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**Thermodynamic Modeling of Calcium Sulfate Hydrates in a CaSO₄-H₂SO₄-H₂O System from 273.15 to 473.15 K up to 5 m Sulfuric Acid**

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ABSTRACT: To prevent scaling and to recycle aqueous solutions in industrial processes, the thermodynamic properties of the CaSO₄−H₂SO₄−H₂O 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 CaSO₄−H₂SO₄−H₂O 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 (CaSO₄·2H₂O), anhydrite (CaSO₄), and hemihydrate (CaSO₄·0.5H₂O), 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 H₂SO₄ concentration, the transformation temperatures of gypsum to anhydrite and hemihydrate will decrease. Thus, gypsum is stable at low temperatures in solutions of low H₂SO₄ concentrations and transforms to anhydrite at high temperatures and in concentrated H₂SO₄ 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. 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. 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 CaSO₄−H₂SO₄−H₂O 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, CaSO₄·0.5H₂O) and dihydrate or gypsum (DH, CaSO₄·2H₂O), in addition to anhydrite (AH, CaSO₄). 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. The solubilities of calcium sulfates in water and electrolyte salt systems have been extensively studied experimentally and theoretically over recent decades ever since the mid-19th century. Several experimental data sets are also focused on the solubilities of calcium sulfates in H₂SO₄ solutions. The aim of this study was to compile and reassess the experimental data of calcium sulfate in sulfuric acid solutions and model the CaSO₄−H₂SO₄−H₂O system up to 473.15 K. The assessment procedure was similar to that in our recent article concerning modeling the CaSO₄−H₂O system. The difference from the earlier assessment for the FeSO₄−H₂SO₄−H₂O and NiSO₄−H₂SO₄−H₂O⁹ systems is the model used for the H₂SO₄−H₂O 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
includes the Pitzer activity coefficient model for the excess Gibbs energy of aqueous solutions. The CALPHAD method was used in the modeling to ensure internal consistency of the thermodynamic database. Furthermore, the modeling results were compared in detail with the previous studies to ensure the accuracy of this model and the completed critical analysis.

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 H$_2$SO$_4$ solutions have attracted many researchers, while that of hemihydrate has gained limited attention due to its metastable nature compared to gypsum and anhydrite.

Wang et al. determined the solubilities of gypsum and insoluble anhydrite in the CaSO$_4$–H$_2$SO$_4$–H$_2$O system at temperatures of 298.15 K, 323.15, 348.15, and 363.15 K in the H$_2$SO$_4$ concentration range of 0–4.6531 molality. Furthermore, Wang et al. studied the kinetics of transformation between gypsum and anhydrite in H$_2$SO$_4$ solutions at 298.15 and 363.15 K. They applied the Pitzer model to the stability regions of calcium with H$_2$SO$_4$ concentrations below 0.41 mol/kg, hemihydrate only in H$_2$SO$_4$ concentrations of 0.51–1.93 mol/kg H$_2$O, and anhydrite with H$_2$SO$_4$ concentrations above 2.64 mol/kg H$_2$O. If hemihydrate was used as the starting material, it was the only primary solid equilibrium phase with H$_2$SO$_4$ concentrations up to 1.93 mol/kg and anhydrite above 2.64 mol/kg H$_2$O.

