

**Thermodynamic Data
for Iron (II) in
High-Saline Solutions at
Temperatures up to 90°C**

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1 Introduction

For natural aqueous systems in general and for the near field of underground nuclear waste repositories in particular thermodynamic properties of iron species and solid phases are of predominant importance. Regardless of the question of the host rock, nuclear waste containment in Germany will be based on massive steel canisters. The total mass of iron present in a repository can be, dependent on the applied variant, sum up to more than 100 000 tons. The overall geochemical milieu including pH and E_H will be dominated by the overall abundance of metallic, ferrous, and ferric iron, their aqueous speciation and solid iron-phases. This milieu is imposed on all other equilibria of interest, including those which determine radionuclide solubility. In addition to this, iron bearing corrosion phases due to their shear mass may exhibit a significant sink for radionuclides in terms of incorporation or sorption.

As to the evolution of E_H it is important to note that application of the Nernst equation requires knowing the electrochemical activities of the involved reactants, e. g. for the redox couple



$$E = E^0 + \frac{RT}{1 \cdot F} \ln \left\{ \frac{a_{\text{Fe}^{3+}} p^{1/2} \text{H}_2}{a_{\text{Fe}^{2+}} a_{\text{H}^+}} \right\} \quad (1.1)$$

For the purpose of calculating activities in high-saline solutions with relevance for nuclear waste disposal the Pitzer formalism is widely used in Germany. Essentially the Pitzer model is a virial expansion of the extended Debye-Hückel model, where in the additional terms specific interactions between two or three species are accounted for with so-called "Pitzer parameters" as coefficients for each individual interaction. For this reason, efforts to determine Pitzer parameters among various aqueous species were undertaken in the past decades to set up a thermodynamic database.

Iron is present in aqueous solutions in two oxidation states: +II (ferrous iron) and +III (ferric iron). Ferric iron exhibits a much more complex speciation behavior than ferrous iron, where from a conceptual point of view many species may be neglected. Ferric iron, on the contrary, is subject to considerable complex formation with chloride, sulfate, and – most importantly – with hydroxide. For this reason, experimental and theoretical treatment of "iron" at GRS in high saline solutions proceeded along two strings,

one for each oxidation state, with the ultimate goal to deliver a thermodynamic model for "iron" in high saline solutions.

The first project was finalized March 2003: " Entwicklung eines Modells zur Beschreibung des geochemischen Milieus in hochsalinaren Lösungen", funding number 02 E 91384. It focused on the development of Pitzer parameters for ferrous iron at 298.15 K in the hexary system Na, K, Mg, Ca – Cl, SO₄ – H₂O /MOO 2004/. It was reported about a particular paucity of data concerning sulfate systems, including those for the binary system Fe(II)-SO₄-H₂O. Part of the project was also concerned with isopiestic studies of acid ferric sulfate and -chloride systems, which were also published /RUM 2004/. Yet, Pitzer parameters obtained in this study can be used in extremely acid solutions only.

Binary and ternary Pitzer parameters for the system Fe(II) - Na, K, Mg, Ca – Cl – H₂O were subsequently published /MOO 2004a/;

As a follow-up of these efforts two new projects were set up, one focusing on the hydrolysis of ferric iron in high saline solutions ("Prognose der Redox Eigenschaften natürlicher wässriger Lösungen", funding number 02 C 1244). The sister project "Thermodynamische Daten für Eisen(II) in hochsalinaren Lösungen bei Temperaturen bis 90 °C", funding number 02 E 10075, focused on an extension of the earlier published results for ferrous iron. This project will be reported about in this document.

2 Experiments

2.1 Corrosion experiments in brine solution

Experiments were conducted at two different temperatures – 25 and 83 °C – with several brines. The following table gives an overview.

Tab. 2.1 Composition of brine types (taken from ref. /DAN 1933/)

Brine Type	g anhydrous salt / 100 g water				Mol / 1000 Mol H ₂ O				density [g /cm ³]
	NaCl	KCl	MgCl ₂	MgSO ₄	Na ₂ Cl ₂	K ₂ Cl ₂	MgCl ₂	MgSO ₄	
T = 25 °C									
M	14.9		11.4	9.35	23	14	21,5	14	1.285
Q	2.21	5.3	36.1	3.4	3.4	6.4	68.3	5.1	1.293
					5.8	5.7	67.1	5.0	1.292
R					0.5	1.0	85.6	8.2	
T = 83 °C									
M	19.3	27.8	6.82	6.62	29.7	33.6	12.9	9.9	1.289
Q					5.4	11.3	85.1	3.0	13221

Completely planar iron slabs were utilized only. The surface was purified from oxide layers mechanically and cut into 7 x 2.5 cm platelets. Near a short side a small hole was drilled. The hole was used for a thread to suspend the platelet inside a round bottom flask. The platelets were immersed almost completely in the brine. The following figure shows some examples.



Fig. 2.1 Round bottom flasks for the corrosion experiments

Left: Q-brine. Middle: M-brine. Right: R-brine. Temperature 83 °C

800 ml of brine was used for any two platelets, which were degreased right before submersion. The density of each solution was checked prior to usage. Furthermore, each solution was passed through a 0.45 μm filter. To avoid precipitation during the experiment, each solution was diluted to 90 mass-%.

Prior to filling the round bottom flasks were pre-heated to the desired temperature. A filling with the solution and suspension of the platelets the flasks were closed, evacuated, and stored at the specified temperature.

For sampling any platelet was carefully removed and rinsed with distilled water to remove precipitated salts. After drying over silica gel in a desiccator corrosion products were investigated with XRD. At all steps precautions were taken to prevent the samples from further oxidation by atmospheric oxygen.

2.2 Isopiestic Experiments

As for this project isopiestic measurements were to be conducted at higher temperatures, the experimental set up from earlier experiments at 25 °C underwent major revi-

sion. Up to 40 °C, isopiestic vessels were placed in an open water bath as shown below.

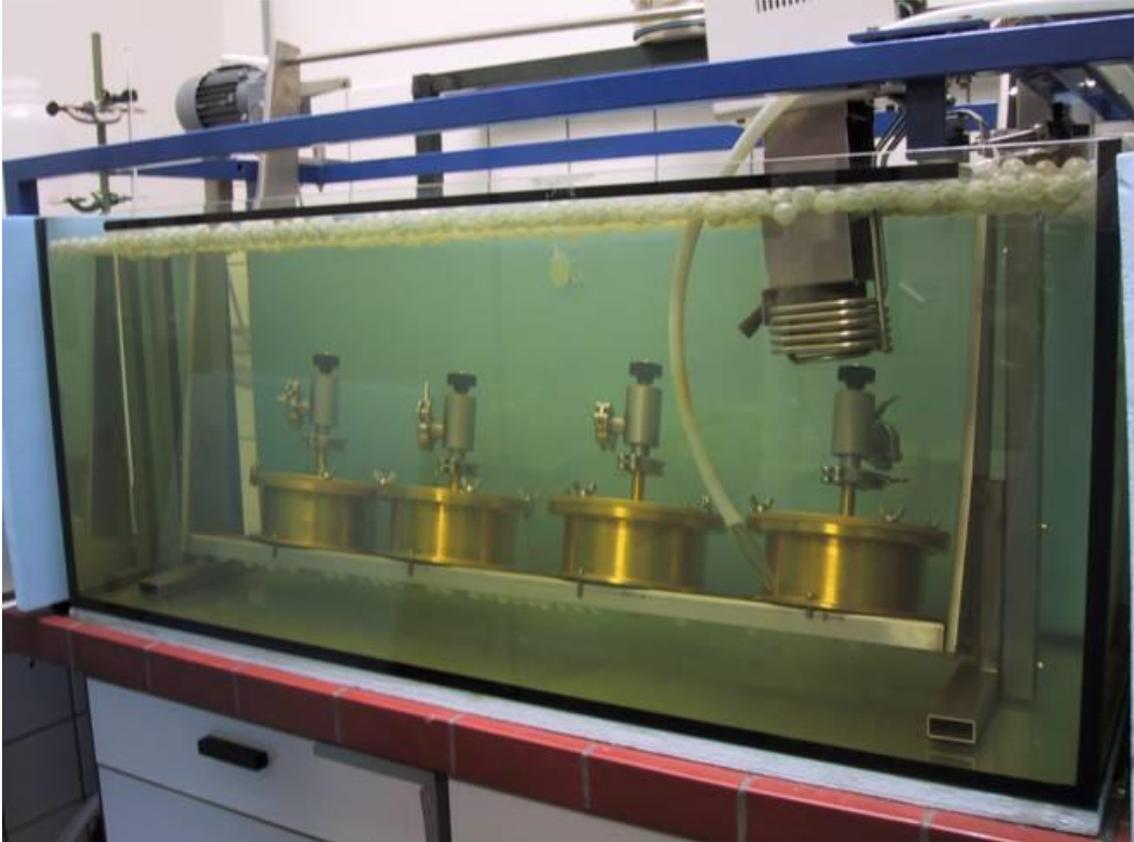


Fig. 2.2 Experimental set up for isopiestic measurements up to 40 °C

For higher temperatures the vessels were stored in tempered ovens at the required temperature. For temperatures above 25 °C the vessel itself had to be redesigned. To avoid condensation of steam in the equilibrated solutions upon cooling it had to be ensured that each cup inside the vessel be tightly closed prior to the removal from the oven (or the water bath at 40 °C, respectively). To accomplish this, a second lid was installed inside the vessel, just above the cups, which on its lower side was covered with a special rubber. Upon removal from the tempered environment, the second lid was lowered immediately using rods going through the first lid and being tightened to keep the vessels airtight.

As it was anticipated the equilibration at higher temperatures should proceed quicker than at 25 °C, the vessels were not rocked inside the ovens (at temperatures higher than 40 °C). However, especially with ferrous sulfate systems, it turned out, that equilibration was extremely sluggish. To accelerate the process, a device was installed inside the ovens to exert a gentle rocking motion on the vessels.



Fig. 2.3 View inside an oven

The isopiestic vessel rests on a metallic board which is connected through an arrangement of rods with a motor at the outside of an oven.



Fig. 2.4 This picture shows a motor fixed at the outside of an oven to exert a gentle rocking motion to the board on which the isopiestic vessels rest

For the project presented here isopiestic measurements at 40, 60 and 90 °C between 0.5 and 2.1 mol/kg FeSO_4 were conducted. Binary stock solutions were prepared from analytical grade suprapur chemicals. Ferrous chloride and -sulfate solutions were prepared by reacting metallic iron with hydrochloric acid or sulfuric acid, respectively. Tertiary solutions were produced by mixing binary solutions in the cups, placed on a balance in a glove box. The compositions of equilibrated solutions were determined by reweighing, taking buoyancy into account. Each cup was visually inspected for clues as to oxidation of the solution, or droplets occurring at the surface of the rubber.

