right] \quad (13)$$

where symbols A_J refer to

$$A_J = \left(\frac{dA_I}{dT} \right)_p \quad (14)$$

and Pitzer parameters are second temperature derivatives of the activity coefficient parameters

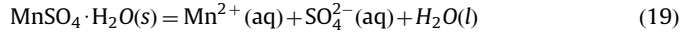
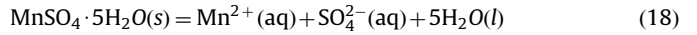
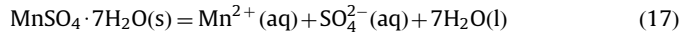
$$\beta^{(i)J} = \left(\frac{d^2 \beta^{(i)}}{dT^2} \right)_p + \frac{2}{T} \left(\frac{d\beta^{(i)}}{dT} \right)_p, \quad i = 0, 1, 2 \quad (15)$$

$$C^{\phi J} = \left(\frac{d^2 C^{\phi}}{dT^2} \right)_p + \frac{2}{T} \left(\frac{dC^{\phi}}{dT} \right)_p \quad (16)$$

The value of the Debye–Hückel parameters used are $A_{\phi}=0.39147$, $A_L=1985.287$ and $A_J=32.64$ at 25 °C.

2.1. Thermodynamic functions

Solubility products of the solid phases are expressed by the following Eqs. (17)–(22):



$$K_{SP7} = \frac{a_{\text{Mn}^{2+}(\text{aq})} \times a_{\text{SO}_4^{2-}(\text{aq})} \times a_{\text{H}_2\text{O}(l)}^7}{a_{\text{MnSO}_4 \cdot 7\text{H}_2\text{O}(s)}} = \gamma_{\pm}^2 \times m^2 \times a_{\text{H}_2\text{O}(l)}^7 \quad (20)$$

$$K_{SP5} = \frac{a_{\text{Mn}^{2+}(\text{aq})} \times a_{\text{SO}_4^{2-}(\text{aq})} \times a_{\text{H}_2\text{O}(l)}^5}{a_{\text{MnSO}_4 \cdot 5\text{H}_2\text{O}(s)}} = \gamma_{\pm}^2 \times m^2 \times a_{\text{H}_2\text{O}(l)}^5 \quad (21)$$

$$K_{SP} = \frac{a_{\text{Mn}^{2+}(\text{aq})} \times a_{\text{SO}_4^{2-}(\text{aq})} \times a_{\text{H}_2\text{O}(l)}}{a_{\text{MnSO}_4 \cdot \text{H}_2\text{O}(s)}} = \gamma_{\pm}^2 \times m^2 \times a_{\text{H}_2\text{O}(l)} \quad (22)$$

where γ_{\pm} is mean activity coefficient, (a_i) is activity of species i and concentration unit m is molality of MnSO_4 (mol/kg of water), which is used throughout this paper.

The temperature dependency equation in MTDATA[®] for heat capacity of a species has the following form:

$$C_p^{\circ} = A + B \left(\frac{T}{K} \right) + C \left(\frac{T}{K} \right)^2 + D \left(\frac{T}{K} \right)^{-2} \quad (23)$$

and the Gibbs energy has the temperature-dependent form

$$G^{\circ}(T) = A_G + B_G \left(\frac{T}{K} \right) + C_G \left(\frac{T}{K} \right) \ln \left(\frac{T}{K} \right) + D_G \left(\frac{T}{K} \right)^2 + E_G \left(\frac{T}{K} \right)^3 + F_G \left(\frac{T}{K} \right)^{-1} \quad (24)$$

The general temperature dependency available in MTDATA[®] for the Pitzer equation parameter (p) is

$$p = A_{\text{Pitz}} + B_{\text{Pitz}} \left(\frac{T}{K} \right) + C_{\text{Pitz}} \left(\frac{T}{K} \right) \ln \left(\frac{T}{K} \right) + D_{\text{Pitz}} \left(\frac{T}{K} \right)^2 + E_{\text{Pitz}} \left(\frac{T}{K} \right)^3 + F_{\text{Pitz}} \left(\frac{T}{K} \right)^{-1} \quad (25)$$

3. Experimental observations

3.1. Solubility data

A large number of solubility measurements have been made at temperatures ranging from –11 to 188 °C [2,3,7,29–69]. The

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