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Thermodynamic Modeling of Calcium Sulfate Hydrates in a CaSO$_4$–H$_2$SO$_4$–H$_2$O System from 273.15 to 473.15 K up to 5 m Sulfuric Acid

Leiting Shen, Hannu Sippola,* Xiaobin Li, Daniel Lindberg, and Pekka Taskinen

ABSTRACT: To prevent scaling and to recycle aqueous solutions in industrial processes, the thermodynamic properties of the CaSO$_4$–H$_2$SO$_4$–H$_2$O system are studied by thermodynamic modeling with the Pitzer model. The published solubility data of calcium sulfate hydrates in sulfuric acid solutions were collected and reviewed critically. Then, the CaSO$_4$–H$_2$SO$_4$–H$_2$O system was modeled using the Pitzer activity coefficient approach from critically selected experimental data to obtain optimized parameters. The model reproduces the solubility data with good accuracy up to 5 m sulfuric acid at temperatures of 283.15–368.15, 283.15–473.15, and 298.15–398.15 K for gypsum (CaSO$_4$·2H$_2$O), anhydrite (CaSO$_4$), and hemihydrate (CaSO$_4$·0.5H$_2$O), respectively. However, at temperatures above 398.15 K and sulfuric acid concentration above 0.5 mol/kg, the solubility of anhydrite predicted by our model deviates significantly from the literature data. Our model predicts that the solubility of anhydrite would first increase but then decrease in more concentrated sulfuric acid solutions, which is in disagreement with the experimental data showing constantly increasing solubilities as a function of increasing sulfuric acid concentration. This discrepancy has been discussed. The transformations of gypsum to anhydrite and hemihydrate were predicted in sulfuric acid solutions. With increasing H$_2$SO$_4$ concentration, the transformation temperatures of gypsum to anhydrite and hemihydrate will decrease. Thus, gypsum is stable at low temperatures in solutions of low H$_2$SO$_4$ concentrations and transforms to anhydrite at high temperatures and in concentrated H$_2$SO$_4$ solutions, while hemihydrate is always a metastable phase. Furthermore, the predicted results were compared with previous experimental studies to verify the accuracy of the model.

1. INTRODUCTION

Calcium sulfate is one of the most common inorganic salts with a high scaling potential existing in many industrial processes.\textsuperscript{1} It mainly precipitates as a solid scale on equipment surfaces or piping networks, causing production losses, downtime, and efficiency decrease. Calcium sulfate scaling appears commonly in industrial processes when treating natural ores containing calcium minerals with sulfuric acid, especially in the hydrometallurgical processes of primary tungsten, copper, nickel, and zinc manufacturing.\textsuperscript{2−7} Despite its negative influences, the small solubility of calcium sulfate is beneficial for recycling aqueous solutions in the processing circuit since it limits the accumulation of calcium and sulfate in the process solutions. Therefore, understanding the detailed thermodynamic properties of the CaSO$_4$–H$_2$SO$_4$–H$_2$O system is of great theoretical and practical importance to prevent scaling and the aqueous process solution circulation.

In aqueous solutions, calcium sulfate forms two hydrates with the chemical names hemihydrate (HH, CaSO$_4$·0.5H$_2$O) and dihydrate or gypsum (DH, CaSO$_4$·2H$_2$O), in addition to anhydrite (AH, CaSO$_4$). The stability regions of calcium sulfates depend on the solution conditions, such as temperature and sulfuric acid concentration, which complicate the prediction and control of calcium sulfate scaling.\textsuperscript{1} The solubilities of calcium sulfates in water and electrolyte salt systems have been extensively studied experimentally and theoretically over recent decades even since the mid-19th century.\textsuperscript{6} Several experimental data sets are also focused on the solubilities of calcium sulfates in H$_2$SO$_4$ solutions.

The aim of this study was to compile and reassess the experimental data of calcium sulfate in sulfuric acid solutions and model the CaSO$_4$–H$_2$SO$_4$–H$_2$O system up to 473.15 K. The assessment procedure was similar to that in our recent article concerning modeling the CaSO$_4$–H$_2$O system.\textsuperscript{7} The difference from the earlier assessment for the FeSO$_4$–H$_2$SO$_4$–H$_2$O and NiSO$_4$–H$_2$SO$_4$–H$_2$O\textsuperscript{9} systems is the model used for the H$_2$SO$_4$–H$_2$O system.

All of the experimental data adopted in the modeling were taken from the published literature and reviewed critically. The optimized thermodynamic model parameters were obtained using thermodynamic equilibrium calculation software MTDATA, which uses a Gibbs energy minimization routine and
used Pitzer parameters for the interactions of calcium with HSO4(−), SO4(2−), Ca2+, and H+. They characterized the solid phase after 2 h of equilibration by X-ray diffraction. They found that when using calcium dihydrate as the starting material, the solid phase is a mixture of gypsum and hemihydrate in H2SO4 concentrations below 0.41 mol/kg H2O, hemihydrate only in H2SO4 concentrations of 0.51–1.93 mol/kg H2O, and anhydrite with H2SO4 concentrations above 2.64 mol/kg H2O. If hemihydrate was used as the starting material, it was the only primary solid equilibrium phase with H2SO4 concentrations up to 1.93 mol/kg and anhydrite above 2.64 mol/kg H2O.

