$MgSO_4 + H_2O$ System at Eutectic Conditions and Thermodynamic Solubility Products of $MgSO_4 \cdot 12H_2O(s)$ and $MgSO_4 \cdot 7H_2O(s)$

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A thermodynamic electrolyte model has been used to investigate the system $MgSO_4 + H_2O$ at temperatures close to the eutectic from (0 to −10) °C. The model was based on the Pitzer aqueous electrolyte activity coefficient model using the interaction parameters proposed by Marion and Farren (Marion, G.; Farren, R. E. Mineral solubilities in the Na-K-Mg-Ca-Cl-SO_4-H_2O system: A re-evaluation of the sulfate chemistry in the Spencer-Møller-Weare model. *Geochim. Cosmochim. Acta* **1999**, *63*, 1305−1318) as well as improved functions that have been derived in this work. Because of its improved data fitting, the model describes the system $MgSO_4 + H_2O$ accurately from (−5 to 50) °C. By making use of solubility data obtained from the literature as well as from additional laboratory experiments, we investigated the magnesium sulfate duodecahydrate solid phase ($MgSO_4 \cdot 12H_2O$). The two characteristic points, which limit the $MgSO_4 \cdot 12H_2O(s)$ region of existence, are the eutectic point between $MgSO_4 \cdot 12H_2O(s)$ and ice and the phase-transition point (peritectic) between $MgSO_4 \cdot 12H_2O(s)$ and $MgSO_4 \cdot 7H_2O(s)$ (epsomite, bitter salt). Both were determined from the solubility experiments and the model. The solubility products (K_{sp}) of $MgSO_4 \cdot 12H_2O(s)$ and $MgSO_4 \cdot 7H_2O(s)$ were calculated as functions of temperature from solubility and phase stability data. These functions improve K_{sp} functions published by Marion and Farren (Marion, G.; Farren, R. E. Mineral solubilities in the Na-K-Mg-Ca-Cl-SO_4-H_2O system: A re-evaluation of the sulfate chemistry in the Spencer-Møller-Weare model. *Geochim. Cosmochim. Acta* **1999**, *63*, 1305−1318). It was experimentally determined that the eutectic occurs at 17.4 mass % $MgSO_4$ and −3.7 °C, and the presented model predicts it at 17.3 mass % $MgSO_4$ and −3.7 °C.

Introduction

Magnesium and sulfate ions are among the most common ions found in natural groundwaters and aquatic environments.[1] Creating a comprehensive solubility model of the system $MgSO_4 + H_2O$ based on its thermodynamic properties is difficult not only because of the large number of crystalline hydrates occurring in the system but also because of the strongly associative nature of the aqueous ions.

Recent interest has risen to recover magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O(s)$) for use as a fertilizer by crystallization from solutions of eutectic composition.[2,3] $MgSO_4 \cdot 12H_2O(s)$ crystallizes at the eutectic and has to be subsequently converted to $MgSO_4 \cdot 7H_2O(s)$ by solution-mediated recrystallization. Therefore, detailed knowledge of the phase diagram in the system $MgSO_4 + H_2O$ is needed. Phase diagrams of electrolytes have often been modeled with ion-interaction, virial expansion expressions for activity coefficients using experimentally determined solubilities as input.[1,4−8]

The Spencer−Møller−Weare (SMW) model[6] is based on the activity-coefficient expressions proposed by Pitzer[9] and describes the system Na + K + Mg + Ca + Cl + SO_4 + H_2O over the temperature range of (−60 to 25) °C. As an extension of the basic interactions proposed by Pitzer,[9] binary and ternary ion-interaction parameters have been derived as functions of temperature.

Marion and Farren[5] improved the SMW model in the FREZCHEM model to include refined interaction parameters for the sulfate ion, notably for sodium sulfate and magnesium sulfate. The model parameters were mostly obtained from solubility data compiled by Bukshtein et al.[10] with additional data from Linke and Seidell[11] and some activity data for dilute solutions.[1,12] Therefore, this model is especially accurate for saturation states.