Azimi et al. measured the solubility of gypsum in 0.5 molality H$_2$SO$_4$ solutions at temperatures of 298.15, 318.15, 343.15, and 363.15 K when researching the solubility of gypsum in the MgSO$_4$–H$_2$SO$_4$–H$_2$O system. Farrah et al. conducted experiments in 36 and 72 g of H$_2$SO$_4$/kg solution to determine the solubilities of gypsum and anhydrite at temperatures from 303.15 to 378.15 K in the MnSO$_4$–H$_2$SO$_4$–H$_2$O system. Zdanovskii et al. measured the solubilities of gypsum from 328.15 to 368.15 K, anhydrite from 323.15 to 334.15 K, and hemihydrate from 298.15 to 368.15 K in 0–40 mass % H$_2$SO$_4$ solutions when studying the dehydration of gypsum. Marshall and Jones determined the solubilities of gypsum from 298.15 to 333.15 K, hemihydrate from 398.15 to 368.15 K, and anhydrite from 398.15 to 623.15 K in 0–4.7 mol/L solutions when assessing the second dissociation constant for sulfuric acid. Cameron and Breazeale measured the solubilities of gypsum in 0–292.92 g/L H$_2$SO$_4$ solutions at 298.15, 308.15, and 316.15 K when studying the ZnSO$_4$–H$_2$SO$_4$–H$_2$O system. Dutrizac 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 H$_2$SO$_4$ solutions and the second one from 293.15 to 353.15 K in 0.8–1.8 mol/L H$_2$SO$_4$ 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 H$_2$SO$_4$ solution. In the second series, a hysteresis behavior was found. When heating gypsum with increasing sulfuric acid concentrations, it remained the only solid phase up to 2.37 mol/L H$_2$SO$_4$ at 313.15 K and above 3.1 mol/L H$_2$SO$_4$ solution.
temperature at different H2SO4 concentrations. The solubility data by Dutrizac used in this work were calculated from the smoothed equations and were not included in the assessment of this work but used in comparison, due to the absence of the original experimental data.

Huang and Luo20 presented the solubility of calcium sulfate in concentrated sulfuric acid (\(-96\) mass % H2SO4) from 283.15 to 473.15 K. Dvegubskii and Shchiponikova21 measured the solubilities and phase transformation of calcium sulfate in concentrated sulfuric acid in the temperature range of 393.15–453.15 K. Tsikaeva22 studied the solubilities of anhydrite in 65–95 mass % sulfuric acid at temperatures of 313.15, 353.15, and 373.15 K. Ostrovskii et al.23 carried out solubility experiments of calcium sulfate in 94, 98, and 100 mass % sulfuric acid solutions from 313.15 to 353.15 K. All of these solubility data are in concentrated sulfuric acid and were not considered in this work.

All of the solubility data for gypsum, anhydrite, and hemihydrate in aqueous sulfuric acid solutions were collected and are classified in Table 1. The unit of all data was converted to molality (mol/[kg H2O]) for the solubilities of calcium sulfates and sulfuric acid concentrations. The values of 136.14, 98.078, and 18.015 g/mol were adopted for the molar masses of CaSO4, H2SO4, and H2O in the data conversion to obtain the accurate data.

Solubility data for the CaSO4–H2O system listed in our previous article7 was also included in the assessment, unchanged. The criteria used to include or exclude data points have been explained later in this article in Section 4.1.

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.24–26 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 Weare27 and Harvie et al.28 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 works29–31 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

\[
\Delta G^\circ(T) = -RT \ln(K_{\text{eq}}) = A_C + B_C(\frac{T}{K}) + C_C(\frac{T^2}{K^2}) + D_C(\frac{T^3}{K^3}) + E_C(\frac{T^4}{K^4}) + F_C(\frac{T^5}{K^5})
\]

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

\[
p = A_{\text{Pitz}} + B_{\text{Pitz}}(\frac{T}{K}) + C_{\text{Pitz}}(\frac{T^2}{K^2}) + D_{\text{Pitz}}(\frac{T^3}{K^3}) + E_{\text{Pitz}}(\frac{T^4}{K^4}) + F_{\text{Pitz}}(\frac{T^5}{K^5})^{-1}
\]

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.28 modification and the mole-fraction-based NPL Pitzer model.32 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

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

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

\[
\text{MAPE} = 100 \left( \frac{1}{N} \sum_{i=1}^{N} \left| \frac{C_i - E_i}{E_i} \right| \right)
\]

---

Table 2. Summary of the Optimization of Pitzer Parameters for the CaSO4–H2SO4–H2O System

