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Thermodynamic Modeling of Calcium Sulfate Hydrates in the CaSO$_4$–H$_2$O System from 273.15 to 473.15 K with Extension to 548.15 K

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ABSTRACT: Calcium sulfate is one of the most common inorganic salts with a high scaling potential. The solubility of calcium sulfate was modeled with the Pitzer equation at a temperature range from 273.15 to 473.15 K from published solubility data, which was critically evaluated. Only two Pitzer parameters, $\beta^{(1)}$ and $\beta^{(3)}$, with simple temperature dependency are required to model the solubility with excellent extrapolating capabilities up to 548.15 K. The stable temperature range for gypsum is 273.15–315.95 K, whereas above 315.95 K the stable phase is anhydrite. Hemihydrate is in the metastable phase in the whole temperature range, and the obtained metastable invariant temperature from gypsum to hemihydrate is 374.55 K. The obtained enthalpy and entropy changes at 298.15 K for the solubility reactions are in good agreement with literature values yielding solubility products of 2.40 $\times$ 10$^{-8}$, 3.22 $\times$ 10$^{-8}$, and 8.75 $\times$ 10$^{-8}$ for gypsum, anhydrite, and hemihydrate, respectively. The obtained Pitzer model for the CaSO$_4$–H$_2$O system is capable of predicting the independent activity and osmotic coefficient data with experimental accuracy. The mean absolute average error of activity coefficient data at 298.15 K is less than 2.2%. Our model predicts the osmotic coefficient on the ice curve within 1.5% maximum error.

1. INTRODUCTION

Scaling or precipitation fouling, mainly forming a solid layer on equipment surfaces or piping networks, is a persistent problem encountered in many industrial processes, causing production losses, standstills, downtime and process efficiency decrease due to the reduction of equipment volume and material flow, increased heat transfer resistance, corrosion, and wearing out of construction materials.¹ Hence, scaling prevention and techniques for evaluating scaling tendencies are of considerable practical and theoretical importance in science and the engineering field.

Calcium sulfate is one of the most common inorganic salts with a high scaling potential in oil and gas production, water desalination, geothermal energy production, sulfur dioxide removal from flue gas by coal-fired power plants,²,³ and hydrometallurgical processes of zinc, nickel, copper, and tungsten.⁴–⁸ The demand for utilization of membrane technology is increasing and thus creating requirement for a better understanding of the solubility behavior of calcium sulfate. Moreover, the demand for process water circulation in hydrometallurgical processes will build up more and more complex and concentrated aqueous solutions, increasing the possibility of scaling. Thus, the need of thermodynamic understanding of a multicomponent aqueous solution is required, since laboratory analyses only, are not enough to comprehend the scaling potential and its variations with temperature and concentration.

In aqueous solutions, calcium sulfate forms stable hydrates with 0, 1/2, and 2 molecules of crystalline water, with the chemical names of anhydrite (AH: CaSO$_4$), hemihydrate (HH: CaSO$_4$·0.5H$_2$O), and dihydrate, i.e., gypsum (DH: CaSO$_4$·2H$_2$O). The stability regions of CaSO$_4$ hydrates depend on solution conditions, and they are influenced by temperature and composition of the aqueous solution. Therefore, understanding the phase equilibria of CaSO$_4$ as a function of temperature and other electrolytes is of great theoretical significance and practical importance, making it possible to estimate its scaling potential and facilitate the synthesis of calcium sulfate materials in industrial processes.

Applying the CALPHAD methodology,⁷ the thermodynamic description of the binary CaSO$_4$–H$_2$O system is fundamental to clarify the thermodynamic behavior of calcium sulfate and its hydrates in aqueous solutions.
The aim of this study was to compile and reassess critically the experimental data of calcium sulfate and model the thermodynamic behavior of the CaSO$_4$-H$_2$O system up to 473.15 K. The assessment procedure was similar as used earlier for FeSO$_4$-H$_2$O, MnSO$_4$-H$_2$O, and NiSO$_4$-H$_2$O systems. All experimental data used in the modeling were taken from the literature and reviewed critically. The resulting thermodynamic model was obtained using the thermodynamic equilibrium calculation program MTDATA, which uses Gibbs energy minimization routine and includes the Pitzer activity coefficient model for aqeous solutions. The CALPHAD method was used in modeling to ensure internal consistency of the thermodynamic data. Furthermore, the modeling results were compared with the experimental data and other similar models to validate the accuracy of the present model and critical analysis in detail.

2. THERMODYNAMIC DATA

A large number of solubility measurements have been carried out for gypsum, hemihydrate, and anhydrite since the middle of 19th century. Most of the solubility data are in agreement with each other, in spite of slight deviations. However, a large controversy exists on transition temperatures between various calcium sulfate hydrates in the CaSO$_4$-H$_2$O system. The main reason for this problem is kinetic hindrance during phase change. Anhydrite does not crystallize with a measurable rate from water below 343.15 K, even in the presence of anhydrite seeds, and does not hydrate in several months to gypsum without gypsum seeds present. Freyer and Voigt reviewed the solubility of gypsum, hemihydrate, and anhydrite in the temperature range (273.15–473.15) K at saturation pressure and pointed out that at low temperatures the stable phase is gypsum, at high temperatures it is anhydrite, whereas hemihydrate remains metastable at all temperatures. The borderslines of the solubility data points yield a transition temperature between gypsum–anhydrite from about 298.15 to 325.15 K. Within the scatter of the solubility data, the possible transition temperature of gypsum–hemihydrate phase change covers a range from less than 353.15 K to nearly 383.15 K.

On the basis of the review of Freyer and Voigt, Present drew the solubility curves for gypsum, hemihydrate, and anhydrite at saturation pressure up to 253.15 K and concluded that in pure water, the gypsum–anhydrite phase transition occurs between 298.15 and 325.15 K on the basis of solubility measurements of the phases, and the gypsum–hemihydrate transition occurs between 352.15 and 382.15 K.

Recently, Krumgalz summarized the solubility of calcium sulfate in the temperature range between 273.15 and 681.15 K covered by 110 publications starting from 1843. He determined that the transition temperatures of gypsum–anhydrite, gypsum–hemihydrate, and hemihydrate–anhydrite transition occurs between 352.15 and 382.15 K.
are 318.76, 373.85, and 471.55 K, respectively, according to the polynomial equation curves. He used a six-order polynomial for the solubility of anhydrite and four-order polynomials for hemihydrate and gypsum. He also gave several reasons for the relatively large scatter of the solubility data of calcium sulfate determined by different authors.