2.3 Solubility experiments

Solubility experiments focused on the binary system Fe(II)-SO_4 . For this purpose special glass vessels were fabricated, as shown in the following figure.

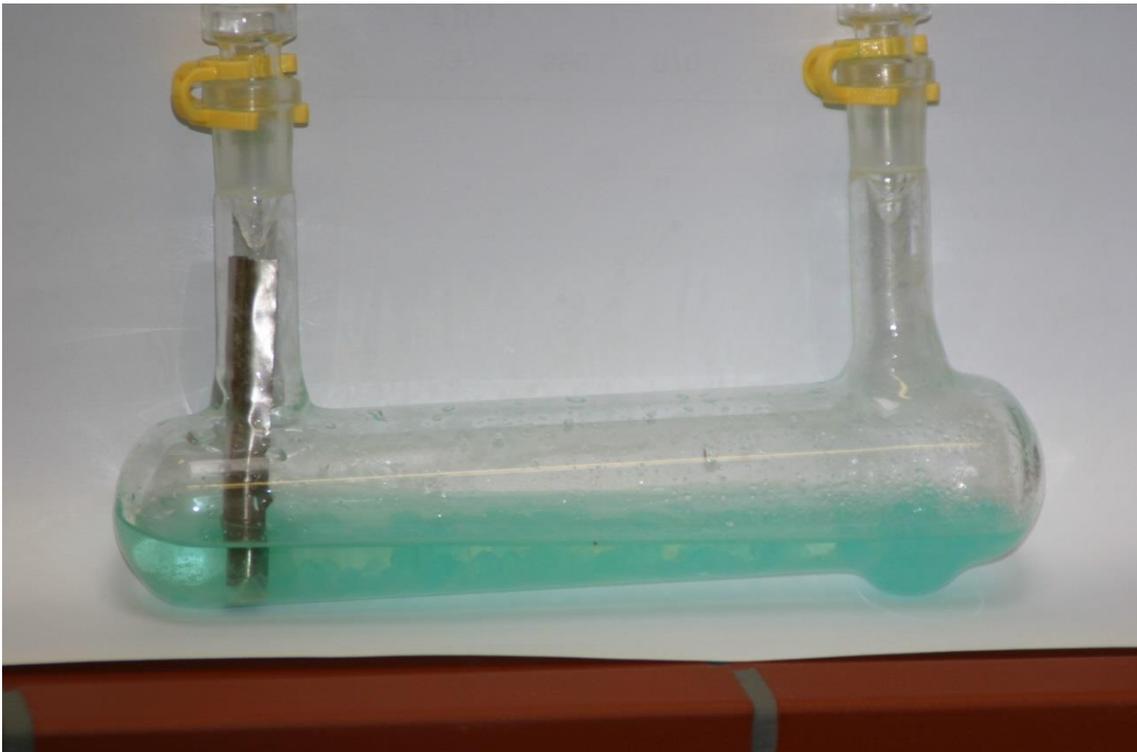


Fig. 2.5 Glass vessel for solubility experiments

Inside the vessel cyan-colored crystals of melanterite can be seen

The glass vessels were equipped with two necks. One neck was used to immerse a Pd-slab, loaded with hydrogen prior to the experiment. This measure ensured reliable, continuous reducing conditions within the vessels. The experiments with ferrous sulfate, due to the very long times necessary for equilibration, generally were run over many months, and our experience with this method is very positive. It was possible to stabilize the solutions over the entire duration of experiment. Sampling was done through the second neck, using a syringe, while through the first neck a gentle stream of Ar was passed through the vessel.

The vessels were immersed in an oil bath. To enhance insulation the necks were muffled.



Fig. 2.6 Glass vessel for solubility experiments immersed in an oil bath

For the experiments ferrous sulfate was synthesized from reaction of elemental iron with sulfuric acid in an Ar atmosphere. Temperature was set as to gain the hydrate for the particular experiment, either $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{FeSO}_4 \cdot 1\text{H}_2\text{O}$. For further stabilization and to minimize the potential formation of ferrous hydroxide the solutions were acidified to $\text{pH} \sim 4$ with sulfuric acid.

3 Concepts and conventions

3.1 Temperature dependence of thermodynamic quantities

The standard molar Gibbs energy change for a given reaction at any temperature is given by:

$$\Delta_r G^0(T) = \Delta_r H^0(T) - T\Delta_r S^0(T) \quad (3.1)$$

The temperature dependence of the Gibbs energy is:

$$\left(\frac{\partial \Delta_r G^0}{\partial T}\right)_p = -\Delta_r S^0(T) \quad (3.2)$$

From the Gibbs-Helmholtz equation, on the other hand, we have:

$$\left(\frac{\partial \Delta_r G^0/T}{\partial T}\right)_p = \frac{-\Delta_r H^0(T)}{T^2} \quad (3.3)$$

The temperature dependences of the molar enthalpy and entropy are given by:

$$\left(\frac{\partial \Delta_r H^0}{\partial T}\right)_p = \Delta_r C_p^0(T); \quad \left(\frac{\partial \Delta_r S^0}{\partial T}\right)_p = \frac{\Delta_r C_p^0(T)}{T} \quad (3.4)$$

After integrating (3.2), (3.3) and (3.4) and introducing them in (3.1), we get:

$$\Delta_r G^0(T) = \Delta_r G^0(T_0) + \int_{T_0}^T \Delta_r C_p^0 dT - T \int_{T_0}^T \frac{\Delta_r C_p^0}{T} dT - (T - T_0)\Delta_r S^0(T_0) \quad (3.5)$$

Reaction constants can be calculated at temperatures different from 298.15 K by extrapolating the standard molar Gibbs energy change according to eq. (3.5). This is only possible, when $\Delta_r S^0(T_0)$, $\Delta_r G^0(T_0)$ or $\Delta_r H^0(T_0)$ and $C_p^0(T)$ are known. The molar heat capacity of reaction species not involving phase transitions is generally expressed by the following dependency:

$$C_p^0(T) = a + bT + cT^2 + jT^3 + d \frac{1}{T} + e \frac{1}{T^2} + k \frac{1}{T^3} + f \ln T + g T \ln T + h \sqrt{T} + i \frac{1}{\sqrt{T}} \quad (3.6)$$

For the temperature region investigated in this work, only few of these coefficients will be required: a, b, c and e.

Thermodynamic properties of ionic species are referred to the hydrogen ion convention, according to which standard partial molar Gibbs energy of formation, entropy and heat capacity of H^+ are set equal to zero at all temperatures. In addition, this convention assumes that $\Delta_f G^0(H^+, aq, T) = 0$. This implies that $\Delta_f S^0(H^+, aq, T) = 0$ and $\Delta_f H^0(H^+, aq, T) = 0$. For calculating the standard entropy of ions other than H^+ according to this convention, the following relation is derived from the formation reaction of hydrogen ion, $\frac{1}{2} H_2(g) \rightarrow H^+ + e^-$:

$$\Delta_f S^0(H^+, aq, T) = S^0(H^+, aq, T) + S^0(e^-, T) - \frac{1}{2} S^0(H_2, g, T) = 0 \quad (3.7)$$

Therefore, according to the convention: $S^0(e^-, T) = \frac{1}{2} S^0(H_2, g, T)$. At 298.15 K and 1 bar, a value of $65.34 \text{ J K}^{-1} \text{ mol}^{-1}$ is extracted from /NEA 1995/. Thus, the temperature dependency of the standard partial molar Gibbs energy of formation can be expressed as:

$$\Delta_f G^0(T) = \Delta_f G^0(T_0) + \int_{T_0}^T \Delta_f C_p^0 dT - T \int_{T_0}^T \frac{\Delta_f C_p^0}{T} dT - (T - T_0) \Delta_f S^0(T_0) \quad (3.8)$$

where

$$\Delta_f S_i^0(T_0) = S_i^0(T_0) + \frac{z}{2} S^0(H_2, g, T_0) - \sum_i \frac{\nu_j}{\nu_i} S_j^0(T_0) \quad (3.9)$$

is a general expression for the calculation of the formation entropy of an ion i where z is the charge of phase constituent (including sign!), ν_j : stoichiometric coefficient and ν_i : stoichiometric coefficient of the element in its reference state (e. g. "2" for O_2). To compare the prediction of thermodynamic data at temperatures different from 298.15 K calculated from experimental data of different reports, the interconversion of thermodynamic data is necessary. This requires adopting in some cases selected auxiliary data, which are listed in Tab. A.1.

3.2 The Pitzer theory

The Pitzer model describes the thermodynamic behavior of electrolyte solutions at high ionic strengths by adding a term accounting for non-electrostatic ion interactions to the expression extended Debye-Hückel equation for the free excess energy:

$$\frac{G^{ex}}{kg_wRT} = f(I) + \sum_{i,j} \lambda_{ij}(I) m_i m_j + \sum_{i,j,k} \mu_{ijk} m_i m_j m_k \quad (3.10)$$

where m_i is the molality of the species i and $f(I)$ is a function of the ionic strength. $\lambda_{ij}(I)$ is the ionic-strength dependent interaction parameter of pairs of species and μ_{ijk} is a concentration independent ternary interaction parameter for ion-triplets. The derivative of function (3.10) leads to expressions of activity and osmotic coefficients of the form:

$$Y_s = f_s(I) + f_s[\alpha_{ij}^{(1)}, \alpha_{ij}^{(2)}, \beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}, C_{ij}^\phi, \theta_{ii}, \Psi_{ijk}] \quad (3.11)$$

where $Y_s: \phi, \ln \gamma_i$. Pitzer equations (3.11) are linear with respect to the unknown interaction parameters and can be written for each individual data set as:

$$Y_n = \sum_i A_{n,P_i} P_i + C_n \quad (3.12)$$

where each A_{n,P_i} is the constant prefactor in the n th data set for the Pitzer parameter P_i and C_n is a constant. The adjustment of semi-empirical Pitzer equations (3.11) to the experimentally accessible quantities was made by minimization of the sum of the relative error:

$$E = \sum_i (\sum_j \frac{A_{i,j} P_j}{Y_i} + \frac{C_i}{Y_i} - 1)_i \quad (3.13)$$

by the generalized reduced gradient method.

The interaction of the investigated Fe(II) with the hexary oceanic system can be graphically represented by an octahedron, the vertices of which are assigned to cations and ions of the oceanic system, while Fe(II) is placed in the center. Inner triangles represent the interaction of ionic triplets; the edges indicate binary interactions. The task is to construct the inner facets by quantifying the interactions of two binary and nine ternary systems containing Fe(II).

Interaction Pitzer parameters and solubility constants of minerals belonging to the hex-ary oceanic salt system were taken from the THEREDA data base.