In this work, we have applied the FREZCHEM model to the $MgSO_4 + H_2O$ system to predict the phase diagram of the system under conditions close to the eutectic, with emphasis given to the $MgSO_4 \cdot 12H_2O(s)$ phase. We propose improved expressions for the dependency of the solubility product of $MgSO_4 \cdot 12H_2O(s)$ and $MgSO_4 \cdot 7H_2O(s)$ with temperature.

Methods

The solubility of a solid phase can be thermodynamically expressed by its solubility product, K_{sp}, the product of the activities of the dissolved species of the solid. For this system, the solubility products of magnesium sulfate duodecahydrate ($MgSO_4 \cdot 12H_2O(s)$), epsomite ($MgSO_4 \cdot 7H_2O(s)$), and ice are defined as

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Table 1. FREZCHEM Parameters for the Pitzer Electrolyte Model

	A	B	C	D	E	F
$\beta^{(0)}{}_{MgSO_4}$	1.678	−0.0055	0.597×10^{-6}	0.156×10^{-7}	0.224×10^{3}	0.0659
$\beta^{(1)}{}_{MgSO_4}$	1.484	0.0063	0.541×10^{-5}	0.884×10^{-7}	0.132×10^{4}	0.3061
$\beta^{(2)}{}_{MgSO_4}$	1.88×10^{2}	−1.039	0.122×10^{-2}	0.349×10^{-5}	0.897×10^{5}	0.679×10^{2}
$C^{\Phi}{}_{MgSO_4}$	0.223	-0.61×10^{-3}	-0.1×10^{-8}	-0.11×10^{-8}	0.427×10^{2}	−0.0179

$$K_{sp,MgSO_4\cdot 7H_2O} = a_{Mg^{2+}} a_{SO_4{}^{2-}} a_w{}^{7} \qquad (1)$$

$$K_{sp,MgSO_4\cdot 12H_2O} = a_{Mg^{2+}} a_{SO_4{}^{2-}} a_w{}^{12} \qquad (2)$$

$$K_{sp,ice} = a_w \qquad (3)$$

These solubilities are strongly dependent on temperature. Their temperature dependencies can be expressed by correlations of the following form:

$$\ln(K_{sp}) = a(T/K)^2 + b(T/K) + c + d(T/K)^{-1} \qquad (4)$$

Activities in eqs 1 to 3 relate to activity coefficients and the osmotic coefficient in the usual way. These are described by the FREZCHEM model. The model uses the Pitzer framework,[9] where the activity coefficient (γ_i) of any ion in solution is expressed by a virial expansion function of terms representing the interaction of this ion with every other ion in solution. An expression for the osmotic coefficient (ϕ) is also provided in a similar fashion. The expressions, in summarized form, can be represented by

$$\ln(\gamma_i) = -z_i{}^2 A_\phi f(I) + \sum_j m_j(2B_{ij} + ZC_{ij}) + |z_i| \sum_c \sum_a m_c m_a C_{ca} \qquad (5)$$

$$\phi = 1 + \frac{2}{\sum_i m_i}\left[-A_\phi \frac{I^{1.5}}{1 + bI^{0.5}} + \sum_c \sum_a m_c m_a (B^{\phi}_{ca} + ZC_{ca})\right] \qquad (6)$$

$$f(I) = \left[\frac{I^{0.5}}{1 + bI^{0.5}} + \frac{2}{b}\ln(1 + bI^{0.5})\right] \qquad (7)$$

$$Z = \sum_i m_i |z_i| \qquad (8)$$

where m_i represents the molalities of the ions in solution; m_j, the molalities of their possible counterions; and m_a and m_c, the molalities of the anions and cations, respectively. b is a universal parameter with a value of 1.2 $(kg/mol)^{0.5}$. I is the ionic strength of the solution, A_ϕ is the Debye−Hückel parameter, z_i is the charge of ion species i, and B_{ij} and C_{ij} (i.e., C_{ca}) are species-dependent binary interaction parameters. B^{ϕ}_{ca} is the species-dependent binary interaction parameter for the osmotic coefficient. The complete expressions are given by Marion and Farren[5] and Pitzer.[9]