<table>
<thead>
<tr>
<th>model</th>
<th>OF</th>
<th>(\beta^{(0)})</th>
<th>(\beta^{(1)})</th>
<th>(\beta^{(2)})</th>
<th>(\beta^{(0)})</th>
<th>(\beta^{(1)})</th>
<th>(C^0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>set-0</td>
<td>0.23</td>
<td>a b T f T</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
</tr>
<tr>
<td>set-1</td>
<td>0.23</td>
<td>D D D D</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
</tr>
<tr>
<td>set-2</td>
<td>0.71</td>
<td>D D D D</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
</tr>
<tr>
<td>set-3</td>
<td>0.30</td>
<td>D D D D</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
</tr>
<tr>
<td>set-4</td>
<td>0.39</td>
<td>D D D D</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
</tr>
<tr>
<td>set-5</td>
<td>0.22</td>
<td>x D D D</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
</tr>
<tr>
<td>set-6</td>
<td>0.16</td>
<td>x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
<td>x x x x x x x</td>
</tr>
</tbody>
</table>

\(^{a}\)The parameters of Gibbs energy changes for forming the solid phase use the A + B \times T + C \times T \ln T form. \(^{b}\)Values of parameters \(\beta^{(1)}\) and \(\beta^{(2)}\) for \(\text{Ca}^{2+}\text{SO}_4^{2-}\) ion interactions are from model D in a previous work and kept unchanged in the assessment.
Table 3. Summary of the Thermodynamic Values of Solubility Reactions at 298.15 K

<table>
<thead>
<tr>
<th>model</th>
<th>gypsum</th>
<th>anhydrite</th>
<th>hemihydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Delta G^\circ)</td>
<td>(\Delta S^\circ)</td>
<td>(\Delta C_p^\circ)</td>
</tr>
<tr>
<td>model D</td>
<td>26 372</td>
<td>−95</td>
<td>−1814</td>
</tr>
<tr>
<td>set-0</td>
<td>26 392</td>
<td>−95</td>
<td>−2063</td>
</tr>
<tr>
<td>set-1</td>
<td>26 394</td>
<td>−95</td>
<td>−2007</td>
</tr>
<tr>
<td>set-2</td>
<td>26 353</td>
<td>−94</td>
<td>−1685</td>
</tr>
<tr>
<td>set-3</td>
<td>26 428</td>
<td>−96</td>
<td>−1968</td>
</tr>
<tr>
<td>set-4</td>
<td>26 416</td>
<td>−94</td>
<td>−1741</td>
</tr>
<tr>
<td>set-5</td>
<td>26 360</td>
<td>−96</td>
<td>−2224</td>
</tr>
<tr>
<td>set-6</td>
<td>26 797</td>
<td>−114</td>
<td>−7080</td>
</tr>
<tr>
<td>HSC558</td>
<td>26 518</td>
<td>−92</td>
<td>−1716</td>
</tr>
<tr>
<td>set-1, this work</td>
<td>26 893</td>
<td>−87</td>
<td>−1130</td>
</tr>
<tr>
<td>CODATA55</td>
<td>26 140</td>
<td>−91</td>
<td>−1130</td>
</tr>
</tbody>
</table>

\(\Delta G^\circ\) and \(\Delta H^\circ\), J/mol; \(\Delta S^\circ\) and \(\Delta C_p^\circ\), J/(mol·K). Clearly deviating values are indicated in bold.

Table 4. Parameters of the Pitzer Model for the CaSO₄−H₂SO₄−H₂O System

<table>
<thead>
<tr>
<th>ion interactions</th>
<th>parameters</th>
<th>(A_{Piz})</th>
<th>(B_{Piz})</th>
<th>(C_{Piz})</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca^{2+}−SO₄²⁻</td>
<td>(\beta^{(1)})</td>
<td>−3.20249</td>
<td>0</td>
<td>−0.27033</td>
<td>1149.4</td>
</tr>
<tr>
<td></td>
<td>(\beta^{(2)})</td>
<td>32.0227</td>
<td>0.096100</td>
<td>0.002074</td>
<td>23.105</td>
</tr>
<tr>
<td>Ca^{2+}−HSO₄⁻</td>
<td>(\beta^{(3)})</td>
<td>1.20201</td>
<td>−0.000420</td>
<td>226.9</td>
<td>31.070</td>
</tr>
<tr>
<td></td>
<td>(\beta^{(1)})</td>
<td>0.7515156</td>
<td>8930</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H⁺−SO₄²⁻</td>
<td>(\beta^{(4)})</td>
<td>0.137684</td>
<td>0</td>
<td>12.04250</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>(\beta^{(5)})</td>
<td>0.24106</td>
<td>0.333982</td>
<td>22.0454</td>
<td>0</td>
</tr>
</tbody>
</table>