The temperature dependence of Pitzer parameters and solubility constants was expressed by the generalized function:

$$Y(T) = Y(T_0) + a \left(\frac{1}{T} - \frac{1}{T_0} \right) + b \ln \left(\frac{T}{T_0} \right) + c(T - T_0) \quad (3.14)$$

where $Y(T)$: $\beta_{ij}^{(0)}(T)$, $\beta_{ij}^{(1)}(T)$, $\beta_{ij}^{(2)}(T)$, C_{ij}^ϕ , $\theta_{ii}(T)$, $\Psi_{ijk}(T)$; $\ln K(T)$, and

$$T_0 = 298.15 \text{ K.}$$

This temperature expansion suits very well in the range of investigated temperatures.

4 Speciation Model

The consideration of complex species in the modeling of iron solutions, though important, would complicate extremely the computing of experimental data: binary systems, for instance, become ternary or of higher order. In geochemical modeling, one of the most pursued goals is the prediction of solid-solution equilibrium at predetermined chemical solution compositions. This can be made by regarding the salt solution as a binary system and the speciation as a particular case of ionic interaction, which can be still treated by the Pitzer formalism. Thus, the formation of iron complexes such as FeA^+ and FeA^{+2} , FeA_2^0 , FeA_2^+ and FeA_3^0 (A: Cl, SO_4) would be equivalent in the Pitzer theory to a statistical predominance of these atom groups arising from ion-pair formation.

Selected formation constants for ferric and ferrous iron are given in the following table. As can be seen the formation of hydroxo-complexes requires a special treatment. Revised Pourbaix diagrams for the Fe- H_2O system published by Beverskog and Puigdomenech /BEV 1996/ let infer that the complexes $\text{Fe}(\text{OH})^{+2}$, $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_3^0$ for Fe(III) and FeOH^+ for Fe(II) are the most relevant for the modeling of near neutral and light acid Fe(III) containing brines. In contrast, comparing the Gibbs free energy of reaction for the formation of hydroxyl-complexes with those for salt anion complexes, it can be inferred, that the hydrolysis of Fe^{2+} can in principle be neglected in the modeling of Fe(II) salt solutions in conditions such as those found in salt rock repositories.

Tab. 4.1 Thermodynamic properties of formation reactions (taken from ref. /HUM 1992/)

Reaction	$\Delta_r G^0$ [kJ mol ⁻¹]	$\Delta_r H^0$ [kJ mol ⁻¹]	$\Delta_r S^0$ [kJ mol ⁻¹]
$\text{Fe}^{2+} + \text{Cl}^- \rightarrow \text{FeCl}^+$	-0.799	-	-
$\text{Fe}^{2+} + \text{SO}_4^{2-} \rightarrow \text{Fe}(\text{SO})_4$	-12.843	13.514	88.403
$\text{Fe}^{3+} + \text{Cl}^- \rightarrow \text{FeCl}^{2+}$	-8.448	23.432	106.924
$\text{Fe}^{3+} + 2\text{Cl}^- \rightarrow \text{FeCl}_2^+$	-12.158	-	-
$\text{Fe}^{3+} + \text{SO}_4^{2-} \rightarrow \text{Fe}(\text{SO})_4^+$	-23.060	16.360	132.219
$\text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{FeOH}^+ + 2\text{H}^+$	54.226	55.229	3.362
$\text{Fe}^{3+} + 2 \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_2^+ + 2\text{H}^+$	32.365	71.548	131.420
$\text{Fe}^{3+} + 3 \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + 3\text{H}^+$	71.693	103.764	107.568
$\text{Fe}^{3+} + 2 \text{SO}_4^{2-} \rightarrow \text{Fe}(\text{SO})_2^-$	-30.709	19.248	167.556

5 Results from Corrosion Experiments

The most important corrosion products found were hematite (Fe_2O_3) and Maghemite ($\gamma\text{-Fe}_2\text{O}_3$). Akageneite $\text{Fe}^{3+}\text{O}(\text{OH},\text{Cl})$ (also referred to as β - FeOOH) and green rust were found in about half of the samples. While hematite, Maghemite, and Akageneite are purely ferric solid phases, green rust, also known as fougurite, contains both ferric and ferrous iron. The composition may be thought of $[\text{Fe}^{\text{II}}_3 \text{Fe}^{\text{III}} (\text{OH})_8]^+ [\text{Cl} \cdot \text{H}_2 \text{O}]^-$ and has a brucite-like structure. It is formed from intermediary formed ferrous hydroxide and is stable only in the absence of oxygen in chloride-rich solutions. Lepidocrocite ($\gamma\text{-FeO}(\text{OH})$) has a boehmite-like structure and is found in three samples only, but in significant proportions. In accordance with theoretical considerations as to their Eh-pH-stability domain, samples either contained lepidocrocite or green rust, but never both. Generally, green rust in the presence of oxygen would react to goethite (α - FeOOH), akageneite (β - FeOOH), or lepidocrocite ($\gamma\text{-FeO}(\text{OH})$), or magnetite, the precise composition depending on the composition of the solution in terms of anions, namely chloride or carbonate. Contrary to findings of Smailos /SMA 1993/ neither amakinite $[(\text{Fe}^{\text{II}}, \text{Mg})(\text{OH})_2]$ nor hibbingite $[(\text{Fe}^{\text{II}}, \text{Mg})_2(\text{OH})_3\text{Cl}]$ were found in any sample, including Q-brine. For this reason, further efforts to study amakinite and hibbingite in high-saline solution, were abandoned.

6 The System Fe(II)-Cl-H₂O

6.1 Data related to vapor pressure

For this system, Moog et al. /MOO 2004/ have reported a compilation of osmotic coefficient data taken from an extensive literature revision at 25 °C, which was completed with own experimental data obtained by using the isopiestic method. Measurements of vapor pressures of solutions at vapor-liquid equilibrium were reported by Susarev et al. /SUS 1976/ at temperatures from 40 °C to 100 °C. The data were adjusted to activity isotherms and correlated with a Clausius-Clapeyron type equation:

$$\log p = 8.9441 + 0.0097m - \frac{(2257.1+15m)}{T} \quad (6.1)$$

With m = concentration in mol kg⁻¹ water. Some data for rounded concentrations were obtained by interpolation of experimental isotherms and reported as a table (see Fig. 6.1). Kangro and Groeneveld /KANN 1962/ have reported similar measurements for 20 °C and 25 °C. Some additional isopiestic data were obtained from the binary ends of isopiestic experiments of ternary systems Fe-Na-Cl-H₂O and Fe-Ca-Cl-H₂O at 40 °C, 60 °C and 90 °C. These points show a good agreement of with those reported by Susarev et al. /SUS 1976/.

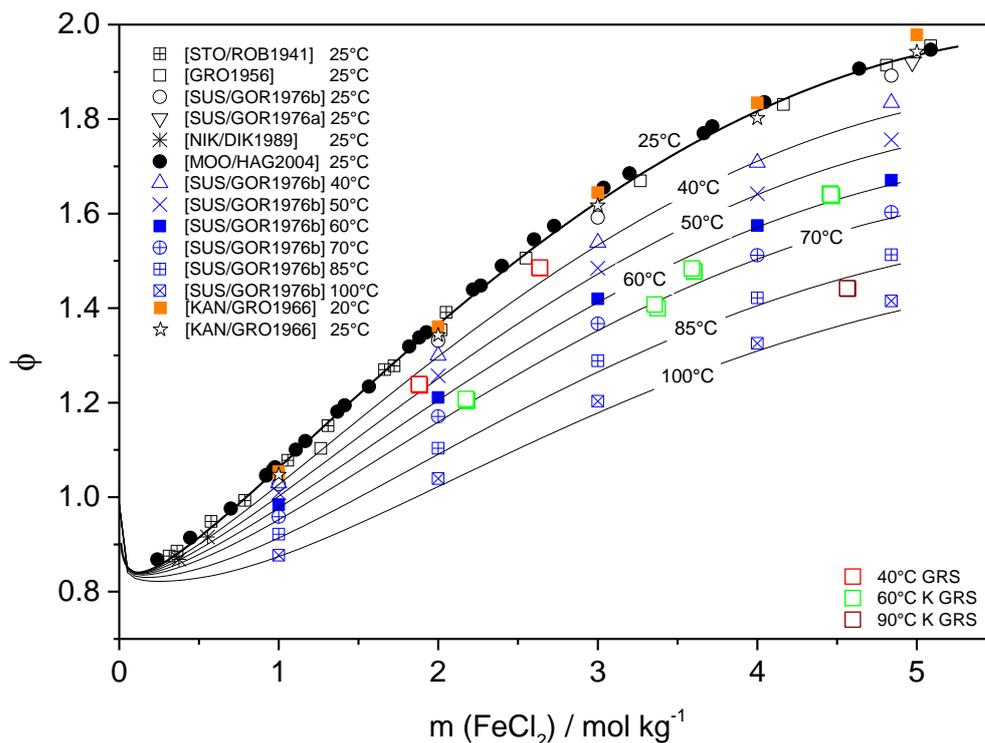


Fig. 6.1 Experimental (points) and calculated (lines) osmotic coefficients for the system $\text{FeCl}_2\text{-H}_2\text{O}$ at different temperatures

6.2 Data related to solubility

In contrast to the availability of isopiestic data, a large amount of solubility data was reported at temperatures higher and lower than 25 °C (see Fig. 6.2). One of the first solubility diagrams for the $\text{Fe-Cl-H}_2\text{O}$ system was determined by Schimmel /SCH 1928/. Two decades later, this author /SCH 1952/ published a study of saturated solutions of the ternary system $\text{FeCl}_2\text{-HCl-H}_2\text{O}$ at different temperatures, from which additional solubility data for the binary end were extracted. Chou and Phan /CHO 1985/ performed solubility experiments for the ternary system $\text{FeCl}_2\text{-NaCl-H}_2\text{O}$ at the temperature interval from 25 °C to 70 °C. They measured the solubility diagram of the binary system $\text{FeCl}_2\text{-H}_2\text{O}$ to calibrate their experimental method and compared it with data published by Schimmel /SCH 1928/. Additional points in the solubility diagram were obtained from the binary ends of a series of published studies of ternary systems /SCH 1949/, /OSA 1927/, /BUR 1975/, /LEG 1967/, /ZDA 1974/, //ATB 1996/, /BUR 1980/, /SHC 1971a/, /SHC 1971b/, /SHC 1964/ and /VID 1978/.

According to the reported data, three temperature domains defined by the stability of the different hydrate forms of iron chloride can be distinguished: At low temperatures (from 0 °C to about 14 °C) the hexahydrate is the stable solid phase in equilibrium with solution; at temperatures ranging from 14 °C to 75 °C, the tetrahydrate form forms and at higher temperatures, the dihydrate becomes the stable solid phase.