In this work, all experimental data were taken from the available literature. The data with less than three experimental data points in one paper or series were not considered in the modeling to obtain reasonable and reliable fitting results depending on temperature. Especially, the experimental data for anhydrite and hemihydrate under metastable conditions were critically analyzed, such as the data from 273.15 to 383.15 K for noncrystalline hemihydrate by D’Ans et al. as well as data for more soluble polymeric forms such as β-anhydrite in the temperature range (278.15−383.15) K by Sborgi and Bianchi and also β-anhydrite and β-hemihydrate in the temperature range (308.15−383.15) K by Power and Fabuss. All of these metastable data were excluded. The solubility of gypsum measured by Farrah et al. is regularly lower than reasons for the relatively large scatter of the solubility data of calcium sulfate in water is collected in Table 1. The values of 136.14 and 18.015 g/mol were adopted for the molar mass of CaSO₄ and H₂O, respectively, in the data conversion to obtain accurate data. The considered solubility data of calcium sulfate in water is collected in Table 1. The temperature ranges of gypsum, anhydrite, and hemihydrate in the table are (273.15−388.15), (273.15−681.15), and (273.15−473.15) K, respectively. All data above 473.15 K were reserved for testing the extrapolation capabilities. The criteria used to exclude or include a data point in the assessment are discussed in Section 4.1 in detail.

3. COMPUTATIONAL METHODS

3.1. Pitzer Interaction Model. The Pitzer model, one of the most widely used activity coefficient models, has been extensively used for modeling thermodynamic properties of aqueous electrolyte systems. Pitzer and his cooperators gave details of the model in the literature. It was developed by combining the expression of 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 the modified Pitzer model to improve the fit in multicomponent systems.

The mathematical expression and internal parameters of the model are clarified in eqs 1−6. Equation 1 reproduces the Debye–Hückel type contribution of the dilute solution domain. Equation 2 describes the stoichiometric mean activity coefficient (γᵢ), eq 3 formulates the osmotic coefficient (ϕ), eqs 4 and 5 give the concentration dependence of the electrolyte specific terms Bᵦ and B, and eq 6 further explains the function g(x) for eq 5.

\[
\ln \gamma_i = z_i M_i z_i f' + 2m \bigg( \frac{V_{M_i} N_i}{\nu} \bigg) B^ϕ_\nu + B_{MX}
\]

\[
\phi - 1 = -A_ϕ z_i M_i \bigg( \frac{1}{1 + b_i T} \bigg) + 2m \bigg( \frac{V_{M_i} N_i}{\nu} \bigg) B^ϕ_\nu
\]

\[
B^ϕ_\nu = \frac{\nu_i^2}{\nu} \exp(-\alpha_i^1/2) + \frac{\nu_i^2}{\nu} \exp(-\alpha_i^1/2)
\]

\[
B_{MX} = \frac{\nu_i^2}{\nu} + \frac{\nu_i^2}{\nu} \exp(\alpha_i^1/2) + \frac{\nu_i^2}{\nu} \exp(\alpha_i^1/2)
\]

\[
g(x) = \frac{2[1 - (1 + x)e^{-x}]}{x}
\]

where A_ϕ is the Debye–Hückel parameter, υ is the sum of the stoichiometric coefficients of cation (ν_M) and anion (ν_X), z is charge, b_i is an electrolyte-dependent constant (b = 1.2), and the parameter values α_i and α_ϕ used for 2−2 electrolyte of the Pitzer model are 1.4 and 12, respectively, in this work.

Thus, the electrolyte specific parameters to be assessed are β_MX, β_MX', β_MX'', and C_ϕ where β_MX'' is used only for 2−2 or higher electrolytes. The C_ϕ parameter is assumed to be concentration independent in the early Pitzer model version and adopted in this work. Archon also suggested concentration dependency for C_ϕ in a similar way to eq 4 but with different values for the internal constants. The constant values used in the above equations are the same as suggested by Pitzer and also adopted by Harvie et al. even though different values have been used in many approaches of the Pitzer formalism.

3.2. Thermodynamic Functions. The solubility products (K) of the solid phases for calcium sulfate hydrates are expressed by the following eqs 7−12.

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

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

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

\[
K_{DH} = \frac{a_{\text{Ca}^{2+}(aq)} a_{\text{SO}_4^{2−}(aq)} a_{\text{H}_2\text{O}(l)}}{a_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(s)}} = \gamma_{\text{Ca}^{2+}}^2 \gamma_{\text{SO}_4^{2−}}^2 a_{\text{H}_2\text{O}(l)}
\]

\[
K_{4H} = \frac{a_{\text{Ca}^{2+}(aq)} a_{\text{SO}_4^{2−}(aq)} a_{0.5\text{H}_2\text{O}(l)}}{a_{\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}(s)}} = \gamma_{\text{Ca}^{2+}}^2 \gamma_{\text{SO}_4^{2−}}^2 a_{0.5\text{H}_2\text{O}(l)}
\]

\[
K_{AH} = \frac{a_{\text{Ca}^{2+}(aq)} a_{\text{SO}_4^{2−}(aq)}}{a_{\text{CaSO}_4(s)}} = \gamma_{\text{Ca}^{2+}}^2 a_{\text{SO}_4^{2−}}
\]
Table 2. Tested Models for the Optimization of Pitzer Parameters in the Assessment

| Model | OF value | Number of fitted terms in parameters | number of fitted terms in parameters |
|-------|----------|--------------------------------------|--------------------------------------|
| C     | 0.70     | 4                                    |                                      |
| D     | 0.12     | 4                                    |                                      |
| E     | 0.10     | 4                                    |                                      |
| F     | 0.07     | 6                                    |                                      |
| G     | 0.08     | 5                                    |                                      |
| H     | 0.08     | 5                                    |                                      |
| I     | 0.13     | 5                                    | 0.15                                 |
| J     | 0.10     | 4                                    | 0.15                                 |
| K     | 0.12     | 4                                    |                                      |

Table 3. Summary for Obtained Thermodynamic Values in the Optimization of Pitzer Parameters

| Model | gypsum | anhydrite | hemihydrate |
|-------|--------|-----------|-------------|
|       | ΔG°(2) | ΔS°(2)    | ΔH°(2)      |
| C     | 30.149 | -101      | 175         |
| D     | 26.372 | -95       | -1814       |
| E     | 26.503 | -145      | -16825      |
| F     | 26.934 | -108      | -5202       |
| G     | 27.390 | -92       | -219        |
| H     | 26.826 | -116      | -7907       |
| I     | 26.349 | -94       | -1790       |
| J     | 25.489 | -137      | -15413      |
| K     | 25.263 | -120      | -10468      |
| HSC   | 25.671 | -92       | -1716       |