Azimi et al.14 measured the solubility of gypsum in 0.5 molality H2SO4 solutions at temperatures of 298.15, 318.15, 343.15, and 363.15 K when researching the solubility of gypsum in the MgSO4·H2SO4·H2O system. Farrah et al.15 conducted experiments in 36 and 72 g of H2SO4/kg solution to determine the solubilities of gypsum and anhydrite at temperatures from 303.15 to 378.15 K in the MnSO4·H2SO4·H2O system. Zdanovskii et al.16,17 measured the solubilities of gypsum from 283.15 to 368.15 K, anhydrite from 283.15 to 323.15 K, and hemihydrate from 289.15 to 368.15 K in 0–40 mass % H2SO4 solutions when studying the dehydration of gypsum. Marshall and Jones18 determined the solubilities of gypsum from 298.15 to 333.15 K, hemihydrate at 398.15 K, and anhydrite from 398.15 to 623.15 K in 0–4.7 mol H2SO4 solution when assessing the second dissociation constant for sulfuric acid. Cameron and Breazeale19 measured the solubilities of gypsum in 0–292.92 g/L H2SO4 solutions at 298.15, 308.15, and 316.15 K.

When studying the ZnSO4·H2SO4·H2O system, Dutrizac5 determined the solubilities of gypsum on heating and cooling in two series of experiments. The first one was carried out from 293.15 to 368.15 K in 0–0.6 mol/L H2SO4 solutions and the second one from 293.15 to 353.15 K in 0.8–1.8 mol/L H2SO4 solutions. Dutrizac used excess gypsum as the raw material and examined the solid phase by X-ray diffraction. He discovered that gypsum was the only solid phase during heating and cooling in the first series up to 368.15 K and up to 0.6 mol/L H2SO4 solution. In the second series, a hysteresis behavior was found. When heating gypsum with increasing sulfuric acid concentrations, it remained the only solid to temperatures varying from 363.15 to 353.15 K. Then, anhydrite was formed, and the solubility dropped. The transition temperature decreased with increasing sulfuric acid concentration. On cooling, the anhydrite remained as a solid phase down to around 323.15 K, where gypsum was formed. Dutrizac further fitted the data for the solubilities and saturated solution densities as a function of temperature.

### 2. THERMODYNAMIC DATA

The experimental data about the solubilities of calcium sulfates in sulfuric acid solutions were collected from the available literature. The solubilities of gypsum and anhydrite in H2SO4 solutions have attracted many researchers, while that of hemihydrate remains as a solid phase down to around 323.15 K, where gypsum was formed. Dutrizac further fitted the data for the solubilities and saturated solution densities as a function of temperature.

#### Table 1. Solubility Data of Calcium Sulfates in H2SO4 Solutions from the Literature

| T, K     | H2SO4 molality | points* | reported experimental error (%) | solid phase                          | reference               |
|----------|----------------|---------|-----------------------------------|--------------------------------------|-------------------------|
| 298.15−363.15 | 0−4.0030       | 20 (20) | 0.1−2                             | CaSO4·2H2O                           | Wang et al.11           |
| 298.15−363.15 | 0.4854−0.4990  | 4 (4)   | 5                                  | CaSO4·2H2O                           | Azimi and Papangelakis14 |
| 303.15−353.15 | 0−0.7931       | 12 (12) | 6                                  | CaSO4·2H2O                           | Farrah et al.15         |
| 298.15−333.15 | 0−4.7000       | 74 (76)b| 4                                  | CaSO4·2H2O                           | Marshall and Jones18     |
| 283.15−368.15 | 0−6.8429       | 31 (44)c| 6                                  | CaSO4·2H2O                           | Zdanovskii et al.16,17  |
| 298.15−316.15 | 0−3.4081       | 2 (26)d | 1.0                               | CaSO4·2H2O                           | Cameron and Breazeale19 |
| 298.15−363.15 | 0−4.6531       | 23 (28)e| 0.1−2                             | CaSO4                                 | Wang et al.11           |
| 363.15−378.15 | 0−0.7922       | 0 (8)   | 6                                  | CaSO4                                 | Farrah et al.15         |
| 398.15−623.15 | 0−1.2090       | 17 (15)f| 4                                  | CaSO4                                 | Marshall and Jones18     |
| 283.15−323.15 | 0−4.3767       | 24 (26)g| 6                                  | CaSO4                                 | Zdanovskii16            |
| 373.15     | 2.64−7.90      | 0 (3)   | 0.45−4.117                         | CaSO4·0.5H2O                         | Ling and Demopoulos13   |
| 398.15     | 0−1.0450       | 12 (12) | 4                                  | CaSO4·0.5H2O                         | Marshall and Jones18     |
| 398.15−368.15 | 0−6.8246       | 27 (32)b| 1.70−7.52                         | CaSO4·0.5H2O                         | Zdanovskii et al.17     |
| 373.15     | 0−1.93         | 14 (14) |                                    | CaSO4                                 | Ling and Demopoulos13   |

*Total number of data points in the parentheses. **Except points 2.384 and 4.7 mol/kg H2SO4 at 313.15 K. \(^{11}\) All points at 283.15 excluded except at 2.5525 mol/kg H2SO4, excluded points from 1.8038 to 6.0811 mol/kg H2SO4 at 298.15 K, excluded 0.8296 mol/kg H2SO4 at 308.15 K, all points excluded at 315.15 K, excluded 4.3781 and 6.8047 mol/kg H2SO4 at 323.15 K, excluded 6.8146 mol/kg H2SO4 at 348.15 K and 6.8429 mol/kg H2SO4 at 368.15 K. \(^{12}\) Included only 0.0831 mol/kg H2SO4 at 298.15 K and 0.0496 mol/kg H2SO4 at 316.15 K. \(^{13}\) Except points 3.0 and 4.5007 mol/kg H2SO4 at 323.15 K, 0.2001 and 3.0021 mol/kg H2SO4 at 348.15 K, and 3.0022 mol/kg H2SO4 at 363.15 K. \(^{14}\) All points included at 398.15 K, included only 0.476−0.564 mol/kg H2SO4 at 423.15 K, included 0.00085−0.0023 and 0.481−0.578 mol/kg H2SO4 at 448.15 K, included 0.00014 and from 0.488 to 0.585 mol/kg H2SO4 at 473.15 K. All data above 473.15 K excluded. \(^{15}\) Included all points except 2.5565 and 4.3767 mol/kg H2SO4 at 323.15 K. \(^{16}\) Included all except points 6.8036 mol/kg H2SO4 at 298.15 K, 4.3872 and 6.8053 mol/kg H2SO4 at 323.15 K, 6.8121 mol/kg H2SO4 at 348.15 K, and 6.8246 mol/kg H2SO4 at 368.15 K.