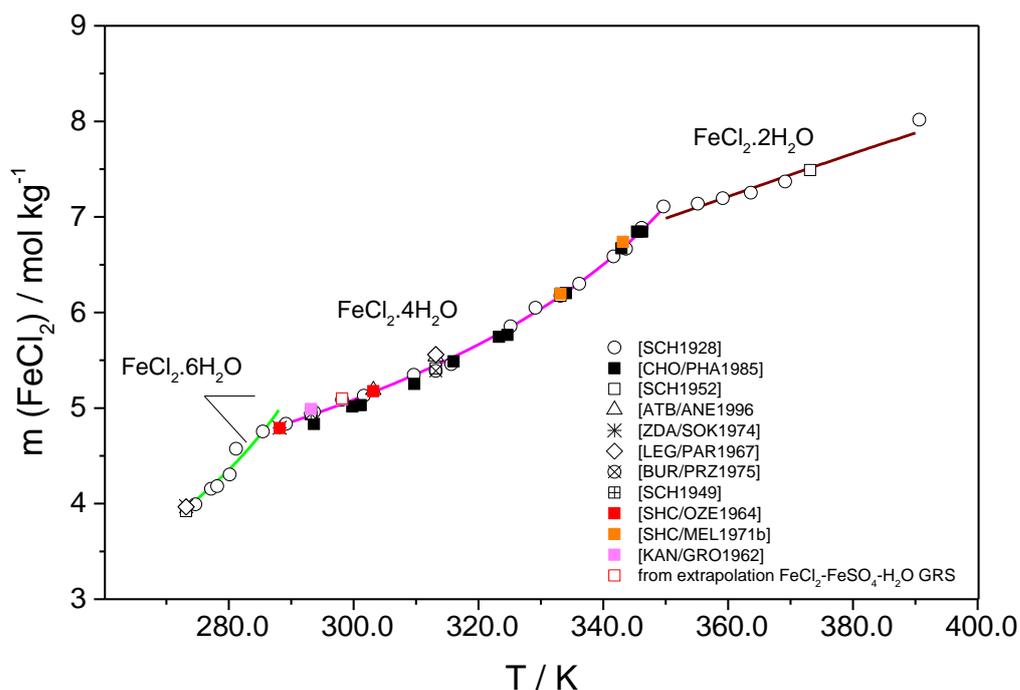


Fig. 6.2 Solubility-temperature diagram for the $\text{FeCl}_2\text{-H}_2\text{O}$ system

Lines: solubility curves calculated taking Pitzer parameters and solubility constants shown in Tab. 6.1 and Tab. 6.2

In a first approach, the temperature coefficients of Pitzer parameters were calculated using the experimental data reported by Schimmel /SCH 1928/. Some points in the Debye-Hückel concentration range ($m < 0.001 \text{ mol kg}^{-1}$) were also added to ensure that the curve of ϕ vs. m adopt the expected limit behavior at $m \rightarrow 0$. The temperature coefficients are listed in Tab. 6.1. The calculated curves reproduce very well the experimental data. The temperature functions were used for correlating the solubility data. Here, $\ln K(T_0)$ and the parameters a , b and c of $\ln K(T)$ (see eq. (3.14)) were taken as adjustable variables. A reasonable reproduction of the solubility diagram in the whole temperature range can be obtained and the temperature parameters of $\ln K$ are shown in Tab. 6.2.

Standard Gibbs energy changes, $\Delta_r G^0(T_0)$, of 15.941 kJ mol⁻¹, 17.068 kJ mol⁻¹ and 21.794 kJ mol⁻¹ for the formation reactions $\text{Fe}^{2+} + 2 \text{Cl}^- + 6\text{H}_2\text{O} \rightarrow \text{FeCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}^{2+} + 2 \text{Cl}^- + 4\text{H}_2\text{O} \rightarrow \text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}^{2+} + 2 \text{Cl}^- + 2\text{H}_2\text{O} \rightarrow \text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ respectively, can be calculated. Using auxiliary data from Tab. A.1, the standard Gibbs free energy of formation of hydrates, $\Delta_f G^0(T_0)$, can be calculated: $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$: -1759.86 kJ mol⁻¹, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$: -1284.46 kJ mol⁻¹ and $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$: -805.45 kJ mol⁻¹.

Values of the change of standard enthalpy for the formation reactions, $\Delta_r H^0(T_0)$, can be calculated by the relation:

$$\Delta_r H^0(T_0) = -RT^2 \left. \frac{\partial \left(\frac{\Delta_r G^0}{T} \right)}{\partial T} \right]_{T_0} = R[b + cT_0 - a] \quad (6.2)$$

Thus, values of the change of reaction enthalpy, $\Delta_r H^0(T_0)$, of -16.730 kJ mol⁻¹, 17.272 kJ mol⁻¹ and 27.467 kJ mol⁻¹ for the formation of $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ respectively were calculated. With the aid of auxiliary data, formation enthalpies of -2155.870 kJ mol⁻¹, -1550.207 kJ mol⁻¹ and 968.352 kJ mol⁻¹ for the hexa- tetra- and dihydrate respectively were calculated.

Tab. 6.1 Pitzer parameters at 298.15 K and their temperature coefficients calculated by regression of isopiestic data reported by Moog and Hagemann /MOO 2004/ and Susarev et al. /SUS 1976/ for the binary system FeCl_2 - H_2O . $\alpha^{(1)} = 2$, $\alpha^{(2)} = 0$, $\beta^{(2)} = 0$

Pitzer Parameter	298.15 K	a	b	c
$\beta^{(0)}$	0.37324	-0.00181	-0.53420	-0.00010
$\beta^{(1)}$	1.13499	-0.00223	0.36537	0.01570
C^\ominus	-0.0215243	0.07883	-0.00378	0.00013

Tab. 6.2 Dissociation constants (as $\ln K$) of iron chloride hydrates at 298.15 K and their temperature coefficients calculated by regression of solubility data using the Pitzer parameters shown in Tab. 6.1

Solid	298.15 K	a	b	c
FeCl ₂ ·6H ₂ O	6.43056	0.00024	-0.03174	0.02274
FeCl ₂ ·4H ₂ O	6.88533	0.00416	-0.65453	-0.02118
FeCl ₂ ·2H ₂ O	8.79169	0.00097	-0.17767	-0.03657

7 The System Fe(II)-SO₄-H₂O

7.1 Data related to vapor pressure

Undersaturated solutions were investigated with isopiestic experiments by Oykova and Balarew /OYK 1974/ and Nikolaev et al. /NIK 1989/. Furthermore there are isopiestic data from Moog and Hagemann /MOO 2004/. All data were determined at 25 °C. Oykova and Balarew /OYK 1974/ measured from 0.1 mol/kg to saturation, Nikolaev et al. /NIK 1989/ in the concentration range of 0.1 to 1.8 mol/kg. In both publications not the raw data were given for water activity; instead they were given for rounded values of molality. There is a large discrepancy between the given data. While water activity data of /OYK 1974/ show a minimum around 0.4 mol/kg with $a_w = 0.508$ followed by an increasing up to $a_w = 0.704$ at saturation, the water activity measured by /NIK 1989/ decreases up to $a_w = 0.392$ at 1.4 mol/kg FeSO₄ and increases to $a_w = 0.545$ at 1.8 mol/kg FeSO₄. Moog and Hagemann /MOO 2004/ measured at 1.4 and 1.5 mol/kg FeSO₄. Their results agree with the data given by Oykova and Balarew /OYK 1974/.

The discrepancy between the different measurements may be the result from different equilibration times. Nikolaev et al. /NIK 1989/ waited only 2 – 3 days, Oykova and Balarew /OYK 1974/ 10 – 15 days and Moog and Hagemann /MOO 2004/ several weeks. Since an equilibration time of more than a few days is necessary measurements of Oykova and Balarew /OYK 1974/ and Moog and Hagemann /MOO 2004/ are preferred.

Beside the isopiestic method direct vapor pressure measurements were used to investigate the water activity. Ojkova /OJK 1982/ and Ojkova and Panajotov /OJK 1978/ published the measured vapor pressure of the saturated solution at 25 °C. Both values agree with the isopiestic results. There are several temperature dependent measurements. One is given by Diesnis /DIE 1937/ who measured the vapor pressure of saturated FeSO₄ solutions between 18 and 32 °C. At 25 °C these measurements are in disagreement with the isopiestic measurements. Apelblat /APE 1993/ measured the vapor pressure of saturated FeSO₄ solutions between 7 and 32 °C. These data are obviously not reliable and excluded from parameter determination. Rudakoff et al. /RUD 1972/ measured the vapor pressure of a saturated FeSO₄ solution at 50 °C. The resulting water activity is questionable.

In case of the mentioned vapor pressure measurements on saturated solutions the FeSO_4 concentration was not specified. It was calculated from solubility experiments, which are described below. Results of isopiestic experiments and also of vapor pressure measurements except data of /APE 1993/ and /RUD 1972/ are plotted in Fig. 7.1. They are also listed in Tab. A.5.

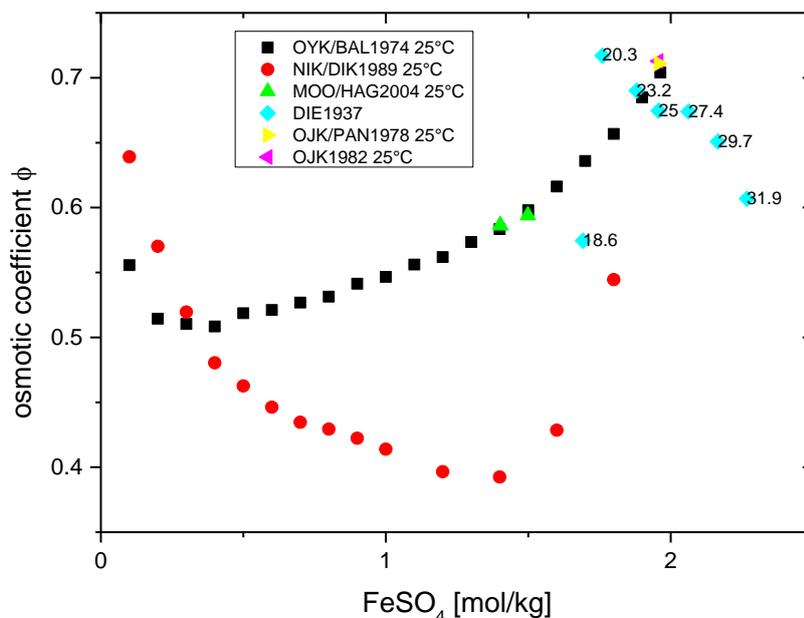


Fig. 7.1 Osmotic coefficient of the system $\text{FeSO}_4\text{-H}_2\text{O}$ at 25 °C, other temperatures are indicated

Own experiments to determine osmotic coefficients in this system at higher temperatures did not yield reliable results. In an initial phase of the project problems with the experimental set up had to be resolved, primarily to ensure the tightness of cup capping and to avoid sputtering of solutions in the cups. After all these difficulties were overcome, another severe problem particularly for sulfate bearing systems turned up: even after several months no equilibration could be ascertained and most of the results had to be discarded from further consideration. In a last effort towards the end of the project, the experimental set up was changed in that the equilibration vessels were slowly rocked to introduce a gentle agitation into the solutions. But even then solutions did not equilibrate. This phenomenon of sluggish equilibration turns up with the system $\text{FeSO}_4\text{-H}_2\text{O}$ and is also reported for other $\text{M}^{\text{II}}\text{-SO}_4\text{-H}_2\text{O}$ systems.