4. RESULTS AND DISCUSSION

4.1. Fitting Parameters. Due to the small values for solubilities of calcium sulfate hydrates in water, a new optimization approach was tested. Instead of comparing the calculated and measured molality, the difference in Gibbs energy was selected to fit the parameters of the Pitzer model. According to eq 13, at solubility limit, ΔG°(T) + RT ln K_{SP} = 0. Thus, we obtain

\[ C_i = \Delta G^°(T) \]

\[ E_i = RT \ln K_{SP} \]

The uncertainty (U_i) was set to 100 J/mol for stable phases, whereas 500 J/mol was used for metastable phases. Only first three parameters A_{Pitz} - C_i were found be adequate to describe ΔG°(T).
Table 4. Binary Parameters for Ca$^{2+}$–SO$_4^{2−}$ Ion Interactions of the Pitzer Model in This Work and Other Authors

| Ca$^{2+}$–SO$_4^{2−}$ | $A_{Pitz}$ | $B_{Pitz}$ | $D_{Pitz}$ | $F_{Pitz}$  | ref |
|----------------------|-----------|-----------|-----------|------------|-----|
| $β^{(0)}$            | 0         | 0         | 0         | 0          | model D, this work (273.15−473.15) K |
| $β^{(1)}$            | −3.20249  | 0         | 0         | 0          | 1149.4 |
| $β^{(2)}$            | 32.0227   | −0.27033  | 0         | 0          | Wang et al., 2013 $^{21}$ (298.15−368.15) K |
| C$^θ$                | 0         | 0         | 0         | 0          | Raju and Atkinson, 1990 $^{53}$ (273.15−573.15) K |
| $β^{(0)}$            | 0.4295755 | −0.00077  | 0         | 0          | |
| $β^{(1)}$            | 1.045953  | 0.00538   | 0         | 0          | |
| $β^{(2)}$            | −324.959265 | 0.9031 | 0         | 0          | |
| C$^θ$                | 0         | 0         | 0         | 0          | |
| $β^{(0)}$            | −0.32521  | 0.002916  | −0.000003872 | 0        | |
| $β^{(1)}$            | 1.219512  | 0.00124   | 0.00001809 | 0          | |
| $β^{(2)}$            | −142.7895661 | 0.8283| −0.001782 | 0          | |
| C$^θ$                | 0         | 0         | 0         | 0          | |

All weights for accepted experiments were set to 1 except for duplicates for which a value of 0.5 was used. Several sets for temperature dependency of Pitzer parameters was tested. If all tested sets failed to model an experimental point within a given uncertainty its weight was changed to zero. However, if any of the tested sets was able to model it properly, its weight was changed to 1.

During the assessment, we discover that the parameter C$^θ$ has no influence on the simulation for CaSO$_4$–H$_2$O system as is customary for dilute solutions and was set to zero. However, it was also found out that the parameter $β^{(0)}$ is unnecessary, even though it was adopted in Pitzer modeling by most researchers, $^{21,24,46,50−53}$ usually with a constant value. Still, the effect of a constant value of 0.15 for $β^{(0)}$ used by Møller $^{21}$ and Spencer et al. $^{51}$ was tested.

The tested parameter sets and obtained objective function values are summed in Table 2, together with the assessed thermodynamic values of reactions in eqs 7−9 shown in Table 3. The four terms in Pitzer parameters are found sufficient to obtain accurate simulation results. An extra term would not improve the assessment significantly. Of the four term sets, the model C is less accurate than models D, E, J, and K according to the OF values. Set E and J have similar values for object function values, but set K produces slightly worse OF values. Set E and J have the lowest OF value of the four term sets, but their assessed Δ$H^o$ and Δ$S^o$ values for the solubility reactions are far away from the values of other sets and those obtained by HSC 9. $^{55}$ (Table 3). Sets D and K have similar values for object function values, but set K produces inappropriate values of Δ$H$ and Δ$S$ for the gypsum solubility reaction. So the parameter set D is considered the best to model the CaSO$_4$–H$_2$O system and adopted in this work.

The optimized Pitzer parameters of model D obtained in this work are given in Table 4, containing the parameters collected from previous works. $^{21,53}$ The total number of fitted terms in Pitzer parameters is only four in our model compared with six terms in the model of Wang et al.$^{21}$ and nine terms in the model of Raju and Atkinson. $^{53}$ Wang et al.$^{21}$ modeled the solubility of CaSO$_4$ in sulfuric acid CaSO$_4$–H$_2$SO$_4$–H$_2$O system in the temperature range from 298.15 to 368.15 K, whereas Raju and Atkinson $^{55}$ modeled the solubility in CaSO$_4$–NaCl–H$_2$O system between 273.15 and 573.15 K. Both Wang et al.$^{21}$ and Raju and Atkinson $^{55}$ used literature values of Pitzer parameters at 298.15 K in their models: Pitzer and Mayorga $^{85}$ and Rogers, $^{85}$ respectively. Raju and Atkinson also extracted the temperature dependency for CaSO$_4$ Pitzer parameters from published values for MgSO$_4$. $^{53,56}$

The HMW $^{50,52}$ and SMW $^{51}$ models also used only four terms in their Pitzer parameters, but they included a neutral ion pair CaSO$_4$(aq) in their model with two to three terms depending on temperature.

The relative errors, $(C_i − E_i)/U_i$, between calculated $(C_i)$ and “experimental” $(E_i)$ values for precipitation reactions of calcium sulfate were plotted in Figure 1, in which the solid symbol means the included value whereas the hollow one means the excluded value in the assessment.

![Figure 1](image.png)

Figure 1. Error between calculated and experimental values of Gibbs energy for calcium sulfate hydrates in the assessment. Error $= (C_i − E_i)/U_i$, where $(C_i − E_i) = ΔG^o + RT\ln(K_{sp})$ and $U_i$ is either 100 or 500 J/mol (see the text). A solid symbol indicates the adopted value, and the hollow, the rejected one.

The uncertainty used for stable-phase equilibrium was 100, and 500 J/mol was used for the unstable one. Most values of the errors were close to zero. The data for gypsum and hemihydrate are in good agreement, whereas the experimental data for anhydrite deviate to some degree at high temperature. Only three anhydrite data points above temperature 373.15 K were accepted in the assessment. Thus, the assessment at about 373.15 K is based mostly on solubility of hemihydrate.