For the Mg−SO_4 + H_2O system, the relevant interaction parameters of the FREZCHEM model are $\beta^{(0)}{}_{MgSO_4}$, $\beta^{(1)}{}_{MgSO_4}$, $\beta^{(2)}{}_{MgSO_4}$, $C^{\Phi}{}_{MgSO_4}$. These parameters are the basis for the calculation of B_{ij}, C_{ij}, and $B^{\phi}{}_{ca}$. They are temperature-dependent according to eq 9 and Table 1.

$$P(T) = A + B(T/K) + C(T/K)^2 + D\cdot(T/K)^3 + E(T/K)^{-1} + F\ln(T/K) \qquad (9)$$

In this work, we have determined improved parameters for the K_{sp} versus T functions of magnesium sulfate heptahydrate and duodecahydrate. The $K_{sp}(T)$ values were derived from measured solubility concentrations in the temperature range of −5 to 50 °C and the respective activity and osmotic coefficients calculated with the FREZCHEM model (i.e., eqs 5 to 8). From these values, the activities of the ionic species and water were obtained. The activities were inserted into eqs 1 to 3 to obtain the solubility products at various temperatures. The empirical equation (eq 4) was fit to reproduce the so-obtained temperature dependence of the solubility products. The FREZCHEM ion-interaction parameters were used without modification. With this approach, the framework of this widely applicable model remains unaltered, and improved solubility predictions in the $MgSO_4$ + H_2O system are derived.

Table 2. Experimental Solubility Data

$100w(MgSO_4)$/ 100 g·g^{-1}	t/°C	solid phase	reference
20.57	−5.20	ice + $MgSO_4\cdot 7H_2O(s)$	this work
16.77	−3.87	ice + $MgSO_4\cdot 12H_2O(s)$	this work
17.12	−3.74	ice + $MgSO_4\cdot 12H_2O(s)$	this work
18.07	−2.80	$MgSO_4\cdot 12H_2O(s)$	this work
17.87	−3.43	$MgSO_4\cdot 12H_2O(s)$	this work
17.59	−3.72	$MgSO_4\cdot 12H_2O(s)$	this work
18.72	−2.00	$MgSO_4\cdot 12H_2O(s)$	this work
19.87	−1.33	$MgSO_4\cdot 12H_2O(s)$	this work
20.21	−0.30	$MgSO_4\cdot 12H_2O(s)$	this work

Experimental Section

Experiments were conducted to determine the solubility of $MgSO_4\cdot 12H_2O(s)$. Measurements were done in a 1-L thermostated jacketed glass vessel with a Teflon propeller-stirrer. $MgSO_4\cdot 7H_2O(s)$ with a purity of ± 99.9 mass % (Baker Analytical Reagent, Baker BV, The Netherlands) and ultrapure water with a specific resistance of 18.2 MΩ were used. The experiments were performed according to the following procedure:

- A carefully weighed solution (20.5 mass % $MgSO_4$) was cooled to below the eutectic temperature to crystallize out the $MgSO_4\cdot 12H_2O(s)$ solid phase.
- The suspension was heated to the temperature at which the solubility was to be measured.
- The temperature was maintained for a minimum of 48 h to ensure that the formation of the stable hydrate phase and the dissolution of any unstable phases was complete.
- Liquid samples were analyzed for Mg and SO_4 using inductively coupled plasma mass spectrometry and ion chromatography, respectively.

Previous tests had shown that an experimental duration of 48 h was sufficient to ensure that the equilibrium state of the system was obtained. The analytical method yielded an uncertainty of 2% of the measured concentration. On the basis of the reproducibility of some of the measured data points with solubilities measured in experiments with longer equilibration times in preliminary tests, the experimental uncertainty is estimated to be in the range of 2 to 3% of the measured concentration. The obtained solubility data points and the corresponding stable solid phase are listed in Table 2.