7.2 Data related to solubility

The solubility of FeSO_4 was determined by many researchers as it is shown in Fig. 7.2 and Tab. A.6. Between -2 and about 55 °C $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Melanterite, is the stable phase. Solubility data for FeSO_4 in water in this temperature range can be found in Belopol'skii and Urusov /BEL 1948/, Kobe and Frederickson /KOB 1956/, Schreinemakers /SCH 1910/, Occleshaw /OCC 1925/, Bursa and Przepiera /BUR 1975/, Legrand und Paris /LEG 1967/, Zdanovskij et al. /ZDA 1974/, Fraenckel /FRA 1907/, Wirth /WIR 1913a/, Ojkova and Makarow /OJK 1978/, Agde and Barkholt /AGD 1926/, Étard /ETA 1894/, Mulder /MUL 1860/, Tobler /TOB 1855/, Novoselova et al. /NOV 1953/, Kulikova and Druzhinin /KUL 1968/, Kononva and Redzhepov /KON 1996, KON 1996b/, Blidin and Andreeva /BLI 1958/, Balarew et al. /BAL 1973/, Mu et al. /MU 2006/, Gorshtein and Silantyeva /GOR 1953/, Družinin and Kajkiev /DRU 1960/, Legrand and Paris /LEG 1966/, Bursa et al. /BUR 1982a/, Bursa et al. /BUR 1982b/, Bursa et al. /BUR 1980/, and Balarew and Karaivanova /BAL 1975/. There are also some publications about solubility studies in ternary systems, for example H_2SO_4 - FeSO_4 - H_2O , (Bullough et al. /BUL 1952/, Belopol'skij and Kolyceva /BEL 1948/, Belopol'skij and Urusov /BEL 1948/, Cameron /CAM 1930/, McLaren White /MCL 1933/, and D'Ans and Freund /DAN 1960/) from which the solubility in pure water can be extrapolated. But since there are enough data for Melanterite without extrapolated this is not necessary.

Most of the data agree very well to each other but there are also exceptions. In older studies from the 18th century (/ETA 1894/ (> 50 °C), /MUL 1860/, /TOB 1855/) the major problem was the oxidation of Fe(II). But also some newer publications (/MU 2006/, /DRU 1960/, /BAL 1975/) had to be excluded from parameter determination since they did not agree with the other published data.

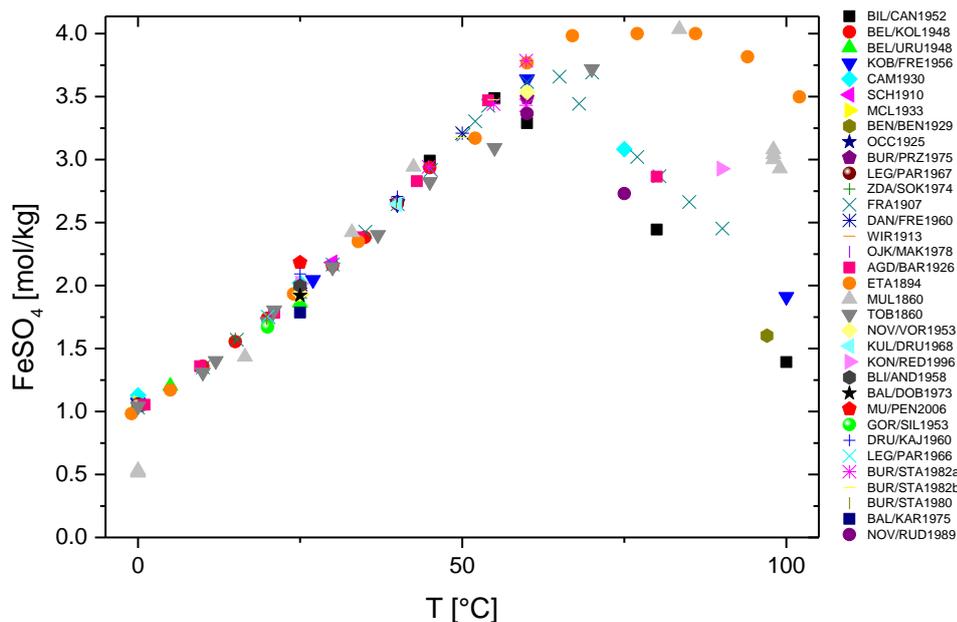


Fig. 7.2 Solubility of FeSO_4 in water: literature data

At temperatures above 55 °C two solids may be precipitated, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (Rozenite) and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ (Szomolnokite). $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ was observed by /BUR 1975/, /FRA 1907/, /NOV 1953/, and /BUR 1982a/ between 60 and 70 °C. Solubility studies of this work, described below, showed that the phase Rozenite is metastable and it converts slowly over years to the stable Szomolnokite.

The solubility of the monohydrated form was investigated by Kobe and Frederickson /KOB 1956/, Benrath and Benrath /BEN 1929/, Fraenckel /FRA 1907/, Agde and Barkholt /AGD 1926/, Étard /ETA 1894/, Kononova and Redzhepov /KON 1996b/, Bursa and Staniszl-Lewicka /BUR 1982a/ and Novikov et al. /NOV 1989/. Furthermore Bullough et al. /BUL 1952/ and Cameron /CAM 1930/ investigated the ternary system $\text{H}_2\text{SO}_4\text{-FeSO}_4\text{-H}_2\text{O}$. From these measurements the solubility of FeSO_4 in pure water was extrapolated.

Data of /ETA 1894/ and /KON 1996b/ agree with no other publication and are questionable. The other publications can be divided into two groups. One includes /FRA 1907/, /CAM 1930/, /AGD 1926/, and /KOB 1956/, the other /BUL 1952/, /BUR 1982a/, /NOV 1989/, and /BEN 1929/. Solubilities measured from the first group around Fraenckel /FRA 1907/ are somewhat lower than solubilities measured from the second group around Bullough et al. /BUL 1952/. The difference between the two groups is, that Fraenckel /FRA 1907/ and the other workers used Melanterite as starting material whereas Bullough et al. /BUL 1952/ and the other workers of the second

group started the experiment with Szomolnokite. The conversion of melanterite to Szomolnokite is a very slow reaction and takes according to Bullough et al. /BUL 1952/ several weeks. But the equilibration time in the studies of the “Fraenckel-group” was in the range of hours to a few days which is too short for a complete conversion. Therefore measurements of these publications are neglected by the calculation of Pitzer parameters.

Results of our solubility studies are also listed in Tab. A.6. For 44.8, 49.8, and 55.0 °C $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was used as starting material. During equilibration this phase did not change. The results agree very well with the mentioned literature data. For temperatures above 66 °C we used the monohydrate as starting material. The results are comparable with those of Bullough et al. /BUL 1952/ who also started the solubility experiments with Szomolnokite. For investigations at 58.0, 59.9, and 63.1 °C we began with Rozenite. In case of the two lower temperatures we waited six and four weeks, respectively. At the end of equilibration the phase we found was still Rozenite. At 63.1 °C in the first six weeks also no conversion could be observed. But in the following time the frequently controlled density changed. After half a year Szomolnokite was found beside Rozenite. After altogether two and a half year the conversion was complete for one of the two samples. This process can be seen in Fig. 7.3.

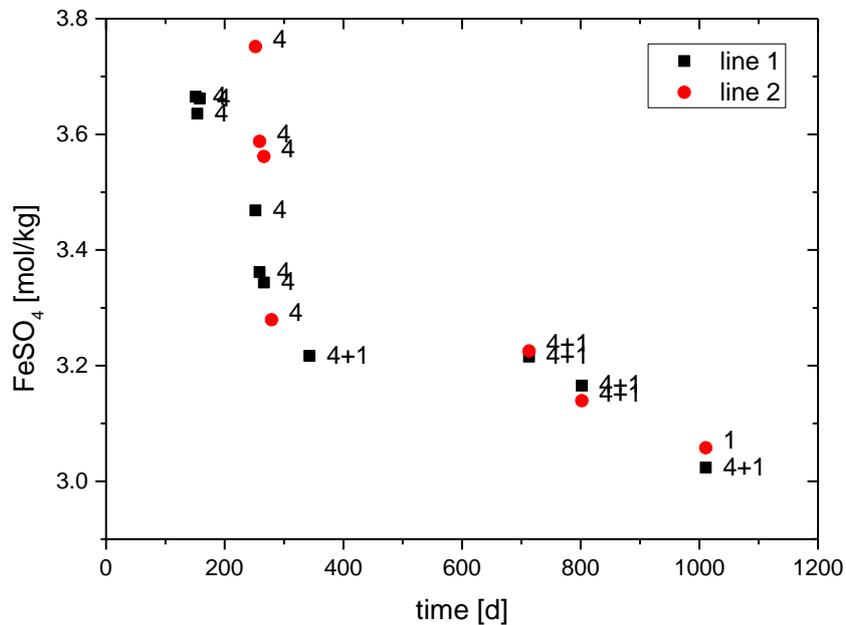


Fig. 7.3 Conversion of Rozenite to Szomolnokite at 63.1 °C

As can be seen in Fig. 7.2 scattering in the solubility data is considerable, due to slow attainment of equilibrium. After careful inspection of all available data, both from the literature and from own experiments, solubility data were identified, to be selected for further consideration. The data are shown in Fig. 7.4. From this figure and from our findings concerning the conversion of Rozenite to Szomolnokite we propose that Rozenite should be regarded as metastable phase for the purpose of thermodynamic equilibrium modeling.