The assessed temperature dependencies of Gibbs energy for CaSO$_4$(s), CaSO$_4$·0.5H$_2$O(s), and CaSO$_4$·2H$_2$O(s) are presented in Table 5. The temperature ranges used in the assessment were 273.15−388.15, 273.15−423.15, and 273.15−473.15 K for gypsum, anhydrite, and hemihydrate, respectively (Table 5).

4.2. Solubility Data. The solubilities of calcium sulfate hydrates in water were calculated in the temperature ranges of 273.15−393.15, 273.15−573.15, and 273.15−473.15 K for gypsum, anhydrite, and hemihydrate, respectively, using the
optimized parameters of this work. The solubility curves of each phase depending on temperature are drawn together with all collected experimental data. Predictions by recent models are also shown. The obtained difference between calculated and experimental molality for calcium sulfate hydrates is also shown in figures, where the solid symbol means the adopted value and the hollow one refers to data rejected in the assessment.

The goodness of the assessment for adopted experimental data is estimated by standard deviation (SD), also known as root mean square error, defined as

\[ SD = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (C_i - E_i)^2} \]  

where \( i \) goes over all experimental points (\( N \)) with nonzero weights in the experimental set and \( C_i \) is the calculated and \( E_i \) is the experimental molality.

The mean absolute percentage error (MAPE), also known as the absolute average relative deviation (AARD %), is used when the focus is on relative deviation

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

The standard deviation values for fitted data are 0.00045 mol/kg for gypsum, 0.00063 mol/kg for anhydrite, and 0.0053 mol/kg for hemihydrate. The mean absolute percentage errors (MAPE), are 2.2, 2.5, and 7.3%, respectively.

4.2.1. Gypsum. As shown in Figure 2a,b, the calculated solubility values for gypsum are consistent with the most experimental solubility data. The temperature dependency of the solubility curve goes through most data points. Most of the differences between calculated and experimental data for gypsum are less than 0.001 mol/kg-H\(_2\)O, with the absolute percentage error within 5%.

However, excluded points show a slight scatter, such as the data points at 273.15 K by D’Ans et al., 273.65 K by Marshall and Slusher, 26 as well as data points at 298.15 K by Block and Waters 26 and at 303.15 K by Bock. 17 Still, the modeled curve around 273.15 K goes between these two rejected data points.

In addition, the excluded data from Farrah et al. 19 are scattered and lower than others. The absolute percentage errors between the calculated and experimental data for these excluded observations are above 5%.

4.2.2. Anhydrite. The calculated phase boundary for anhydrite performs excellently with the optimized parameters in the temperature range of 273.15–573.15 K, as presented in Figure 3a,b, even though the assessment of Gibbs energy according to solubility data shows high scatter at temperatures above 373.15 K in Figure 1.

The data sets with temperature ranges of 324.65–337.65 K by Innorta et al., 28 high-temperature ranges of 373.15–398.15 and 448.15–548.15 K by Marshall et al. 33,34 373.15 and 403.15–493.15 K by Partridge and White, 17 373.15–473.15 K by D’Ans et al., 16 414.15–568.15 K by Hall et al., 38 and 373.15–480.15 K by Booth and Bidwell 18 were not included in the assessment. However, even though the high-temperature data was not included in the assessment, the difference between calculated and experimental data for anhydrite is less than 0.0005 mol/kg-H\(_2\)O (Figure 3c). The extrapolating capacity over 473.15 K is also excellent (Figure 3b). The absolute percentage errors for molalities are within 5% for the adopted data.

4.2.3. Hemihydrate. Compared with gypsum and anhydrite, hemihydrate is considered as the metastable phase and attracts...
less attention from other researchers. The assessed solubility and differences with predicted and measured solubilities are presented in Figure 4a,b from 273.15 to 473.15 K. The calculated phase boundaries agree with the experimental data very well. All data, except the data points at 463.15 and 473.15 K by D’Ans et al.,16 were included in the assessment. The difference between the calculated and experimental saturation boundaries is a little larger at low temperatures, whereas the absolute percentage errors were less than 10%, due to the large values of solubility. Most of the absolute percentage errors were still within 5%, showing a good modeling capability of the present parameter set.

4.3. Transition Temperature. The transformations of calcium sulfate hydrates are of significant importance for CaSO4−H2O system to predict and control calcium sulfate formation. However, a large controversy exists between the phase equilibria regarding the various calcium sulfate hydrates in the CaSO4−H2O system. The transition temperatures for calcium sulfate dehydration are summarized and listed in Table 6.

From the solubility curves calculated in this work (Figure 5), the estimated transition temperature of gypsum to anhydrite is 315.95 K. This agrees with the research result of 315.15 ± 2 K from Azimi,1 D’Ans,16,57 Hill,36 Posnjak,58 Kelly et al.,59 Macdonald,60 Zen,65 Cruft and Chao,66 Grigor’ev and Shamaev,67 Corti and Fernandez-Prini,68 and Kontrec et al.,69 and is in the temperature intervals determined by Freyer and Voigt7 and Present.74

The transition temperature of gypsum to hemihydrate has drawn less attention and it is in this study determined at 374.55 K, in agreement with Krumgalz’s15 value of 373.95 K but a little bit higher as obtained by Posnjak’s. Still, the stable temperature range is 273.15−315.95 K for gypsum and above 315.95 K for anhydrite whereas hemihydrate is in a metastable phase in the whole temperature range.

The transition temperature of anhydrite to hemihydrate suggested recently by Krumgalz73 is considered incorrect since after 471.55 K, hemihydrate would be in a stable phase instead.
of anhydrite, which is most unlikely and has never been reported to our knowledge.

4.4. Comparison with Previous Works. The CaSO$_4$–H$_2$O system has been assessed with the Pitzer model by many authors, but most of them calculated the solubilities of gypsum and anhydrite only and did not include hemihydrate. Møller$^{50}$ described a chemical equilibrium model for CaSO$_4$–H$_2$O system on the basis of Pitzer equations, with gypsum from 298.15 to 383.15 K and anhydrite and hemihydrate from 298.15–498.15 K. But the parameter $\beta^{(0)} = 0.15$ is different from the later obviously mistyped value of 0.015 reported by Greenberg and Møller.$^{52}$ Moreover, they have used the ion pair CaSO$_4$(aq) in their model with two separate temperature ranges and parameter sets. So their model was not used to compare the observation in this work.

The assessed model of Wang et al.$^{21}$ and the one by Raju and Atkinson$^{53}$ were used to compare the parameterization of this work. Wang et al.$^{21}$ modeled CaSO$_4$–H$_2$O system in the temperature range 298.15–363.15 K as a subsystem of the CaSO$_4$–H$_2$SO$_4$–H$_2$O system, and Raju and Atkinson,$^{53}$ in the temperature range 273.15–573.15 K as a subsystem of the CaSO$_4$–NaCl–H$_2$O system.