The solubilities of gypsum and anhydrite in H2SO4 solutions have attracted many researchers, while that of hemihydrate remains as a solid phase down to around 323.15 K, where gypsum was formed. Dutrizac further fitted the data for the solubilities and saturated solution densities as a function of temperature.
Table 2. Summary of the Optimization of Pitzer Parameters for the CaSO₄−H₂SO₄−H₂O System

| Model | OF | β⁽¹⁾ | β⁽²⁾ | β⁽³⁾ | β⁽⁴⁾ | β⁽⁵⁾ | β⁽⁶⁾ | Cg |
|-------|----|------|------|------|------|------|------|----|
| set-1⁰ | 0.23 | D | D | D | D | x | x | x | x |
| set-2⁰ | 0.23 | D | D | D | D | x | x | x | x |
| set-3⁰ | 0.71 | D | D | D | D | x | x | x | x |
| set-4⁰ | 0.39 | D | D | D | D | x | x | x | x |
| set-5⁰ | 0.22 | x | x | D | D | x | x | x | x |
| set-6 | 0.16 | x | x | x | x | x | x | x | x |

The parameters of Gibbs energy changes for forming the solid phase use the A + B × T + C × T ln T form. Values of parameters β⁽¹⁾ and β⁽²⁾ for Ca²⁺−SO₄²⁻ ion interactions are from model D in a previous work and kept unchanged in the assessment.

3. MODELING THE AQUEOUS SOLUTIONS

The Pitzer model, one of the most used activity coefficient models, has been extensively used for modeling thermodynamic properties of aqueous electrolyte systems. Pitzer and co-workers have provided the details of the model in the literature. It was developed by combining the expression of the Debye–Hückel electrostatic theory for long-range interactions and composition for short-range ion-specific interactions with a virial-type expansion. Harvie and Weare and Harvie et al. further included unsymmetrical electrostatic mixing terms in their modified Pitzer models to improve the fit in multicomponent systems. All of the necessary Pitzer model equations, variables, and parameters have been explained in the Supporting Information, where the typographical error in eq A-15 existing in previous works has been corrected. This correction does not have any effect on results presented in this work.

3.1. Thermodynamic Functions. The consistent concentration unit in aqueous solutions is molality of CaSO₄ and H₂SO₄ (mol/kg of water), used throughout this paper. The temperature dependency of Gibbs energy change for forming a solid phase has the following form

\[ \Delta G°(T) = -RT \ln(K_{eq}) = A_C + B_C \left( \frac{T}{K} \right) + C_C \ln\left( \frac{T}{K} \right) + D_C \left( \frac{T}{K} \right)^2 + E_C \left( \frac{T}{K} \right)^3 + F_C \left( \frac{T}{K} \right)^{-1} \]

The general temperature dependency of the parameters for the Pitzer equation parameter (p) available in MTDATA is

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

3.2. Parameter Optimization. MTDATA version 6.0 was used for parameter fitting in this work. In MTDATA, there are several excess models available, including the Pitzer equation with Harvie et al.’s modification and the mole-fraction-based NPL Pitzer model. MTDATA solves thermodynamic equilibrium using the Gibbs energy minimization technique and also includes several thermodynamic databases for pure substances and several excess Gibbs energy models for different kinds of solutions. It also has an assessment module to fit model parameters from many types of experimental data. The objective function (OF) used in MTDATA is

\[ OF = \sum_{i=1}^{N} w_i \left[ \frac{C_i - E_i}{U_i} \right]^2 \]

where \( w_i \) is the weight of the experimental value, \( C_i \) is the calculated value, \( E_i \) is the experimental value, and \( U_i \) is the uncertainty. All weights for the adopted experimental data, except for the rejected values, were set to 1 in the assessment and parameterization. For duplicates, the weight was set to 0.5.

In this work, the mean absolute percentage error (MAPE), also known as the absolute average relative deviation (AARD %), is used in the comparison between the experimental data and the predicted values of this study

\[ MAPE = \frac{100}{N} \left( \sum_{i=1}^{N} \frac{|C_i - E_i|}{E_i} \right) \]
Table 3. Summary of the Thermodynamic Values of Solubility Reactions at 298.15 K

| ion interactions | coefficients | $A_{Pit}$ | $B_{Pit}$ | $P_{Pit}$ | reference |
|------------------|--------------|-----------|-----------|-----------|-----------|
| Ca$^{2+}$−SO$_4^{2−}$ | $β^{(1)}$ | −3.20249 | 0 | 1149.4 | model D$^7$ |
| Ca$^{2+}$−HSO$_4^{−}$ | $β^{(2)}$ | 32.027 | −0.27033 | 0 | set-1, this work |
| H$^{+}$−SO$_4^{2−}$ | $γ^{(2)}$ | −6.53747 | 0.096100 | 8930 | Sippola and Taskinen$^{31}$ |
| H$^{+}$−HSO$_4^{−}$ | $γ^{(3)}$ | −0.7515156 | 0.00207479 | 0 | −30.395 |

Table 4. Assessed Temperature Dependences of Gibbs Energy Changes (J/mol) for Formation of the Equilibrium Solid Phases in This Work

| phase | $A$ | $B$ | $C$ | temperature range (K) |
|-------|-----|-----|-----|-----------------------|
| CaSO$_4$·2H$_2$O | −59 567.2 | 1287.94 | −206 522 | 273.15−368.15 |
| CaSO$_4$ | −75 436.6 | 1548.65 | −303 855 | 273.15−473.15 |
| CaSO$_4$·0.5H$_2$O | −56 468.74 | 1518.79 | −246 924 | 273.15−473.15 |

4. RESULTS AND DISCUSSION

4.1. Fitted Parameters. In a ternary system, the parameters of binary systems are very important. According to the Calphad methodology, the binary systems are fitted first. After critical evaluation of the binaries, the critical evaluation of the ternary system is based on the binaries. Sometimes, during the assessment of the ternary system, it becomes obvious that either Gibbs energies or activity coefficient parameters obtained from binary systems need to be refitted. So, the assessment of the ternary system will also serve as a quality test for binary assessments. As far as solubility is concerned, there is only one experimental data point for each temperature in the binary system, while in the ternary system, there can be several.