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 3. continued
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 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
describe the H$_2$SO$_4$–H$_2$O system equally well in the temperature range of 273.15–323.15 K. Finally, Sippola and Taskinen$^{31}$ reassessed the H$_2$SO$_4$–H$_2$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 CaSO$_4$–H$_2$SO$_4$–H$_2$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 CaSO$_4$–H$_2$SO$_4$–H$_2$O system. No change in the weights for the solubility in the CaSO$_4$–H$_2$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 CaSO$_4$–H$_2$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 $\Delta G^o(T) + RT \ln(K_{sp}) = 0$. Thus, we obtain

$$C_i = \Delta G^o(T)$$ (5)
the CaSO₄ and water in an aqueous solution. The solubility product calculated from the activities of calcium and sulfate ions is much lower than the one in the literature. Also, the entropy change (ΔS°) 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 273.15–368.15, 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 Breazeale at 298.15 and 316.15 K were also included in the assessment.

### Table 6. Comparison of the Experimental Data for Solubility of Gypsum from Dutrizac and the Predicted Values of This Work in the CaSO₄–H₂SO₄–H₂O System

<table>
<thead>
<tr>
<th>H₂SO₄</th>
<th>298.15 K</th>
<th>323.15 K</th>
<th>348.15 K</th>
<th>363.15 K</th>
<th>all</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPE</td>
<td>0–1.8 mol/L</td>
<td>1.8%</td>
<td>1.9%</td>
<td>3.6%</td>
<td>4.7%</td>
</tr>
</tbody>
</table>

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

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

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

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

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 Δ\( G^\circ \) 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. Only the first three parameters \( A_i – C_i \) were found adequate to describe Δ\( G^\circ \)(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 Ca⁴⁺–HSO₄⁻ ion interaction, \( \beta^1 \), \( \beta^2 \), and \( C_i \), were included in all sets, but the temperature dependency used varied from one set to another. In most sets, the values of parameters \( \beta^1 \) and \( \beta^2 \) for the Ca⁴⁺–SO₄⁻ ion interaction were from model D in the previous work and were kept unchanged in the assessment. The parameter \( \beta^0 \) for the Ca⁴⁺–SO₄⁻ 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 \( C_i \) 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 Ca⁴⁺–SO₄⁻ 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 Ca⁴⁺–SO₄⁻ ion interaction parameters, but the resulted enthalpy change (Δ\( H^\circ \)) for gypsum is much lower than the one in the literature. Also, the entropy change (Δ\( S^\circ \)) 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 273.15–368.15, 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 Breazeale 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.\textsuperscript{11} and Zdanovskii et al.\textsuperscript{16} were included in the assessment. Also, individual data points by Marshall and Jones\textsuperscript{18} were included in the assessment despite the scattering points. Solubility data for anhydrite by Ling and Demopoulos\textsuperscript{13} and Farrah et al.\textsuperscript{15} were excluded completely.

All of the solubility data for the hemihydrate in sulfuric acid from Ling and Demopoulos\textsuperscript{13} and Marshall and Jones\textsuperscript{18} were accepted. Most of the data by Zdanovskii et al.\textsuperscript{17} were included except for 4.38228 mol H\textsubscript{2}SO\textsubscript{4}/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 H\textsubscript{2}SO\textsubscript{4}/kg.

4.2. Solubility of Calcium Sulfate in Water. A comparison of calculated solubilities of gypsum between set-1 and our previous model D\textsuperscript{7} is presented in Figure 2, with the experimental data from the literature.\textsuperscript{18,34} The difference with the models is that the HSO\textsubscript{4}\textsuperscript{−} ion and the Pitzer parameters for Ca\textsuperscript{2+}–HSO\textsubscript{4}\textsuperscript{−} 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 CaSO\textsubscript{4}–H\textsubscript{2}O.