The temperature dependencies of Pitzer parameters and forming Gibbs energy changes of solid phases are listed in Tables 4 and 5.

The simulation results were drawn in Figures 2–4, together with the experimental data collected in this work. Wang et al.$^{21}$ simulated gypsum and anhydrite primary phase fields with a temperature range of 298.15–363.15 K. We extended the temperature ranges from 273.15 to 393.15 and 273.15 to 573.15 K for gypsum and anhydrite, respectively. The model of Wang et al. shows excellent trends and is close to our results. But the extrapolated solubilities for anhydrite calculated by parameters of Wang et al. at low temperatures of 273.15–298.15 K are larger than the experimental data whilst our model predicts lower values.

Raju and Atkinson$^{53}$ present an insufficient model for gypsum at 273.15–393.15 K and anhydrite at 273.15–573.15 K. The solubilities of gypsum from Raju and Atkinson are smaller than the experimental data, the data calculated by

### Table 6. Transition Temperatures for Calcium Sulfate Dehydration

| reaction | transition temperature (K) | source |
|----------|----------------------------|--------|
| CaSO$_4$·2H$_2$O $\Rightarrow$ CaSO$_4$ + 2H$_2$O | 315.95 | this work |
| | 317.85$^a$ | Wang et al., 2013$^{21}$ |
| | 333.05 | Raju and Atkinson, 1990$^{53}$ |
| | 313.15 $\pm$ 2 | Azimi, 2010$^1$ |
| | 318.76 | Krumgalz, 2018$^{11}$ |
| | $\approx$313.15 | D’Ans, 1933$^{12}$ |
| | 315.15 $\pm$ 2 | Hill, 1937$^{13}$ |
| | 315.15 $\pm$ 2 | Posnjak, 1938$^{14}$ |
| | 313.15 | Kelly et al., 1941$^{15}$ |
| | 315.15 | Macdonald, 1953$^{16}$ |
| | 322.65 $\pm$ 2.5 | Innorta et al., 1980$^{17}$ |
| | 322.65 $\pm$ 2.5 | Møller, 1988$^{18}$ |
| | 328.65 $\pm$ 1.5 | Knacke and Gans, 1977$^{19}$ |
| | 331.15 $\pm$ 2 | Hardie, 1967$^{20}$ |
| | 329.15 $\pm$ 3 | Blount and Dickson 1973$^{21}$ |
| | 333.05 | Raju and Atkinson 1990$^{53}$ |
| | 336.65 | Van’t Hoff et al., 1903$^{22}$ |
| | 319.15 $\pm$ 2.5 | Zen, 1965$^{23}$ |
| | $\approx$313.15 | Cruff and Chao, 1970$^{24}$ |
| | $\approx$313.15 | Grigor’ev and Shamaev, 1976$^{25}$ |
| | 315.75 $\pm$ 0.4 | Corti and Fernandez-Prini, 1983$^{26}$ |
| | 313.15 | Kontrec et al., 2002$^{27}$ |
| | 374.55 | this work |
| | 373.95 | Krumgalz, 2018$^{11}$ |
| | 370.15 $\pm$ 1 | Posnjak, 1938$^{14}$ |
| | 363.65 | Ostroff, 1964$^{28}$ |
| | 471.55$^b$ | Krumgalz, 2018$^{11}$ |

$^a$Value calculated by MTDATA with Wang et al. parameters, value of about 315 K reported by Wang et al. 2013. $^b$Considered as incorrect, hemihydrate is in metastable phase at all temperature ranges.

Figure 5. Solubility curves of calcium sulfate hydrates in water calculated in this work. Solubility over 473.15 K is extrapolated. Solubility curves calculated by parameters by Wang et al.$^{21}$ and Raju and Atkinson$^{53}$ models are also shown for comparison. The transition temperatures predicted by the models are also shown.
calculated by model of Raju and Atkinson are closer to NBS gypsum and anhydrite, the enthalpy and entropy changes calculated for the solubility reaction of gypsum by Wang et al. do not agree well with the literature data whereas our values are closer to literature values, too. For our model is in good agreement with literature values. For previous studies is summarized in Table 8. Our model uses the their values are based on literature values.

The thermodynamic properties of solubility reactions calculated from parameter values in Table 5 are collected in Table 7. As can be seen from the table, enthalpy and entropy changes calculated for the solubility reaction of gypsum by Wang et al. do not agree well with the literature data whereas neither of these data sets or similar data was used in the assessment; only solubility data was used. The calculated activity coefficient compared with values obtained by Lilley and Briggs is shown in Figure 6 with the estimated experimental error. Lilley and Briggs used a value of \(-352.6 \text{ mV}\) for standard electrode potential of the \((\text{Hg})\text{Pb/PbSO}_4\) electrode when obtaining values for the activity coefficient. We also recalculated their results using the recent value of \(-352.0 \pm 0.5 \text{ mV}\) for this electrode determined by

### Table 7. Thermodynamics for Calcium Sulfate Solubility Reaction at 298.15 K

| Reference                  | \(\Delta G^\circ_{298}\) (kJ/mol) | \(\Delta H^\circ_{298}\) (kJ/mol) | \(\Delta S^\circ_{298}\) (J/(K mol)) | \(K\) |
|----------------------------|----------------------------------|----------------------------------|----------------------------------|------|
| Raju and Atkinson, 1990    | 26.241                           | -577\(^a\)                      | -89.95\(^a\)                     | 2.53 \times 10^{-5} |
| Wang et al., 2013          | 26.284                           | 5217\(^a\)                      | -70.66\(^a\)                     | 2.48 \times 10^{-5} |
| this work                  | 26.372                           | -1814                           | -94.54                           | 2.40 \times 10^{-5} |
| HSC 9\(^a\)               | 25.671                           | -1716                           | -91.86                           | 3.18 \times 10^{-5} |
| NBS \(^a\)               | 24.893                           | -1130                           | -87.28                           | 4.36 \times 10^{-5} |
| CODATA \(^a\)           | 26.140                           | -1130                           | -91.46                           | 2.63 \times 10^{-5} |

\(\Delta G^\circ_{298}\) and \(\Delta S^\circ_{298}\) are calculated from temperature dependence of the given \(\Delta G^\circ\) equation.