Figure 1. Difference between calculated and experimental values of Gibbs energy for calcium sulfates in sulfuric acid solutions in the assessment. Error = ($C_i - E_i$)/$U_i$ (solid symbol, adopted value; open symbol, unadopted in the assessment).

Figure 2. Comparison between set-1 and model D for the CaSO$_4$−H$_2$O system.
Figure 3. continued
Sulfuric acid dissociates completely to hydrogen and bisulfate ions, while bisulfate does not further dissociate completely to

Figure 3. Assessed and experimental solubilities of gypsum in the CaSO₄–H₂SO₄–H₂O system at (a) 283.15 K, (b) 298.15 K, (c) 303.15 K, (d) 308.15 K, (e) 313.15 K, (f) 315.15 K, (g) 316.15 K, (h) 318.15 K, (i) 323.15 K, (j) 333.15 K, (k) 343.15 K, (l) 348.15 K, (m) 353.15 K, (n) 363.15 K, and (o) 368.15 K.

experimental data points at the same temperature as a function of the third component’s concentration. Sulfuric acid dissociates completely to hydrogen and bisulfate ions, while bisulfate does not further dissociate completely to
hydrogen and sulfate ions except in very dilute solutions. Sippola et al. critically evaluated six different equilibrium constants ($K_2$) for the dissociation of the bisulfate ion in the $\text{H}_2\text{SO}_4^{-}\text{H}_2\text{O}$ system and discovered that four of them can

Figure 4. Assessed and experimental solubilities of anhydrite in the CaSO$_4$–H$_2$SO$_4$–H$_2$O system at (a) 283.15 K, (b) 298.15 K, (c) 308.15 K, (d) 315.15 K, (e) 323.15 K, (f) 348.15 K, (g) 363.15 K, (h) 368.15 K, (i) 373.15 K, (j) 378.15 K, (k) 398.15 K, (l) 423.15 K, (m) 448.15 K, and (n) 473.15 K.
describe the $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ system equally well in the temperature range of 273.15$-$323.15 K. Finally, Sippola and Taskinen$^{31}$ reassessed the $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ system using the Pitzer equation in the temperature range of 273.15$-$443.15 K up to 6 $m$ sulfuric acid. They fitted simultaneously the dissociation constant of the bisulfate ion as well as Pitzer parameters. The number of used Pitzer parameters was four, and the total number of used terms was only eight. Recently, we critically assessed the solubility data of gypsum, anhydrite, and hemihydrate in the available literature up to 473.15 K and obtained an excellent Pitzer model$^7$ using only two Pitzer parameters, $\beta^{(1)}$ and $\beta^{(2)}$, with simple temperature dependency consisting of only two fitted terms in each. Our model for the $\text{CaSO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ system will be based on these two critically fitted binary systems.

The critically evaluated solubility data of calcium sulfate in sulfuric acid solutions listed in Table 1 as well as the solubility in water$^{18,34,52}$ applied in a previous work$^7$ were used in the assessment of the $\text{CaSO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ system. No change in the weights for the solubility in the $\text{CaSO}_4 - \text{H}_2\text{O}$ system was made.$^7$

Due to the small values for solubilities of calcium sulfate hydrates in aqueous solutions, the same optimization technique was applied as in the assessment of the $\text{CaSO}_4 - \text{H}_2\text{O}$ system.$^7$ Instead of comparing the calculated and measured solubilities, the difference in Gibbs energy was selected to fit the parameters of the Pitzer model. According to eq 1, in the solubility limit $\Delta G^\circ(T) + RT \ln(K_{sp}) = 0$. Thus, we obtain

$$C_i = \Delta G^\circ(T)$$  

Figure 5. Assessed and experimental solubilities$^{13,17,18}$ of hemihydrate in the $\text{CaSO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ system at (a) 298.15 K, (b) 323.15 K, (c) 348.15 K, (d) 368.15 K, (e) 373.15 K, and (f) 398.15 K.
Table 6. Comparison of the Experimental Data for Solubility of Gypsum from Dutrizac5 and the Predicted Values of This Work in the CaSO4–H2SO4–H2O System

| H2SO4 | 298.15 K | 323.15 K | 348.15 K | 363.15 K | all      |
|-------|-----------|-----------|-----------|-----------|----------|
| MAPE  | 0±1.8 mol/L | 1.8% | 1.9% | 3.6% | 4.7% | 3.0% |

Figure 6. Transformation of gypsum to anhydrite and hemihydrate in the CaSO4–H2SO4–H2O system.

\[ E_i = -RT \ln(K_{eq}) \] (6)

where \( \Delta G^\circ \) is the Gibbs energy change for each of the reactions

\[ \text{CaSO}_4 \cdot 2\text{H}_2\text{O}(s) = \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) + 2\text{H}_2\text{O}(l) \] (7)

\[ \text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}(s) = \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) + 0.5\text{H}_2\text{O}(l) \] (8)

\[ \text{CaSO}_4(s) = \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) \] (9)

In this approach, \( C_i \) and \( E_i \) do not present the calculated and experimental solubilities, respectively. \( C_i \) presents the calculated standard Gibbs energy change \( \Delta G^\circ \) based on thermodynamic difference in standard state values for the solubility reaction, and \( E_i \) presents the Gibbs energy change calculated from the solubility product calculated from the activities of calcium sulfate and water in an aqueous solution. \( U_i \) will serve as an acceptable difference between these two values.