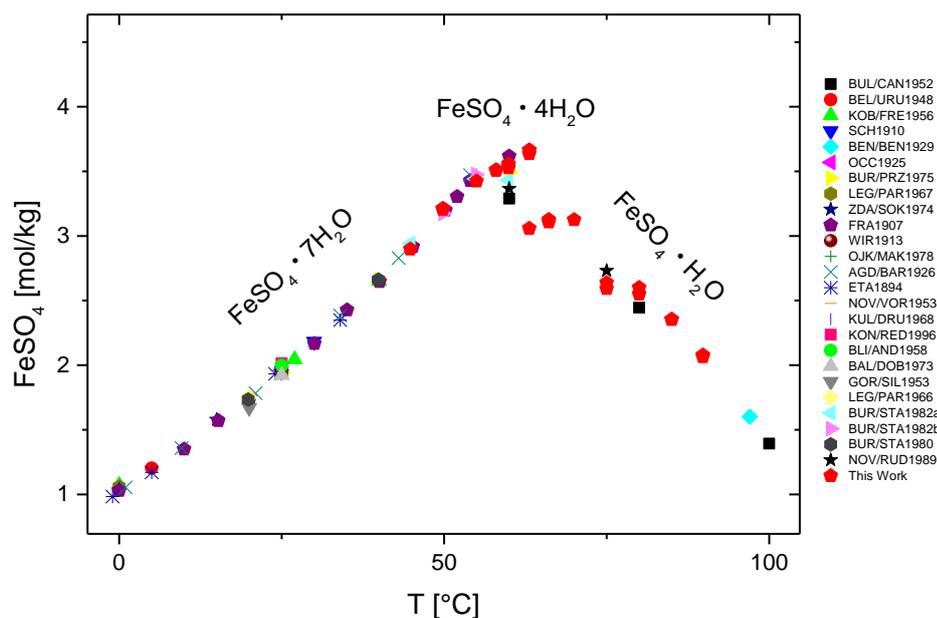


Fig. 7.4 Solubility data in the system FeSO₄-H₂O from literature and this work, to be selected for further consideration

Recently, Kobylin et al. /KOB 2011/ published their results about an extensive review of data concerning the binary ferrous sulfate system. Their results agree with ours with regard to the paucity of binary ferrous sulfate activity data. In fact, the solubility data as compiled in this report are more comprehensive. However, Kobelyn et al. in their work also processed other types of data for the derivation of Pitzer parameters. With regard to higher temperatures they included heat capacity data of ferrous sulfate solutions for up to 91.6 °C. Applying their set of Pitzer parameters to our data, even though they were not known to Kobylin et al., yielded a satisfiable agreement with our solubility data. As far as real activity data are concerned (which in this case means water activities) Kobylin et al. present few data between 18.6 and 31.9 °C, the course of which could not be reproduced well.

In the following table we document the Pitzer parameters given by Kobylin et al..

Tab. 7.1 Binary Pitzer parameters from /KOB 2011/ for the interaction $\text{Fe}^{2+} - \text{SO}_4^{2-}$ as temperature functions

For comparison the computed value for 298.15 K is compared to those from /MOO 2004/.
 $\alpha^{(1)} = 1.4$, $\alpha^{(2)} = 12$

	T^0	T	T^2	$1/T$	298.15 K	
					/KOB 2011/	/MOO 2004/
$\beta^{(0)}$	5.1934	-0.0161	0.000018349	-508.3	0.31944	0.28863
$\beta^{(1)}$	15.8514	0.0085	-6.0442E-05	-3205.3	2.26215	2.70661
$\beta^{(2)}$	-16.2142	0	0	0	-16.21420	-42
C^\ominus	-0.0588	0	0	12.8	-0.01587	0.00748

Note: values in table 6 in /KOB 2011/ must be multiplied with the factors given in the header line, and not with their reciprocal value!

8 The System Fe(II)-OH-H₂O

8.1 Thermodynamic properties

Formation energies for iron hydroxyl compounds were reported by Vasilenko /VAS 1981/ for 373 K, 473 K and 573 K (see Tab. 8.1). These data were calculated by modeling the solubility data of Fe(OH)₂ at temperatures between 25 °C and 300 °C by applying the Helmholtz relation (3.5) and a reaction schema involving the species: Fe(OH)₂ (aq), Fe²⁺(aq), FeOH⁺(aq), Fe(OH)₂ (s), Fe(OH)₃⁻ (aq) and OH⁻(aq). Mean partial molal heat capacities in the integration range were calculated by applying the correspondence method (see below).

Tab. 8.1 Thermodynamic data reported by /VAS 1981/

Species	S ⁰ (298 K) [J K ⁻¹ mol ⁻¹]	ΔG _f ⁰ (298 K) [kJ mol ⁻¹]	ΔG _f ⁰ (373 K) [kJ mol ⁻¹]	ΔG _f ⁰ (473 K) [kJ mol ⁻¹]	ΔG _f ⁰ (573 K) [kJ mol ⁻¹]
Fe(OH) ₂ (s)	87.5	-483.99	-491.28	-502.96	-513.72
Fe(OH) ₂ (aq)	44.97	-454.69	-455.36	-455.06	-451.8
Fe ²⁺	-108.44	-84.99	-76.83	-66.32	-56.4
FeOH ⁺	-35	-269.34			
OH ⁻	-10.55	-157.48	-155.5	-149.34	-139.09

Slobodov et al. /SOL 1988/ have calculated Gibbs energies of formation by using the Helmholtz relation (3.5) and mean partial molal heat capacities calculated by means the *correspondence principle* postulated by Criss and Cobble /CRI 1964/. This principle is based on the assumption that the ion entropy is mainly determined by solvent interactions and that the entropy of given groups of ions show analogous linear temperature dependencies with respect to a reference state, expressed as:

$$S^0(t_2) = a(t_2) + b(t_2)S^0(t_1) \quad (8.1)$$

The constants $a(t)$ and $b(t)$ are tabulated for different temperatures and ion-groups (simple cations, simple ions and OH⁻, oxyanions and acid oxyanions) in /CRI 1964/. The linearity condition is attained, provided the standard state entropy of H⁺(aq) is adjusted at each temperature.

According to eq. (8.1), the following expression for the mean partial molal heat capacity can be written:

$$\overline{C_p}^0 \Big|_{25}^{t_2} = \frac{a(t_2) - S^0(25)[1 - b(t_2)]}{\ln(T_2/298.15)} = \alpha(t_2) + \beta(t_2)S^0(25) \quad (8.2)$$

Tab. 8.2 Heat capacity constants corresponding to equation (8.2) in [J mol⁻¹K⁻¹] /CRI 1964/

Temperature [°C]	Cations		OH- and anions	
	$\alpha(t)$	$\beta(t)$	$\alpha(t)$	$\beta(t)$
60	146.53	-1.716	-192.59	-1.172
100	192.59	-2.302	-242.83	0.000
150	192.59	-2.470	-255.39	-0.126
200	209.34	-2.637	-272.14	-0.167

Slobodov et al. /SOL 1988/ were able to predict experimental solubility data of magnetite as a function of pH by using the estimated thermodynamic properties shown in Tab.

8.3.

Tab. 8.3 Thermodynamic data reported by /SOL 1988/

Values at T > 298.15 K were calculated by applying the correspondence principle

Species	S ⁰ (298 K) [J K ⁻¹ mol ⁻¹]	ΔG _f ⁰ [kJ mol ⁻¹]						
		T [K]						
		298.15	373.15	423.15	473.15	523.15	573.15	623.15
FeO	59.8	-251.2	-256.1	-259.8	-263.9	-208.2	-272.8	-277.6
Fe(OH) ₂	88	-486.2	-493.7	-499.5	-505.9	-512.9	-520.5	-528.5
Fe ²⁺	-106.6	-85.3	-73.2	-64	-53.7	-41.7	-26.2	0.7
FeOH ⁺	-33.4	-268.2	-264.3	-261.9	-259.5	-257.2	-254.8	-250.7
Fe(OH) ₂ (aq)	60.1	-438.6	-443.7	-447.6	-452.2	-457	-462.2	-467.6
H ⁺	0	0	2	3.9	6.4	9.8	15.5	28.4
OH ⁻	-10.71	-157.256	-157.417	-157.237	-156.683	-155.781	-154.18	-151.6
H ₂ O	69.95	-237.141	-243.037	-247.618	-252.643	-258.066	-263.84	-269.94

Beverkog and Puigdomenech /BEV 1996/ have reported Pourbaix diagrams of iron valid in the temperature range from 25 °C to 300 °C. The Gibbs reaction energies were calculated by taking a temperature function of C_p^0 extracted from a comprehensive literature revision and presented in the form: $C_p^0(T) = a + bT + cT^{-2}$ (see Tab. 8.4) and by applying equation (3.8). Values of $\Delta_f G^0(T_0)$ and $S^0(T_0)$ were taken from a careful selection of reported data. For aqueous species, the coefficient a was taken as the standard partial molar heat capacity at 25 °C, while the temperature function was calculated by the revised Helgeson-Kirkham-Flowers model (HKF) /HEL 1981/. Results for $T > 298.15$ K were reported in graphical form.

Tab. 8.4 Thermodynamic data for the Fe(II)-H₂O system as reported in /BEV 1996/

Species	ΔG_f^0 [kJ mol ⁻¹]	S^0 (298 K) [J K ⁻¹ mol ⁻¹]	C_p^0 [J K ⁻¹ mol ⁻¹]		
			a	b × 10 ³	c × 10 ⁻⁶
Fe(OH) ₂ (s)	-491.98	88	116.064	8.648	-2.874
Fe ²⁺	-91.88	-105.6	-2		
FeOH ⁺	-270.8	-120	450		
Fe(OH) ₂ (aq)	-447.43	-80	435		