4.3. Solubility in H\textsubscript{2}SO\textsubscript{4} 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 H\textsubscript{2}SO\textsubscript{4} 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.\textsuperscript{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 four around H\textsubscript{2}SO\textsubscript{4} 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 Papangelakis\textsuperscript{14} are very close to the calculated curves but slightly lower at higher temperatures. Farrah et al.\textsuperscript{15} presented data points very close to the calculated ones, even though only two solubility data points in solutions of different H\textsubscript{2}SO\textsubscript{4} concentrations are reported at each temperature set. Only data at 353.15 K deviate from our prediction.

The gypsum solubility data points reported by Marshall and Jones\textsuperscript{18} 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 H\textsubscript{2}SO\textsubscript{4} solutions above 1.0 mol/kg.

The gypsum solubility data in H\textsubscript{2}SO\textsubscript{4} concentration solutions by Zdanovskii et al.\textsuperscript{16,17} agree with the others’ and the calculated data in this work, despite several slightly scattered points. The
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

\begin{table}[h]
\centering
\caption{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}
\begin{tabular}{|c|c|c|c|c|}
\hline
 & Schafer and Hunger\textsuperscript{56} & Beremzhanov and Kruchenko\textsuperscript{57} & Zhang and Muhammed\textsuperscript{58} & Calmanovici et al.\textsuperscript{59} \\
\hline
& 298.15 K & 298.15 K & 323.15 K & 298.15 K & 293.15 K & 323.15 K & 343.15 K \\
\hline
MAPE & 4.1% & 1.1% & 2.0% & 4.9% & 7.4% & 6.8% & 3.6% \\
\hline
\end{tabular}
\end{table}
and Demopoulos\textsuperscript{13} agree well at 373.15 K solutions with the assessed solubility curve. The solubility data at 398.15 K of Marshall and Jones\textsuperscript{18} 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.\textsuperscript{11} 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.\textsuperscript{16} gave those points in H$_2$SO$_4$ concentrations of 0.316, 1.261, 2.554, and 5.257 mol/kg at temperatures of 315.15, 308.15, 298.15, and 283.15 K, respectively.

Zdanovskii et al.\textsuperscript{16} 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 298.15 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.\textsuperscript{11} and Zdanovskii et al.\textsuperscript{16,17} 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.\textsuperscript{5} 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\textsuperscript{5} 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\textsuperscript{5} are collected in Table 6. Wang et al.\textsuperscript{41} 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\textsuperscript{5} at temperatures of 298.15, 323.15, 348.15, and 363.15 K are shown in Figure 7. Wang et al.\textsuperscript{41} 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,\textsuperscript{66–59} 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 parameterization of this work. The deviation plots for the data of Dutrizac\textsuperscript{5} at 423.15 K based on the data of Marshall and Jones\textsuperscript{18} 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\textsuperscript{17} Compared to the Literature Values ($K_{2,lit}$) at Various Temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_{2,MJ}$</th>
<th>$K_{2,lit}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15 K</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>313.15 K</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>323.15 K</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>333.15 K</td>
<td>1.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Figure 9. Reﬁtted solubility of anhydrite at 423.15 K based on the data of Marshall and Jones\textsuperscript{18} only. The predicted solubility by the original model is also included.
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 the temperature range of 393.15–283.15 K, our model is in agreement with their solubility data for anhydrite above 393 K in aqueous sulfuric acid are needed to predict the measured osmotic coefficient, which was not included 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 experimental data, but at higher temperatures, their value for K₂ is about double compared to the literature data (Table 8). Möller and later Greenberg and Möller modeled the system Na−K−Ca−Cl−SO₄−H₂O system to high temperatures and concentrations. They used β₁ 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)

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Figure 10. Predicted solubility of gypsum by our model in dilute sulfuric acid in the temperature range of 273.15−298.15 K.
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Notes

The authors declare no competing financial interest.

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