The uncertainty value (\( U_i \)) was set to 100 J/mol for stable phases, while 500 J/mol was used for metastable states. Only the first three parameters \( A_{ij} = C_{ij} \) were found adequate to describe \( \Delta G^\circ(T) \).

The critical evaluation of the solubility data for the CaSO4–H2SO4–H2O system was performed during the assessment using the following procedure:

1. If all of the tested sets failed to model an experimental data point within given uncertainty, its weight was changed to zero.
2. If any of the tested sets were able to model it within a given uncertainty, its weight was changed to or retained as 1.
3. After changing the weights in solubility data, all parameter sets were refitted.
4. This procedure was repeated until no change was made in weights.

As a result, we considered achieving an internally consistent solubility data for the calcium sulfate in sulfuric acid.

Different sets of Pitzer parameters were tested in the assessment. The Pitzer parameters for the CaSO4–HSO4− ion interaction, \( \beta^{(1)} \), \( \beta^{(2)} \), and \( C^\circ \), were included in all sets, but the temperature dependency varied from one set to another. In most sets, the values of parameters \( \beta^{(1)} \) and \( \beta^{(2)} \) for the Ca\(^{2+}\)–SO\(_4^{2-}\) ion interaction were from model D in the previous work and were kept unchanged in the assessment. The parameter \( \beta^{(0)} \) for the Ca\(^{2+}\)–SO\(_4^{2-}\) ion interaction was included in set-5, and all parameters of the Pitzer model in set-6 were released and refitted. In all of the sets, the parameters of Gibbs energy changes for forming the solid phase were refitted but described with the same temperature dependency as \( A + B \times T + C \times T \ln T \) as in model D.

The summary of the assessment results for different Pitzer parameter sets is shown in Tables 2 and 3, indicating that set-1 is the best in the assessment with an OF value of 0.23, and its thermodynamic values are very close to other sets and the HSC-9 database in addition to NBS tables and CODATA values. Even though set-0 has also an equally small OF value, it uses one extra term for the \( C^\circ \) parameter. Moreover, analyzing the results revealed that the calculated activity of water with this set in some cases was exceeding 1. Including parameter \( \beta^{(0)} \) for the Ca\(^{2+}\)–SO\(_4^{2-}\) ion interaction in set-5 improves the assessment so slightly that one extra parameter cannot be justified. Set-6 has the smallest OF value with released Ca\(^{2+}\)–SO\(_4^{2-}\) ion interaction parameters, but the resulted enthalpy change (\( \Delta H^\circ \)) for gypsum is much lower than the one in the literature. Also, the entropy change (\( \Delta S^\circ \)) differs distinctly from other values obtained with other sets as well as literature values. As a conclusion, six calcium ion interaction Pitzer parameters with 12 terms are required for the assessment of the CaSO4–H2SO4–H2O system.

The optimized Pitzer parameters of set-1 obtained in this work are given in Table 4, together with the parameters of the binary systems used in this work.

The accessed temperature dependences of Gibbs energy change for solubility reactions for CaSO4(s), CaSO4⋅0.5H2O(s), and CaSO4⋅2H2O(s) are presented in Table 5. The experimental temperature ranges in the assessment were 273.15–378.15, 273.15–473.15, and 273.15–473.15 K for gypsum, anhydrite, and hemihydrate, respectively, with the H2SO4 concentrations covering the range of 0–5.0 mol/kg. The maximum differences in Gibbs energy change compared to model D in a previous work for gypsum, anhydrite, and hemihydrate are (temperature in parenthesis) −35 J/mol (331.15 K), 306 J/mol (473.15 K), and 184 J/mol (473.15 K), respectively. The average changes were 0.1, −0.2, and 0.1%, respectively.

The errors between experimental and calculated values of Gibbs energy changes for calcium sulfates in the assessment with optimized parameters are shown in Figure 1, in which the solid symbol means an adopted point, while the hollow means a point not used in the assessment of Pitzer parameters.

The adopted solubility data of gypsum in sulfuric acid solutions were from the data sets by Wang et al.,11 Farrah et al.,15 and Azimi and Papangelakis,14 most data were from Zdanovskii et al.16,17 and Marshall and Jones.18 Few individual points by Cameron and Breazeale19 at 298.15 and 316.15 K were also included in the assessment.
Most of the solubility data of anhydrite in sulfuric acid from Wang et al.11 and Zdanovskii et al.16 were included in the assessment. Also, individual data points by Marshall and Jones18 were included in the assessment despite the scattering points. Solubility data for anhydrite by Ling and Demopoulos13 and Farrah et al.15 were excluded completely.

All of the solubility data for the hemihydrate in sulfuric acid from Ling and Demopoulos13 and Marshall and Jones18 were accepted. Most of the data by Zdanovskii et al.17 were included except for 4.38228 mol H₂SO₄/kg at 323.15 K and five points at temperatures of 298.15, 323.15, 348.15, and 368.15 K, where the sulfuric acid concentration was over 5 mol H₂SO₄/kg.

4.2. Solubility of Calcium Sulfate in Water. A comparison of calculated solubilities of gypsum between set-1 and our previous model D7 is presented in Figure 2, with the experimental data from the literature.18,34 The difference with the models is that the HSO₄⁻ ion and the Pitzer parameters for Ca²⁺−HSO₄⁻ ion interactions are also included in the set-1 model. There is no significant change in the solubility of gypsum, but at lower temperatures, the metastable solubilities of anhydrite and hemihydrate are slightly increased due to the small change in thermodynamic values for solubility reactions, thus improving the accuracy. This also verifies that set-1 is capable of modeling the binary CaSO₄−H₂O.