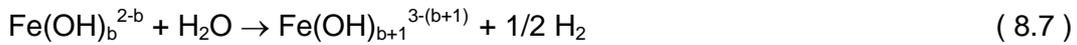
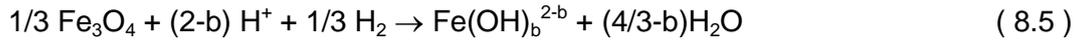
The HKF model considers the standard partial molal properties of ions as a combination of intrinsic properties and electrostriction contributions. The intrinsic properties, considered as not electrostatic, are determined by the interaction of the local solvent structure and the solvation of the ion. Solvation contributions, on the other hand, are modeled by a modified Born transfer equation, in which the electrostatic radius is a function of pressure and temperature. As a result of a long theoretical treatment /HEL 1974/, /HEL 1974b/, /HEL 1976/ /HEL 1981/ /SHO 1988/, the following semi-empiric equations for the Gibbs free energy and enthalpy of aqueous species results:

$$\begin{aligned}
 \Delta G^0 = & \Delta_f G^0 - S_{P_r, T_r}^0 (T - T_r) - c_1 \left[T \ln \left(\frac{T}{T_r} \right) - T + T_r \right] + a_1 (P - P_r) + \\
 & a_2 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) - c_2 \left\{ \left[\left(\frac{1}{T - \theta} \right) - \left(\frac{1}{T_r - \theta} \right) \right] \left(\frac{\theta - T}{\theta} \right) - \frac{T}{\theta^2} \ln \left(\frac{T_r (T - \theta)}{T (T_r - \theta)} \right) \right\} + \left(\frac{1}{T - \theta} \right) \left[a_3 (P - P_r) + \right. \\
 & \left. a_4 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right] + \omega \left(\frac{1}{\epsilon} - 1 \right) - \omega_{P_r, T_r} \left(\frac{1}{\epsilon_{P_r, T_r}} - 1 \right) + \omega_{P_r, T_r} Y_{P_r, T_r} (T - T_r) \quad (8.3)
 \end{aligned}$$

$$\begin{aligned}
\Delta H^0 = & \Delta_f H^0 - c_1(T - T_r) - c_2 \left[\left(\frac{1}{T-\theta} \right) - \left(\frac{1}{T_r-\theta} \right) \right] + a_1(P - P_r) + a_2 \ln \left(\frac{\Psi+P}{\Psi+P_r} \right) - \\
& \left(\frac{2T-\theta}{(T-\theta)^2} \right) \left[a_3(P - P_r) + a_4 \ln \left(\frac{\Psi+P}{\Psi+P_r} \right) \right] + \omega \left(\frac{1}{\epsilon} - 1 \right) + \omega T \gamma - T \left(\frac{1}{\epsilon} - 1 \right) \left(\frac{\partial \omega}{\partial T} \right)_P - \\
& \omega_{P_r, T_r} \left(\frac{1}{\epsilon_{P_r, T_r}} - 1 \right) - \omega_{P_r, T_r} T_r \gamma_{P_r, T_r} \quad (8.4)
\end{aligned}$$

where a_i ($i = 1..4$) and c_i ($i = 1..2$) are ion specific pressure- and temperature independent parameters. T_r and P_r refers to reference temperature and pressures, $\theta = 228$ K and $\psi = 2600$ bar /SHO 1988/. The ion parameters for the species Fe^{2+} , OH^- and FeOH^+ were taken from work of Shock et al. /SHO 1997/.

Tremaine and Leblanc /TRE 1980/ reported values of Gibbs free energy of formation, standard entropies and partial molal heat capacities (see Tab. 8.5 and Tab. 8.6) obtained by adjusting experimental magnetite solubility data at 373, 423, 473, 523 and 573°K to a model described by the following dissolution reactions:



The speciation of solution is described by the corresponding solubility constants given by:

$$m[\text{Fe}(\text{OH})_b^{Z-b}] = \frac{K_b^Z [a(\text{H}^+)]^{Z-b} p(\text{H}_2)^{\left(\frac{4}{3} - \frac{Z}{2}\right)}}{\gamma_{Z-b}} \quad (8.8)$$

where the activity coefficient γ_{Z-b} was calculated by using the extended Debye-Hückel equation. The Calculation of thermodynamic data was made under the assumption of a constant heat capacity of reaction, i. e.:

$$\begin{aligned}
-RT \ln K_b^Z = & \Delta_r G^0[\text{Fe}(\text{OH})_b^{Z-b}, T] \approx \\
& \Delta_r G^0[\text{Fe}(\text{OH})_b^{Z-b}, 298.15\text{K}] - \Delta_r S^0[\text{Fe}(\text{OH})_b^{Z-b}][T - 298.15] \quad (8.9)
\end{aligned}$$

From the adjustment of solubility data to the reaction scheme given by (8.5) and (8.6), the following thermodynamic data were derived:

Tab. 8.5 Thermodynamic data corresponding to reactions (8.5) and (8.6) as reported by /TRE 1980/

$\Delta_r S^0$ is a mean value over the temperature range 100 to 300 °C.

Species	$\Delta_r G^0$ (298 K) [kJ mol ⁻¹]	$\Delta_r S^0$ [J K ⁻¹ mol ⁻¹]
Fe ²⁺	-62.70±0.43	-51.53±3.29
FeOH ⁺	-4.30±1.77	-108.96±17
Fe(OH) ₂	56.03±0.78	-102.35±3.61

Tremaine and LeBlanc /TRE 1980/ calculated the values of $\Delta_r G^0$, S^0 and C_p^0 at 25 °C from the experimental reaction data shown in Tab. 8.5. Values of $\Delta_r G^0$ are shown in Tab. 8.6.

Tab. 8.6 Gibbs free energies of formation derived from experimental solubility experiments by /TRE 1980/

Species	$\Delta_f G^0$ [kJ mol ⁻¹]
Fe ²⁺	-88.92±0.53
FeOH ⁺	-268.0±4.9
Fe(OH) ₂	-441.0±0.8

The value of $\Delta_f G^0$ of -88.92 kJ mol⁻¹ for Fe²⁺ differs from the value of -90.536 kJ mol⁻¹, we adopted as auxiliary data. The authors had erroneously introduced a value of $S^0(T_0)$ and C_p^0 instead of $\Delta_r S^0$ and $\Delta_r C_p^0$ in expression (3.8) for the computing of experimental data. For instance, the reprocessing of the $\Delta_f G^0$ data with the corrected expression yields a formation entropy $\Delta_r S^0 = -2.037$ J K⁻¹mol⁻¹ ($S^0_{Fe^{2+}} = -101.36$ J K⁻¹mol⁻¹), a mean $\Delta_r C_p^0_{Fe^{2+}} = 188.06$ J K⁻¹mol⁻¹ and $\Delta_f G^0_{Fe^{2+}} = -88.92$ kJ mol⁻¹.

Nemer et al. /NEM 2011/ have reported values of solubility constants of Hibbingite, log K = 17.12 and Fe(OH)₂, log K = 12.95, in acid solutions and at 298.15 K according to the reactions:



respectively. These values were obtained by extrapolation to infinite dilution of the mass product measured for different ionic strengths. From the reaction (8.11) a value of $\Delta_f G^0 (298,15) = 491.94 \text{ kJ mol}^{-1}$ for $\text{Fe}(\text{OH})_2$ can be calculated from the reported solubility constant and the auxiliary thermodynamic data (as made by /NEM 2011/) from the work of Refait et al. /REM 2008/.

Leussing and Kolthoff /LEU 1953/ reported values of the dissociation constants for the species $\text{Fe}(\text{OH})_2$ and FeOH^+ at 25 °C of 8.00×10^{-16} ($\text{Fe}(\text{OH})_2 \rightarrow \text{Fe}^{2+} + 2\text{OH}^-$) and 4.00×10^{-10} ($\text{FeOH}^+ \rightarrow \text{Fe}^{2+} + \text{OH}^-$) respectively. Taking auxiliary data recommended in ref. /MOO 2004/, a value of $\Delta_f G^0 (298,15) = -491.19 \text{ kJ mol}^{-1}$ and $-301.40 \text{ kJ mol}^{-1}$ can be calculated for $\text{Fe}(\text{OH})_2$ and FeOH^+ respectively.

Johnson and Bauman /JOH 1978/ have determined the equilibrium constants for the reactions $\text{Fe}(\text{OH})_2 \rightarrow \text{Fe}^{2+} + 2\text{OH}^-$ and $\text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{FeOH}^+ + \text{H}^+$ by using a titration method. Values of $\log K = -14.39$ and -9.23 were reported for 298.15 K. Values of $\Delta_f G^0 (298,15) = -487.15 \text{ kJ mol}^{-1}$ and $\Delta_f G^0 (298,15) = -274.95 \text{ kJ mol}^{-1}$ can be calculated using auxiliary data recommended in /MOO 2004/. These authors carried out additional measurements of the equilibrium constants at 1 and 40 °C. From them, they calculated values of $\Delta_f H^0 (298,15) = 35 \text{ kJ mol}^{-1}$ and $19.67 \text{ kJ mol}^{-1}$ for the reactions indicated above respectively. Using auxiliary data reported in /NEA 1995/ and /VAS 1985/ (see CHI 2004), formation enthalpies $\Delta_f H^0 (298,15) = -531.46 \text{ kJ mol}^{-1}$ and $-341.93 \text{ kJ mol}^{-1}$ respectively can be calculated.

Sweeton and Baes /SWE 1970/ have performed solubility experiments of pure magnetite in alkaline to acid solutions at temperatures between 50 and 300 °C. From their results a temperature function for the equilibrium constant of the general dissolution equation (8.5) of the form:

$$-R \ln K_i(T) = -\frac{A_i}{T} + B_i[\ln(T) - 1] + D_i \quad (8.12)$$

was derived for each species i. The solubility was modeled considering the species Fe^{2+} , FeOH^+ , $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3^-$. The reported constants A_i , B_i and D_i are listed in Tab. 8.7.

Tab. 8.7 Constants for the temperature function (8.12) reported in /SWE 1970/

Species (i)	A _i	B _i	D _i
Fe ²⁺	-112.5298	0.04107	-0.34002
FeOH ⁺	-49.1260	0.01402	-0.17886
Fe(OH) ₂	19.3230	0	-0.09868

Zhuk /ZHU 1973/ has observed a linear correlation of the logarithm solubility constant of a series of slight soluble compounds with T^{-1} . For Fe(OH)₂, he has reported a solubility constant of 9×10^{-14} obtained by extrapolation of a value of 4.8×10^{-16} at 18 °C and 1.65×10^{-15} at 25 °C quoted in /SPR 1964/. Accordingly, values of the Gibbs free energy of reaction: 85.39 kJ mol⁻¹, 84.38 kJ mol⁻¹ and 80.71 kJ mol⁻¹ for 18, 25 and 50 °C can be calculated.

The present review shows that there are no direct measurements of the thermodynamic properties of iron species in neutral and acid solutions as a function of the temperature. Beverslog and Puigdomenech /BEV 1996/ introduced reliable temperature functions of heat capacity for the solid phases and used the HKF-Modell to predict the temperature dependence of the heat capacity of solution species upon modeling the solubility of magnetite. Reliable thermodynamic values for the system Fe(II)-OH-H₂O are listed in the following table.