### Table 8. Comparison of the Pitzer Models between This Work and Previous Studies

| Reference                  | number of terms in Pitzer parameters | parameter temperature range (K) | \(\Delta H\)–\(\Delta H\) (K) | \(\Delta H\)–\(\Delta H\) (K) |
|----------------------------|-------------------------------------|---------------------------------|-----------------------------|-----------------------------|
| this work                  | 4                                   | 273.15–473.15                  | 315.95                      | 374.55                      |
| Wang et al., 2013          | 6                                   | 298.15–363.15                  | 317.85\(^a\)               | 332.05                      |
| Raju and Atkinson, 1990    | 9                                   | 273.15–473.15                  | 333.05                      |                            |

Value calculated by MTDATA with Wang et al. parameters, value of about 315 K reported by Wang et al. 2013.

Wang et al. and this work, whereas the solubilities of anhydrite from 273.15 to 373.15 K are much larger. Furthermore, neither Wang et al. nor Raju and Atkinson assessed the solubilities of hemihydrate.

The thermodynamic properties of solubility reactions calculated from parameter values in Table 5 are collected in Table 7. As can be seen from the table, enthalpy and entropy changes calculated for the solubility reaction of gypsum by Wang et al. do not agree well with the literature data whereas our model is in good agreement with literature values. For anhydrite, our values are closer to literature values, too. For gypsum and anhydrite, the enthalpy and entropy changes calculated by model of Raju and Atkinson are closer to NBS and CODATA literature values, which is not surprising since their values are based on literature values.

The comparison of Pitzer modeling between this work and previous studies is summarized in Table 8. Our model uses the least Pitzer parameters and gives an excellent agreement for gypsum of 273.15–393.15 K, anhydrite of 273.15–573.15 K, and also hemihydrate of 273.15–473.15 K. All these verify that the assessment of this work is simple and accurate.

### 4.5. Comparison with Independent Data. The quality of our model is tested by comparing calculated activity coefficient data with experimental data at 298.15 K as well as activity of water on the ice curve. Neither of these data sets or similar data was used in the assessment; only solubility data was used.

![Figure 6. Experimentally obtained and calculated activity coefficient of calcium sulfate at 298.15 K. Experimental data is from Lilley and Briggs as well as estimated experimental error lines.](image-url)
The difference by measured and calculated activity coefficients is shown in Figure 7.

![Figure 7](image)

**Figure 7.** Deviation plot of the calculated and experimentally obtained activity coefficient \( \Delta \gamma = \gamma_{\text{exp}} - \gamma_{\text{calc}} \) obtained by two different values for standard potential for lead amalgam-leadsulfate electrode (see the text).

The MAPE (AARD%) values for original and recalculated data for the activity coefficient are 2.15 and 2.06%, respectively. Both Pitzer and Mayorga and Rogers used activity or osmotic coefficient data from the literature in their assessment of Pitzer parameters for CaSO4 at 298.15 K. Their Pitzer parameters yield MAPE (AARD%) values for Lilley and Briggs original data to 1.53 and 1.65% and for recalculated data to 1.53 and 0.93%, respectively. All of these results favor a value $-352.0 \text{ mV}$ for the standard electrode potential of the \((\text{Hg})\text{Pb|PbSO}_4\) electrode.

Brown and Prue measured the freezing point depression of CaSO4 with a precision of $\pm 0.0002 \text{ K}$. The measured freezing point depression and the calculated osmotic coefficient on the ice curve are put together in Table 9.

As can be seen from the table, our model predicts both measured osmotic coefficients and thermodynamically estimated osmotic coefficients with a standard deviation (SD) of 0.004 and a maximum error of 1.43%.

![Figure 8](image)

**Figure 8.** Comparison of calculated to experimental and thermodynamically estimated activities of water on the ice curve.

### Table 9. Osmotic Coefficient on the Ice Curve as a Function of CaSO4 Molality

| \( T \) (K) | \( m \) (mol/kg) | \( \phi_{\text{BP}} \) | \( \phi_{\text{ST}} \) | \( \phi - \phi_{\text{BP}} \) | \( \phi - \phi_{\text{ST}} \) |
|-----------|----------------|----------------|----------------|----------------|----------------|
| 273.1376  | 0.00418        | 0.7974         | 0.7980         | 0.0004         | -0.0002        |
| 273.1359  | 0.00487        | 0.7781         | 0.7888         | 0.0077         | 0.0070         |
| 273.1348  | 0.00526        | 0.7672         | 0.7773         | 0.0034         | 0.0023         |
| 273.134   | 0.00560        | 0.7672         | 0.7685         | 0.0073         | 0.0061         |
| 273.1324  | 0.00625        | 0.7548         | 0.7574         | 0.0018         | 0.0082         |
| 273.131   | 0.00670        | 0.7612         | 0.7627         | -0.0013        | -0.0028        |
| 273.13    | 0.00714        | 0.7549         | 0.7534         | 0.0002         | 0.0013         |
| 273.1294  | 0.00742        | 0.7540         | 0.7467         | 0.0055         | 0.0048         |
| 273.1282  | 0.00782        | 0.7498         | 0.7497         | -0.0026        | -0.0026        |
| 273.1251  | 0.00915        | 0.7318         | 0.7319         | 0.0023         | 0.0022         |
| 273.1244  | 0.00937        | 0.7352         | 0.7348         | -0.0031        | -0.0027        |
| 273.1243  | 0.00952        | 0.7266         | 0.7260         | 0.0042         | 0.0048         |
| 273.1218  | 0.01046        | 0.7240         | 0.7250         | -0.0011        | -0.0021        |
| 273.1207  | 0.01092        | 0.7206         | 0.7216         | -0.0013        | -0.0023        |
| 273.1206  | 0.01100        | 0.7197         | 0.7188         | 0.0041         | 0.0037         |

In a dilute solution, the accuracy of concentration measurements is greater. The difference of modeled water activity on the ice curve from experimental and theoretical activity of water is displayed in Figure 8. As can be seen, our model predicts the activity of water on the ice curve as better than $3 \times 10^{-6}$.