4.3. Solubility in H₂SO₄ Solution. The solubilities of calcium sulfates in 0−5.0 mol/kg sulfuric acid solutions were calculated in the temperature ranges of 273.15−368.15, 273.15−473.15, and 273.15−398.15 K for gypsum, anhydrite, and hemihydrate, respectively, using the optimized parameters of this work. The solubility curves of each phase as a function of the H₂SO₄ concentration at different temperatures are shown in Figures 3−5, respectively, together with the compiled experimental data.

4.3.1. Gypsum. In Figure 3, the calculated solubility values for gypsum in sulfuric acid solutions are presented at different temperatures, compared with the experimental data. The temperature dependency of the solubility curve reproduces well most data points. Wang et al.11 carried out excellent experiments on the solubility of gypsum in sulfuric acid solutions at 298.15, 323.15, and 348.15 K. At 363.15 K, two data points of around H₂SO₄ molalities 1.5 and 4.0 mol/kg scatter. The same result can be observed in their own modeling, but the data points are around molalities 1.5 and 3.0 mol/kg. However, at this temperature, metastable gypsum is easily transformed to stable anhydrite in sulfuric acid solutions.

The gypsum solubility data points reported by Azimi and Papangelakis14 are very close to the calculated curves but slightly lower at higher temperatures. Farrah et al.15 presented data points very close to the calculated ones, even though only two solubility data points in solutions of different H₂SO₄ concentrations are reported at each temperature set. Only data at 353.15 K deviate from our prediction.

The metastable gypsum solubility study carried out by Marshall and Jones18 at low temperatures of 298.15−333.15 K gives remarkable data sets in sulfuric acid solutions. Their data are in excellent agreement with our model but scatter slightly in H₂SO₄ solutions above 1.0 mol/kg.

The gypsum solubility data in H₂SO₄ concentration solutions by Zdanovskii et al.16,17 agree with the others’ and the calculated data in this work, despite several slightly scattered points.
data sets by Cameron and Breazeale\textsuperscript{19} are very scattered and show larger values than other researchers’ data and the calculated values of this work.

4.3.2. Anhydrite. The calculated solubility curves of anhydrite in sulfuric acid solutions are shown in Figure 4 at different temperatures, together with all experimental data. The data sets by Wang et al.\textsuperscript{11} are in good agreement with the calculated points but scatter little around the calculated values. Farrah et al.\textsuperscript{15} gave the solubility data in \(\sim 0.38\) and \(\sim 0.79\) mol/kg H\(_2\)SO\(_4\) solutions at the temperature range of 363.15–378.15 K, which deviate from other studies and the calculated values of this work. Their data are constantly higher than predicted values.

The results obtained by Ling and Demopoulos\textsuperscript{13} for the solubility of anhydrite at 373.15 K are much higher than those in our model maybe due to the short time of 2 h used in their experiments. Furthermore, since their focus was on the solubility of gypsum and hemihydrate, they did not use anhydrite as a starting material in their dissolution experiment.

Marshall and Jones\textsuperscript{18} carried out a solubility study of anhydrite at temperatures over 398.15 K. In dilute solutions, our model agrees with their data, but at higher concentrations, our model predicts that the solubility of anhydrite will decrease as it does at lower temperatures, while according to their data, the solubility of anhydrite continues to increase. Marshall and Jones\textsuperscript{18} pointed out that the experimental solubility data at high temperatures and high pressures may lose accuracy due to the negligible density changes caused by the loss of H\(_2\)O and H\(_2\)SO\(_4\) to the vapor phase, and at times, the high-pressure vessels may have leaked. Moreover, the stirring time at temperatures of 150–200 K in sulfuric acid concentrations above 0.5 mol/kg was only 1.5 h, which could be too short a time to attain equilibrium.

Zdanovskii et al.\textsuperscript{16} investigated the solubility data of anhydrite at low temperatures in H\(_2\)SO\(_4\) solutions. The data at 308.15, 315.15, and 323.15 K are in agreement with our model, but the metastable solubility data at 283.15 and 298.15 K are below our predictions and the experimental data by Wang et al.\textsuperscript{11}

4.3.3. Hemihydrate. The assessed solubility of hemihydrate as a function of sulfuric acid concentration is demonstrated in Figure 5 at different temperatures, together with the experimental data. The solubility study carried out by Zdanovskii et al.\textsuperscript{17} in sulfuric acid solutions gives important data for hemihydrate solubility at temperatures of 298.15, 323.15, 348.15, and 368.15 K, even though the data show slight scatter. The data by Ling

| Table 7. Comparison of the Experimental Data for Solubility of Gypsum from the Literature\textsuperscript{56–59} and the Predicted Values of This Work in the CaSO\(_4\)–H\(_2\)SO\(_4\)–H\(_2\)O System |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
|                                | Schäfer and Hunger\textsuperscript{56} | Beremzhanov and Kruchenko\textsuperscript{57} | Zhang and Muhammed\textsuperscript{58} | Calmanovici et al.\textsuperscript{59} |
|                                | 298.15 K        | 298.15 K        | 298.15 K        | 293.15 K        |
|                                | 323.15 K        | 323.15 K        | 323.15 K        | 343.15 K        |
| MAPE                           | 4.1%            | 1.1%            | 2.0%            | 4.9%            |
|                                |                 | 7.4%            | 6.8%            | 3.6%            |
and Demopoulos also agree well at 373.15 K solutions with the assessed solubility curve. The solubility data at 398.15 K of Marshall and Jones also agree well with the predicted values of this work. Considering the metastable nature of hemihydrate, the modeling of this work is adequate for predicting the solubility of hemihydrate.