Table 3. Fit Parameters for ln(K_{sp}) of the Solid Phases According to Equation 4

	a	*b*	*C*	*d*	R^2
		Marion et al.[5]			
$MgSO_4·7H_2O(s)$			3.956	-0.2471×10^4	NA
$MgSO_4·12H_2O(s)$		0.08852	−29.58		NA
		This Work			
$MgSO_4·7H_2O(s)$	-2.420×10^{-4}	0.1650	−32.03		0.996
$MgSO_4·12H_2O(s)$		0.0926	−30.62		0.951

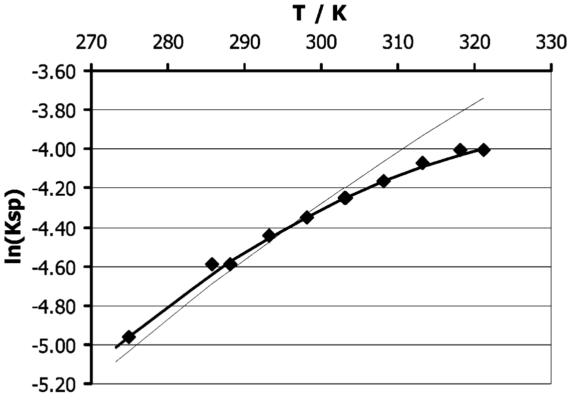

Figure 1. ln(K_{sp}) vs temperature for $MgSO_4·7H_2O(s)$. The bold line represents the K_{sp} function derived in this work, and the thin line represents the K_{sp} function of the FREZCHEM model. ◆, Experimental data from Seidell and Linke,[11] Gmehlin,[13] and this work.

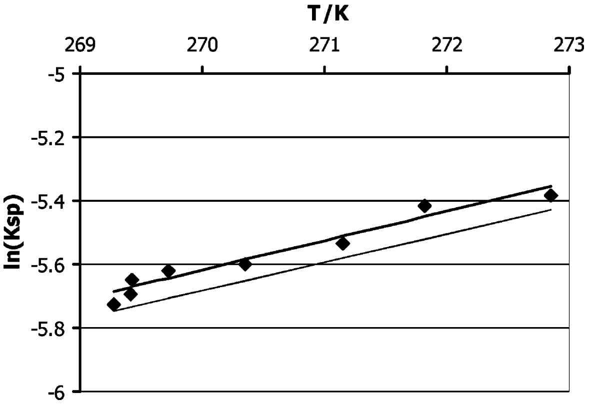

Figure 2. ln(K_{sp}) vs temperature for $MgSO_4·12H_2O(s)$. The bold line represents the K_{sp} function derived in this work, and the thin line represents the K_{sp} function of the FREZCHEM model. ◆, Experimental data from this work.

Results

Salt Lines. The thermodynamic solubility products of epsomite ($MgSO_4·7H_2O(s)$) and magnesium sulfate duodecahydrate ($MgSO_4·12H_2O(s)$) at several temperatures were experimentally determined from the measured solubilities and the FREZCHEM model. The K_{sp} versus T dependencies were adjusted to eq 4 using the parameters shown in Table 3. Figures 1 and 2 show that the proposed correlations compare well with the experimental data over the whole range investigated. It has to be pointed out that the Pitzer interaction parameters were fit only for temperatures up to 25 °C[5] (i.e., the temperature range of (25 to 50) °C of our data is outside the designated range of this Pitzer model). The good agreement of the solubility prediction by our solubility line as well as that of the FREZCHEM model to the experimental data in this extrapolated range indicates how well the solution interactions are reproduced by the used Pitzer model.

For comparison, the correlations used in the FREZCHEM model are shown in Table 3 as well as in Figures 1 and 2.