5. SUMMARY AND CONCLUSIONS

The aim of this study is to give an accurate thermodynamic description of the CaSO4–H2O system and clarify its detailed thermodynamic properties for solution chemistry. The Pitzer activity coefficient approach was used to model the CaSO4–H2O system, and its parameters were assessed from critically evaluated solubility data with MTDATA software. Nine different parameter sets with varying temperature dependencies were tested. It was found that Pitzer parameter $\beta^{(0)}$ is unnecessary for modeling and its value was set to zero, even though it has been adopted in Pitzer modeling by most researchers. Thus, only Pitzer parameters $\beta^{(1)}$ and $\beta^{(2)}$ with simple temperature dependency are required to describe the CaSO4–H2O system from 273.15 to 473.15 K with good extrapolating capabilities.
The model of this work is in good agreement with experimental data up to 393.15, 473.15, and 548.15 K for gypsum (CaSO₄·2H₂O), hemihydrate (CaSO₄·0.5H₂O), and anhydrite (CaSO₄), respectively. The absolute average relative deviations between calculated values and adopted experimental data were 2.2, 2.5, and 7.3% for gypsum, anhydrite, and hemihydrate, respectively. The transformation temperatures of CaSO₄·2H₂O to CaSO₄·(s) and CaSO₄·0.5H₂O are determined as 315.95 and 374.55 K, respectively, agreeing with most previous researches. The stable temperature range is 273.15–315.95 K for gypsum and above 315.95 K for anhydrite, whereas hemihydrate is a metastable phase in the whole temperature range.

The model of this work was also compared with other previous Pitzer models. The model of Wang et al.²¹ agrees well with solubility data but fails to predict correctly the thermodynamic properties of the gypsum solubility reaction. The CaSO₄·H₂O model by Raju and Atkinson³³ is based on thermodynamic values of solubility reactions and Pitzer parameters obtained from the literature. Even their model describes the NaCl–CaSO₄·H₂O system adequately; it fails to predict the solubility in binary system CaSO₄·H₂O, especially in metastable regions. Both these models use more than four terms in their Pitzer parameters.

The model was verified using independent activity coefficient and osmotic coefficient data not used in the assessment, which was based only on solubility data. Our model predicts the activity coefficient at 298.15 K with mean absolute percentage error (MAPE) 2.15% and activity of water on the ice curve better than 3 × 10⁻⁶. These results suggest that using the Gibbs energy difference as a dependent variable, the new optimizing strategy was successful.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.9b00112.

Calculated solubility of CaSO₄ from 273.15 K up to 473.15 K (XLSX)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Azimi, G. Evaluating the Potential of Scaling Due to Calcium Compounds in Hydrometallurgical Process. Ph.D. Thesis, University of Toronto, 2010.

(2) Lee, K.; Teong, B.; Subhash, M. J.; Abdul, R. Preparation and characterization of CaO/CaSO₄/coal fly ash sorbent for sulfur dioxide (SO₂) removal: Part I. Energy Sources 2006, 28, 1241–1249.

(3) Dathe, H.; Jentys, A.; Haider, P.; Schreier, E.; Fricke, R.; Lercher, J. A. On the trapping of SOx on CaO–Al₂O₃–based novel high capacity sorbents. Phys. Chem. Chem. Phys. 2006, 8, 1601–1613.

(4) Azimi, G.; Adams, J. F.; Jones, M.; Liu, H.; Papangelakis, V. G. Chemical Modeling of Calcium Sulphate Solubility in Hydrometallurgical Process Solutions. In Advanced Processing of Metals and Materials Volume 3: Thermo and Physicochemical Principles: Special Materials-Aqueous and Electrochemical Processing, Soino International Symposium, 2006; pp 419–426.

(5) Dutrizac, J. E. Calcium sulphate solubilities in simulated zinc processing solutions. Hydrometallurgy 2002, 65, 109–135.

(6) Dutrizac, J. E.; Kuiper, A. The solubility of calcium sulphate in simulated nickel sulphate-chloride processing solutions. Hydrometallurgy 2006, 82, 13–31.

(7) Dutrizac, J. E.; Kuiper, A. The solubility of calcium sulphate in simulated copper sulphate-electro-refining solutions. Hydrometallurgy 2008, 92, 54–68.

(8) Li, X. B.; Shen, L. T.; Qiu, S. Z.; Peng, Z. H.; Liu, G. H.; Tian, G. Q. Scheelite conversion in sulfuric acid together with tungsten extraction by ammonium carbonate solution. Hydrometallurgy 2017, 171, 106–115.

(9) Spencer, P. J. A brief history of CALPHAD. CALPHAD: Comput. Coupling Phase Diagrams Thermochem. 2008, 32, 1–8.

(10) Kobylin, P. M.; Sippola, H.; Taskinen, P. A. Thermodynamic modelling of aqueous Fe(II) sulfate solutions. CALPHAD: Comput. Coupling Phase Diagrams Thermochem. 2011, 35, 499–511.

(11) Kobylin, P. M.; Taskinen, P. A. Thermodynamic modelling of aqueous Mn(II) sulfate solutions. CALPHAD: Comput. Coupling Phase Diagrams Thermochem. 2012, 38, 146–154.

(12) Kobylin, P. M. Thermodynamics of Concentrated Aqueous Solution of NiSO₄·6H₂O, Wiley, 2011; Vol. 3, pp 957–974. ISBN 978-3-940276-38-4.

(13) Freyer, D.; Voigt, W. Crystallization and phase stability of calcium sulfate. Monatsh. Chem. 2003, 134, 693–719.

(14) Present, T. M. Single Crystal Gypsum Dehydration in Saturated Brine Conditions. Doctoral Dissertation, Pennsylvania State University, 2011.

(15) Krumgalz, B. S. Temperature Dependence of Mineral Solubility in Water. Part 3. Alkaline and Alkaline Earth Sulfates. J. Phys. Chem. Ref. Data 2018, 47, No. 023101.

(16) D’Ans, J.; Bredtscheider, D.; Eick, H.; Freund, H. E. Untersuchungen uber die calciumsulfate. Kali Steinsalz 1955, 9, 17–38.

(17) Sborgi, U.; Bianchi, C. The solubilities, conductivities and X-ray analyses of anhydrous and semihydrated calcium sulphate. Gazz. Chim. Ital. 1940, 70, 823–835.

(18) Power, W. H.; Fabuss, B. M. Transient solubilities in the calcium sulfate-water system. J. Chem. Eng. Data 1964, 9, 437–442.

(19) Farrah, H. E.; Lawrance, G. A.; Wanless, E. J. Solubility of calcium sulfate salts inacindic manganese sulfate solutions from 30 to 105 °C. Hydrometallurgy 2007, 86, 13–21.

(20) Sun, J.; Wang, L. S.; Yu, G. M. Effect of Na, Ca, Mg, and Al chloride salts on dissolution and phase stability of calcium sulfate dehydrate in aqueous solutions at 278.15 K to 308.15 K. J. Chem. Eng. Data 2015, 60, 2559–2566.