4.4. Phase Transformation. The transformation points of calcium sulfates in sulfuric acid solutions are important in predicting and controlling calcium sulfate formation in its solutions. When the concentration of sulfuric acid increases in the solution at a given temperature, the activity of water will decrease. So although gypsum is the most stable phase in pure water, addition of sulfuric acid with decreasing water activity will change the most stable phase to a less hydrated one. Thus, the transition temperature from gypsum to anhydrite or hemihydrate will decrease in ternary CaSO$_4$−H$_2$SO$_4$−H$_2$O with increasing sulfuric acid concentration.

Wang et al. reported that gypsum is generally stable in H$_2$SO$_4$ solutions at relatively low temperatures and low sulfuric acid concentrations. As temperature or concentration of sulfuric acid rises, the stable phase will change to insoluble anhydrite. In pure water, the transition temperature is 315 K and it will decrease as a function of increasing sulfuric acid concentration. In H$_2$SO$_4$ concentrations of 1.8, 3.2, and 4.6 mol/kg, the transition temperatures are 308, 298, and 283 K, respectively. Zdanovskii et al. gave those points in H$_2$SO$_4$ concentrations of 0.316, 1.261, 2.551, and 5.257 mol/kg at temperatures of 315.15, 308.15, 298.15, and 283.15 K, respectively.

Zdanovskii et al. also determined the transformation points of gypsum to hemihydrate locating in H$_2$SO$_4$ concentrations of 1.391, 3.968, 7.091, and 9.804 mol/kg at 368.15, 348.15, 323.15, and 363.15 K, respectively.

The curves of phase transformations calculated in this work using the obtained parameterization are shown in Figure 6. The results agree well with those of Wang et al. and Zdanovskii et al.. The above results confirm that gypsum is stable at low temperatures in solutions of low H$_2$SO$_4$ concentrations and transformed to anhydrite at high temperatures and in concentrated H$_2$SO$_4$ solutions, while hemihydrate is always a metastable phase. This is also in agreement with experimental X-ray predictions by Dutrizac. Furthermore, the transformation temperatures of gypsum to anhydrite and hemihydrate will decrease on increasing the H$_2$SO$_4$ concentration.

4.5. Comparison with Previous Works. As mentioned previously, the solubility data of gypsum measured by Dutrizac were used to compare with the parameterization of this work. The experimental data of Dutrizac were calculated from the quadratic equations of volumetric concentration and solution density as a function of temperature in his study. Dutrizac had obviously some difficulties in transforming his data to quadratic equations since he used two sets of parameters in three sulfuric acid concentrations of 0.025, 0.8 and 1.0 mol/L.

The calculated mean absolute percentage errors (MAPEs) for our model at temperatures of 298.15, 323.15, 348.15, and 363.15 K in comparison to the experimental solubility of gypsum by Dutrizac are collected in Table 6. Wang et al. also compared their model against this data, but they did not compare the entire data set of Dutrizac; thus, MAPE was not calculated for their model. The deviation plots for the data of Dutrizac at temperatures of 298.15, 323.15, 348.15, and 363.15 K are shown in Figure 7. Wang et al. data are included in the figures, too.

As can be seen from Table 6, the MAPE increases with increasing temperature and metastability of gypsum.

After the assessment was made, we became aware of additional solubility data of gypsum, which was not included in the assessment, so we used them for comparison. The deviation plots are shown in Figure 8, with the calculated MAPE being presented in Table 7. As can be seen in Figure 8, the predicted solubilities differ from −3 to 1.5 mmol/L from the experimental values.

5. SUMMARY AND CONCLUSIONS

The aim of this study is to give an accurate thermodynamic description for the CaSO$_4$−H$_2$SO$_4$−H$_2$O system for a better understanding of its detailed thermodynamic properties of solution chemistry to prevent scaling and to recycle aqueous solutions in industrial processes. The experimental solubility data of calcium sulfates in sulfuric acid solutions previously published in the literature were reviewed and selected critically for parameter optimization.

The Pitzer activity coefficient approach was adopted to model the CaSO$_4$−H$_2$SO$_4$−H$_2$O system by assessing the adopted experimental data with MTDATA software. Gypsum was found to be stable at low temperatures, while hemihydrate is always a metastable phase. This is also in agreement with experimental X-ray predictions by Dutrizac. Furthermore, the transformation temperatures of gypsum to anhydrite and hemihydrate will decrease on increasing the H$_2$SO$_4$ concentration.

Figure 9. Refitted solubility of anhydrite at 423.15 K based on the data of Marshall and Jones only. The predicted solubility by the original model is also included.

Table 8. Ratio of the Second Dissociation Constant (K$_{2,MJ}$) of Sulfuric Acid by Marshall and Jones Compared to the Literature Values (K$_{2,Lit}$) at Various Temperatures

| (K$_{2,MJ}$/K$_{2,Lit}$) | 298.15 K | 313.15 K | 323.15 K | 333.15 K |
|-------------------------|---------|---------|---------|---------|
| Matsushima and Okuwaki  | 1.0     | 1.2     | 1.2     | 1.4     |
| Dickson et al.          | 0.9     | 1.1     | 1.1     | 1.3     |
| Christov and Meller     | 0.9     | 1.1     | 1.1     | 1.3     |
| Lietzke et al.          | 1.0     | 1.1     | 1.1     | 1.2     |
| Knopf et al.            | 1.0     | 1.0     | 1.0     | 1.0     |
| Hovey and Hepler        | 1.0     | 1.1     | 1.2     | 1.4     |
| Sippola and Taskinen    | 0.9     | 1.1     | 1.1     | 1.3     |

| (K$_{2,MJ}$/K$_{2,Lit}$) | 398.15 K | 423.15 K | 448.15 K | 473.15 K |
|-------------------------|---------|---------|---------|---------|
| Matsushima and Okuwaki  | 2.1     | 1.8     | 1.9     | 2.1     |
| Dickson et al.          | 2.1     | 1.8     | 1.9     | 2.1     |
| Christov and Meller     | 2.1     | 1.8     | 1.9     | 2.1     |
| Lietzke et al.          | 1.7     | 1.5     | 1.6     | 1.8     |
| Knopf et al.            | 1.4     | 1.2     | 1.3     | 1.5     |
| Hovey and Hepler        | 2.7     | 2.5     | 2.9     | 3.4     |
| Sippola and Taskinen    | 3.0     | 2.9     | 3.6     | 4.4     |
to be stable at low temperatures in low H₂SO₄ concentrations and transformed to anhydrite at high temperatures and in more concentrated H₂SO₄ solutions, while hemihydrate is always a metastable phase. The transformation temperatures of gypsum to anhydrite and hemihydrate will decrease with increasing H₂SO₄ concentration.