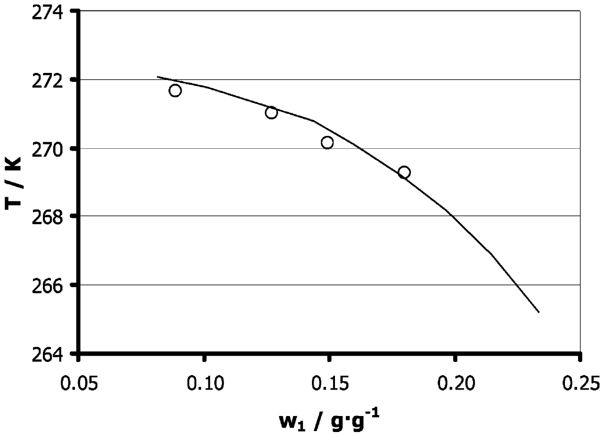

Figure 3. Ice line in $MgSO_4$ solution. The line represents the ice line of the FREZCHEM model. ○, Experimental data from Gmehlin.[13]

For $MgSO_4·7H_2O$, the solubility data used by Marion and Farren[5] is restricted to a narrower temperature range (i.e., (0 to +25) °C) than the data used in this work (i.e., (−5 to +50) °C). $MgSO_4·7H_2O$ solubility data from Seidell and Linke,[11] Gmehlin,[13] and this work was used. The data listed by Gmehlin [13] and Seidell and Linke [11] had been compiled from the work of Schröder,[14] Ting and McCabe,[15] Robson,[16] Benrath,[17] and Smits, Rinse, and Louwe-Kooymans.[18] Figure 1 shows that the solubility product function proposed here extrapolates slightly better outside the fitted range of the Pitzer model (i.e., above 25 °C) than the original correlation of Marion and Farren;[5] see also Figure 5.

The FREZCHEM correlation for $MgSO_4·12H_2O$ yields a fit that lies below our measurements, probably because of the experimental data of Bukshtein et al.[10] used for the fitting of their solubility line. Marion and Farren[5] acknowledge that their estimate was based on scarce data and that hydrates of magnesium sulfate recrystallize slowly, making the evaluation and verification of existing experimental data, based only on the description of the experimental procedures, a difficult task.

Ice Line. As before, the thermodynamic solubility of ice was experimentally determined from the measured solubilities and the FREZCHEM model. The K_{sp} versus T dependency originally proposed in the FREZCHEM model follows eq 9 with the parameters shown in Table 4. The correlation corresponds satisfactorily to experimental data from Gmehling;[12] see Figure 3. Therefore, no refinement of the ice line was applied in this work.

The ice line predicted by the FREZCHEM model was verified not only against our experimental data but also against vapor-pressure data of ice and supercooled water given by Mason[19] and Gibbs free energy of freezing data given by Leyendekkers et al.[20] The ice line of the FREZCHEM model matches those obtained from these data sets excellently, and the FREZCHEM ice line was used unaltered in our model.

Salt Lines and Ice Line: The Phase Diagram. Figure 4 shows experimental and calculated solubility lines and