(21) Wang, W. L.; Zeng, D. W.; Chen, Q. Y.; Yin, X. Experimental determination and modeling of gypsum and insoluble anhydrite solubility in the system CaSO₄–H₂SO₄–H₂O. Chem. Eng. Sci. 2013, 101, 120–129.
of gypsum and anhydrite in simulated laterite pressure acid leach solutions up to 250 °C. Hydrometallurgy 2010, 102, 1–13.

(24) Li, Z. B.; Demopoulos, G. P. Solubility of CaSO4 phase in aqueous HCl + CaCl2 solutions from 283 K to 353 K. J. Chem. Eng. Data 2005, 50, 1971–1982.

(25) Innotra, G.; Rabbi, E.; Tomadin, L. The gypsum–anhydrite equilibrium by solubility measurements. Geochim. Cosmochim. Acta 1980, 44, 981–997.

(26) Marshall, W. L.; Slusher, R. Thermodynamics of calcium sulfate dehydrate in aqueous sodium chloride solutions, 0–110°. J. Phys. Chem. 1966, 70, 4015–4027.

(27) Ostroff, A. G.; Metler, A. V. Solubility of calcium sulfate dehydrate in the system NaCl–MgCl2–H2O from 28 °C to 70 °C. J. Chem. Eng. Data 1966, 11, 346–350.

(28) Power, W. H.; Fabuss, B. M. Transient solute concentrations and phase changes of calcium sulfate in aqueous sodium chloride. J. Chem. Eng. Data 1966, 11, 149–154.

(29) Bock, E. On the solubility of anhydrous calcium sulphate and of gypsum in concentrated solutions of sodium chloride at 25 °C, 30 °C, 40 °C, and 50 °C. Can. J. Chem. 1961, 39, 1746–1754.

(30) Block, J.; Waters, O. B. The CaSO4–Na2SO4–NaCl–H2O system at 25° to 100 °C. J. Chem. Eng. Data 1968, 13, 336–344.

(31) Hill, A. E.; Wills, J. H. Ternary systems. XXIV. Calcium sulfate, sodium sulfate and water. J. Am. Chem. Soc. 1938, 60, 1647–1655.

(32) Hill, A. E. Ternary systems. XIX. Calcium sulfate, potassium sulfate and water. J. Am. Chem. Soc. 1934, 56, 1071–1078.

(33) Marshall, W. L.; Jones, E. V. Second dissociation constant of sulfuric acid from 25 to 350° evaluated from solubilities of calcium sulfate in sulfuric acid solutions. J. Phys. Chem. 1966, 70, 4028–4040.

(34) Marshall, W. L.; Slusher, R.; Jones, E. V. Aqueous systems at high temperature XIV. Solubility and Thermodynamic Relationships for CaSO4 in NaCl–H2O Solutions from 40 to 200 °C, 0 to 4 Molar NaCl. J. Chem. Eng. Data 1964, 9, 187–191.

(35) Booth, H. S.; Bidwell, R. M. Solubilities of salts in water at high temperatures. J. Am. Chem. Soc. 1950, 72, 2567–2575.

(36) Hill, A. The transition temperature of gypsum to anhydrite. J. Am. Chem. Soc. 1939, 61, 2242–2244.

(37) Partridge, E. P.; White, A. H. The solubility of calcium sulfate from 0 to 200°. J. Am. Chem. Soc. 1929, 51, 360–370.

(38) Hall, R. E.; Robb, J. A.; Coleman, C. E. The solubility of calcium sulfate at boiler-water temperatures. J. Am. Chem. Soc. 1926, 48, 927–938.

(39) Seidell, A. Solubilities of Inorganic and Metal Organic Compounds, 3rd ed.; D. Van Nostrand: NY, 1940; p I.

(40) Zdanovskii, A. B.; Vlasov, G. A.; Sotnikova, L. I. Dehydration of Gypsum in Sulphuric acid solutions. Russ. J. Inorg. Chem. 1968, 13, 1418–1420.

(41) Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical basis and general equations. J. Phys. Chem. 1973, 77, 268–277.

(42) Pitzer, K. S.; Mayorga, G. Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. J. Phys. Chem. 1973, 77, 2300–2308.

(43) Pitzer, K. S.; Mayorga, G. Thermodynamics of electrolytes. III. Activity and osmotic coefficients for 2-2 electrolytes. J. Solution Chem. 1974, 3, 539–546.

(44) Harvie, C. E.; Weare, J. H. The prediction of mineral solubilities in natural waters: the Na–K–Mg–Ca–SO4–Cl–H2O system from zero to high concentration at 25 °C. Geochim. Cosmochim. Acta 1980, 44, 981–997.

(45) Harvie, C. E.; Metler, A. V.; Weare, J. H. The prediction of mineral solubilities in natural waters: the Na–K–Mg–Ca–H–Cl–SO4–OH–HCO3–CO3–CO2–H2O system to high ionic strengths at 25 °C. Geochim. Cosmochim. Acta 1984, 48, 723–751.

(46) Archer, D. G. Thermodynamic properties of the NaNO3–H2O system. J. Phys. Chem. Ref. Data 2000, 29, 1141–1156.

(47) Archer, D. G.; Rard, J. A. Isoptiestic investigation of the osmotic and activity coefficients of aqueous MgSO4 and the solubility of MgSO4.7H2O(cr) at 298.15 K: thermodynamic properties of the MgSO4 + H2O system to 440 K. J. Chem. Eng. Data 1998, 43, 791–806.
(70) Ostroff, A. G. Conversion of gypsum to anhydrite in aqueous salt solutions. Geochim. Cosmochim. Acta 1964, 28, 1363−1372.
(71) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttal, R. L. The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units; NBS: Washington, 1982; p 392.
(72) Cox, J.; Wagman, D. D.; Medvedev, V. A. CODATA Key Values for Thermodynamics; Hemisphere Publishing Corporation: NY, 1989; p 271.
(73) Lilley, T.; Briggs, C. C. Activity coefficients of calcium sulphate in water at 25 °C. Proc. R. Soc. London, Ser. A 1976, 349, 355−368.
(74) Sippola, H.; Taskinen, P. Thermodynamic Properties of Aqueous Sulfuric Acid. J. Chem. Eng. Data 2014, 59, 2389−2407.
(75) Brown, P.; Prue, J. A study of ionic association in aqueous solutions of bi-bivalent electrolytes by freezing-point measurements. Proc. R. Soc. London, Ser. A 1955, 232, 320−336.
(76) Sippola, H.; Taskinen, P. Activity of Supercooled Water on the Ice Curve and Other Thermodynamic Properties of Liquid Water up to the Boiling Point at Standard Pressure. J. Chem. Eng. Data 2018, 63, 2986−2998.