The parameters were fitted to obtain an accurate Pitzer model for the solubility of calcium sulfates in 0−5.0 mol/kg H₂SO₄ solutions from 273.15 to 473.15 K. The obtained model is in good agreement with most experimental data in sulfuric acid concentrations up to 5.0 mol/kg, at temperatures of 283.15−368.15, 283.15−473.15, and 298.15−473.15 K for gypsum (CaSO₄·2H₂O), anhydrite (CaSO₄), and hemihydrate (CaSO₄·0.5H₂O), respectively.

At higher temperatures, our predicted solubility deviates significantly from the solubility data of Marshall and Jones. At 398.15 K, our model is in agreement with their solubility data for anhydrite (Figure 4k) and hemihydrate (Figure 5f). However, in sulfuric acid concentrations above 0.5 mol/kg, the solubility of anhydrite predicted by our model deviates significantly from the solubility data of Marshall and Jones at temperatures of 423.15, 448.15, and 473.15 K. Our model predicts that the solubility of anhydrite would first increase and then decrease in more concentrated sulfuric acid solutions as it does at lower temperatures. This behavior is confirmed with experimental data at higher concentrations of sulfuric acid where the measured solubility is less than the solubility of anhydrite in dilute sulfuric acid. For example, when studying the solubility of anhydrite in 50−97 wt % sulfuric acid, Dveugubski and Shchiponikova discovered that the measured solubilities of anhydrite at temperatures of 393.15 and 413.15 K in 60 wt % (15 mol/kg) sulfuric acid are 0.03 and 0.06 g/100 g solution (0.006 and 0.011 mol/kg), respectively. However, the experimental data by Marshall and Jones does show this phenomenon. Their measured solubility increased in the whole concentration range up to around 1 m sulfuric acid at the measured temperature range of 398.15−623.15 K.

We modeled the solubility data by Marshall and Jones alone in the temperature range of 393.15−473.15 K releasing all of the binary Pitzer parameters (β⁰, β¹, β², and C⁰) for Ca²⁺−SO₄²⁻ and Ca²⁺−HSO₄⁻ interactions as well as the Gibbs energy change for the solubility reaction. Only the thermodynamic description of sulfuric acid was retained. We were able to get a better fit for the experimental data, but the solubility of CaSO₄ drops to zero around 2 m sulfuric acid solution in every case (Figure 9).

We found three possible explanations for this discrepancy.

(a) Our Pitzer model for sulfuric acid is incorrect.

(b) An associate CaSO₄(aq) should be included in the Pitzer model.

(c) The precipitated substance is not insoluble anhydrite but something else, for example, soluble anhydrite, or the precipitated substance is insoluble anhydrite, but the measured solubility is incorrect.

At 473.21 K, our model for the sulfuric acid−water system can predict the measured osmotic coefficient, which was not included in the assessment of the model, quite well. The predicted values are 0.009 higher on average, and the mean absolute average error (MAPE) is 1.45%. It is also one of the few Pitzer models that can predict at 298.15 K the standard state potentials of electrochemical cells generally used in the assessment of sulfuric acid within experimental accuracy.

Marshall and Jones used their solubility data to predict the second dissociation constant (K₂) for sulfuric acid. At lower temperatures, their value for K₂ agrees well with the literature data, but at higher temperatures, their value for K₂ is about double compared to the literature data (Table 8). Møller and later Greenberg and Møller modeled the system Na−K−Ca−Cl−SO₄−H₂O system to high temperatures and concentrations. They used β(2) in the temperature range 298.15−348.15 K to improve the fit to the pure gypsum−water data. The CaSO₄(aq) complex was also included with two temperature ranges: from 273.15 to 423.15 K and from 424.15 to 523.15 K. Still, they had severe problems in fitting the higher order systems including CaSO₄ with consistent thermodynamic data. They also found that reasonable values of the θ parameter have little effect on solubilities of gypsum and anhydrite in potassium sulfate solutions.

Our conclusion is that more solubility measurements of anhydrite above 393 K in aqueous sulfuric acid are needed to ensure the solubility of calcium sulfate in aqueous sulfuric acid at higher temperatures.

According to our model at lower temperatures, the solubility of gypsum will first decrease in dilute sulfuric acid concentrations. At 298.15 K, this phenomenon disappears, as can be seen in Figure 10.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.9b00829.

Pitzer equation (PDF)

Calculated solubilities of gypsum, anhydrite, and hemihydrate as a function of sulfuric acid up 5 m solution (XLSX)

#### AUTHOR INFORMATION

**Corresponding Author**

Hanna Sippola — Clean Technologies Research Group, School of Chemical Engineering, Aalto University, Espoo 02150, Finland; FCG Design and Engineering, FI-00601 Helsinki, Finland; orcid.org/0000-0001-8137-4677; Email: hanna.sippola@aalto.fi

**Authors**

Leiting Shen — Metallurgical Thermodynamics and Modeling Research Group, School of Chemical Engineering, Aalto University, Espoo 02150, Finland; School of Metallurgy and Environment, Central South University, Changsha 410083, China; orcid.org/0000-0001-5994-600X
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