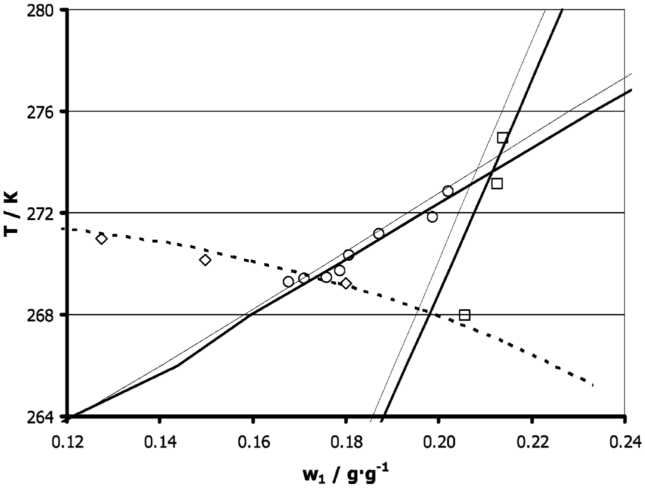

Figure 4. Solubility lines of the system around the eutectic and the peritectic points; the bold lines represent the solubility lines of $MgSO_4 \cdot 7H_2O$(s) and $MgSO_4 \cdot 12H_2O$(s) derived from the model of this work, the thin lines represents the solubility lines of $MgSO_4 \cdot 7H_2O$(s) and $MgSO4 \cdot 12H_2O$(s) derived from the FREZCHEM model, and the broken bold line represents the ice line of the FREZCHEM model. ◇, Experimental data for the ice line from Gmehlin;[13] □, experimental data for the $MgSO_4 \cdot 7H_2O$(s) solubility line from Seidell and Linke,[11] Gmehlin,[13] and this work; ○, experimental data for $MgSO_4 \cdot 12H_2O$(s) solubility line from this work.

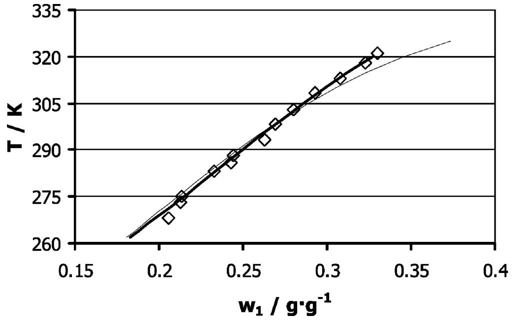

Figure 5. Comparison of the predicted epsomite ($MgSO_4 \cdot 7H_2O$(s)) solubility lines with solubility data. The bold line represents the solubility line derived in this work, and the thin line represents the solubility line derived from the FREZCHEM model. ◇, Experimental data from Seidell and Linke,[11] Gmehlin,[13] and this work. Model values above 298.15 K are extrapolations.

Table 4. Fit Parameters for the Ice Line in the FREZCHEM Model According to Equation 9 with $P(T) = K_{sp,ice}(T)$

	A	B	C	D	E	F
$K_{sp,ice}$	1.834	-1.787×10^{-2}	6.213×10^{-5}	-2.885×10^{-8}		

the ice line for conditions around the eutectic point. The solubility lines predicted by the FREZCHEM model are also shown in the Figure. It was found in our experiments that the eutectic point of the system is at 17.4 mass % $MgSO_4$ and −3.7 °C. Our model predicts the eutectic as 17.3 mass % $MgSO_4$ and −3.7 °C. The FREZCHEM model predicted the eutectic at 17.3 mass % $MgSO_4$ and −3.6 °C.

It can be noted that there is a deviant point in the experimental data of Figure 4 that occurs at approximately 20.5 mass % $MgSO_4$ and −5.15 °C. It is most probably the metastable eutectic point of epsomite ice that has been measured here. The prediction of our model for this point is 19.7 mass % $MgSO_4$ and −5.2 °C, and the FREZCHEM model predicts 19.6 mass % $MgSO_4$ and −5.0 °C. Linke and Seidell[11] gave a eutectic point for epsomite ($MgSO_4 \cdot 7H_2O$(s)) ice as 17.0 mass % $MgSO_4$ and −3.5 °C. It appears that they misidentified the duodecahydrate as heptahydrate. The transition point between epsomite and the duodecahydrate phase is predicted by the model of this work at 21.1 mass % $MgSO_4$ and 0.6 °C. The FREZCHEM prediction is 20.8 mass % $MgSO_4$ and 0.61 °C.

The above results show that our model accurately describes the solubility lines and predicts the two eutectics and the peritectic of the system.

Conclusions

An equilibrium thermodynamic model that accurately describes the $MgSO_4 + H_2O$ system at temperatures close to the eutectic from (−5 to 25) °C was developed using the FREZCHEM model of Marion and Farren[5] as the framework.

On the basis of our solubility data, new correlations were proposed to describe the dependence of the solubility products of $MgSO_4 \cdot 12H_2O$ and $MgSO_4 \cdot 7H_2O$ on temperature. With these correlations, an improved fit to the experimental results is obtained with regard to the results from the original FREZCHEM model. The eutectic point and the peritectic point were correctly predicted.

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