Tab. 8.8 Selected thermodynamic data for the calculation of the temperature function of the Gibbs free energy of formation, $\Delta_f G^0(T)$, for species involved in the system Fe(II)-OH-H₂O

Species	$\Delta_f G^0(298,15K)$ [kJ mol ⁻¹]	$S^0(298,15K)$ [J mol ⁻¹ K ⁻¹]	C_p^0 [J mol ⁻¹ K ⁻¹]					Ref.
			a	b	c × 10 ⁻⁶	e × 10 ³	i	
Fe ²⁺ (aq)	-90.5±1.0	-101.6±3.7	-869.356	5.0433	-1.678×10 ⁻¹¹	-7.605		/PAR 1995/ Cp ⁰ : HKF-model
FeOH ⁺ (aq)	-270.80	-120.0	-816.317	3.744	16.17	-4.713		/BEV 1996/ Cp ⁰ : HKF-model
Fe(OH) ₂ (cr)	-491.96	87.864	116.064	8.648×10 ⁻³	-2.874	-	-	/CHA 1998/ Cp ⁰ : /BEV 1996/
Fe(cr)	0	27.28	28.18	-7.32×10 ⁻³	-0.290	25.04×10 ⁻³		/CHA 1998/
H ₂ (g)	0	130.680	32.086	-0.0073	-0.1388	5.555×10 ⁻³		/NEA 1995/ Cp ⁰ : /CHA 1998/
O ₂ (g)	0	161.059	29.531	-0.0058	-0.5×10 ⁻⁶	0.01796		/NEA 1995/ Cp ⁰ : /CHA 1998/
OH ⁻ (aq)	-157.220	-10.900	7187.272	-6.811	-1.329×10 ⁻⁹	-0.2160	-9.1348×10 ⁴	/NEA 1995/ Cp ⁰ : HKF-model
H ₂ O(l)	-237.140	69.950	53.5227	0.0093	1.0453	0.0822		/NEA 1995/ Cp ⁰ : /CHA 1998/

These data are consistent with the NEA-data **displayed** in Tab. A.1 with the exception of FeOH⁺(aq), which is not part of the NEA database. Coefficients for C_p⁰ refer to eq. (3.6).

8.2 Ionic interactions

There is, to the best of our knowledge, no published data of Pitzer parameters for the species FeOH^+ in solutions of the oceanic salt system. But, the concentration of the species FeOH^+ in concentrated solutions of salts of the oceanic system remains some orders of magnitude lower than the free cation concentration and thus its activity can be calculated by the temperature function of the hydrolysis constant and the activities of Fe^{2+} , H_2O and H^+ . Millero and Hawke /MIL 1992/ have developed a model for the estimation of activity coefficients of complexes of divalent metals based on a combination of the Pitzer and ion pairing model /MIL 1982/. From the main assumption of an equality of the activity coefficients of similar ion pairs with the same charge at the same ionic strength, the activity coefficient of a anion pair MX can be calculated from the equation:

$$\ln K_A^* = \ln K_A + Z_A^2 f^\gamma + B_A^0 \times I + f^1 B_A^1 + C_A \times I^2 = \ln K_A + \ln \frac{\gamma_M \times \gamma_X}{\gamma_{MX}} \quad (8.13)$$

where K_A^* and K_A are the stoichiometric and the thermodynamic stability constants respectively. B_A^0 , B_A^1 and C_A are constants containing Pitzer parameters and $Z_A^2 = Z_M^2 + Z_X^2 - Z_{MX}^2$. f^1 is the Debye-Hückel term given by:

$$f^\gamma = -A \left[\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2} \ln(1 + 1.2\sqrt{I}) \right] \quad (8.14)$$

and f^1 is a function of the ionic strength given by:

$$f^1 = 1 - \exp(-2\sqrt{I})(1 + 2\sqrt{I} - 2I) \quad (8.15)$$

γ_M and γ_X are the activity coefficients of the free cations and anions, which can be calculated by the modified Pitzer equation:

$$\ln \gamma_i = Z_i^2 f^\gamma + B_i^0 \times I + f^1 B_i^1 + C_i \times I^2 \quad (8.16)$$

introduced by Millero and Schreiber /MIL 1982/ by using the mean salt convention. This model was introduced to predict the activity of metal complexes in natural waters, where NaCl predominates in their compositions. Tab. 8.9 shows a list of coefficients extracted from the publication of Millero and Hawke /MIL 1992/ for the estimation of various relevant iron complex species.

Tab. 8.9 Coefficients for the estimation of activity coefficients of metal complexes (eq. (8.13) and (8.16))

Species	$\ln K_A$	Z_A^2	B_A^0	B_A^1	C_A
FeSO ₄	5.07	8.0	0.6344	1.5021	0.02449
FeHCO ₃ ⁺	3.38	4.0	-0.0777	0.9644	0.02487
FeCO ₃	12.54	8.0	0.7175	1.7668	0.02470
Fe(CO ₃) ₂ ²⁻	16.50	8.0	-0.4450	2.4528	0.01946
FeCl ⁺	0.74	4.0	0.5463	1.1868	0.02868
FeOH ⁺	10.34	4.0	1.3259	1.1734	0.03807
Fe(OH) ₂	17.01	6.0	1.3822	1.2661	0.04620
			B_i^0	B_i^1	C_i
Fe ²⁺			1.31964	1.08069	0.02994
Cl ⁻			0.0967	0.1061	-0.00126
OH ⁻			0.1363	0.0927	0.00813
SO ₄ ²⁻			-0.3664	0.4214	-0.00545
CO ₃ ²⁻			-0.3221	0.6861	-0.00524

9 The system Fe(II)-HCO₃-H₂O

This system actually was not part of the project FeT90, but is included here for two reasons. First, siderite represents an important solid phase of ferrous iron in natural systems. Second, a survey of available data in the literature had already been conducted in an earlier project. This chapter shortly describes some considerations and gives an account which data are going to be selected for the THEREDA database.

9.1 Short survey about literature with regard to Siderite

A value for the solubility constant of Siderite (FeCO₃) $\log K = -10.8 \pm 0.2$ was reported by Bruno et al. /BRU 1992/. This value was calculated from solubility experiments of Siderite at different pH's values and considering the formation of carbonate complexes: Fe(CO₃)₂²⁻ and FeCO₃(aq).

Taking a value of $\Delta_f G^\circ(\text{CO}_3^{2-}) = -527.899 \text{ kJ mol}^{-1}$ /NEA 1995/ and $\Delta_f G^\circ(\text{Fe}^{2+}) = -90.536 \text{ kJ mol}^{-1}$, a value of $\Delta_f G^\circ(\text{FeCO}_3) = -680.081 \text{ kJ mol}^{-1}$ can be calculated.

Chivot /CHI 2004/ recommended the thermodynamic values for Siderite compiled by Holland and Powell /HOL 1990/: $\Delta_f H^\circ = -761.18 \text{ kJ mol}^{-1}$, $S^\circ = 95.5 \text{ J K}^{-1} \text{ mol}^{-1}$ and $C_p^\circ = 82.3 \text{ J K}^{-1} \text{ mol}^{-1}$.

From a carefully revision of reported solubility data carried out by Preis and Gamsjäger /PRE 2002/ the following thermodynamic values result: $\Delta_f H^\circ = -752.0 \pm 1.2 \text{ kJ mol}^{-1}$, $S^\circ = 95.47 \pm 0.15 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta_f G^\circ = -678.9 \pm 1.2 \text{ kJ mol}^{-1}$.

The free Gibbs energy of formation was calculated as before, taking $\Delta_f G^\circ(\text{CO}_3^{2-}) = -527.899 \text{ kJ mol}^{-1}$ /NEA 1995/ and $\Delta_f G^\circ(\text{Fe}^{2+}) = -90.536 \text{ kJ mol}^{-1}$ /PAR 1995/.

The formation enthalpy calculated by Preis and Gamsjäger /PRE 2002/ from solubility experiments is very close to that determined by Chai and Navrotsky /CHA 1994/ from calorimetric measurements: $\Delta_f H^\circ = -750.6 \pm 1.1 \text{ kJ mol}^{-1}$.

More recently, Bénézech et al. /BEN 2009/ performed solubility experiments in the temperature region of 25 to 250 °C. From the regression of their experimental data results: $\log K(T/K) = 175.568 + 0.0139 \cdot T - 6738.483 \cdot T^{-1} - 67.898 \cdot \log T$ (FeCO₃(s) → Fe²⁺ + CO₃²⁻).

From this function, values of $\Delta_f H^\circ = -749.59 \pm 2 \text{ kJ mol}^{-1}$, $S^\circ = 109.54 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta_f G^\circ = -680.71 \pm 2 \text{ kJ mol}^{-1}$ were obtained.

The values of heat capacity at 298.15 K were found to be in agreement with those previously reported in /HOL 1990/, /CHA 1994/, and /PRE 2002/ and that reported by Wagman et al. /WAG 1982/ and Robie et al. /ROB 1984/ and Robie and Hemingway /ROB 1995/.

The value of entropy reported by Robie et al. /ROB 1984/, obtained from calorimetric experiments at low temperatures, should be preferred to that from calculated by Bénézech et al. /BEN 2009/ from the second derivative of the temperature function of the solubility constant versus the reciprocal of temperature.

A temperature function of the heat capacity for siderite was reported by Robie et al. /ROB 1984/ as $C_p^0(T) = 257.38 - 0.04620 \cdot T - 3081.9 \cdot T^{-0.5} + 1.523 \times 10^6 \cdot T^{-2}$ between 298.15 K and 600 K.

9.2 Speciation

Prior to the selection of thermodynamic data a decision is necessary as to the speciation of ferrous iron in carbonate-containing solutions. For the precipitation of siderite the following formation reaction is assumed:



Assuming this reaction only, however, cannot describe the dependence of solubility on pH and $p\text{CO}_2$. The following figure displays experimental data along with a calculation using a modified Nagra/PSI-database.

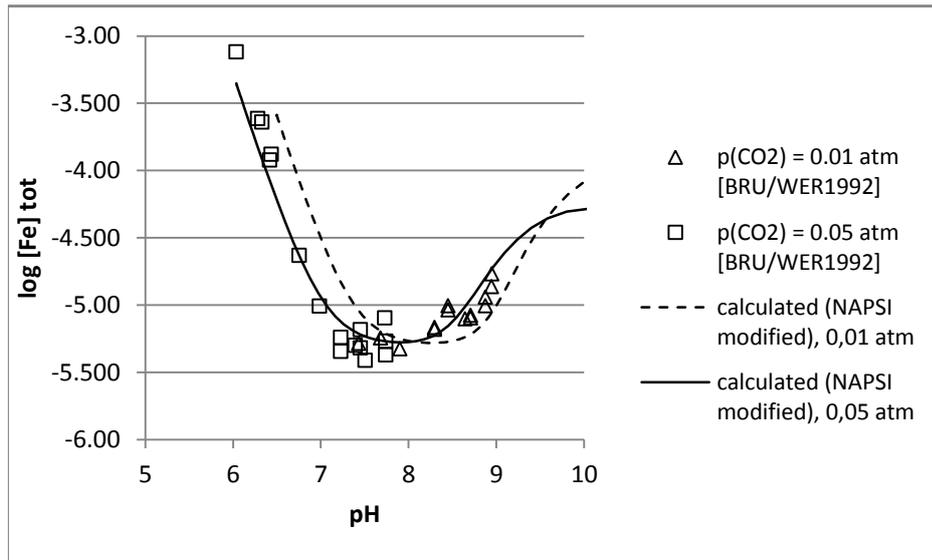


Fig. 9.1 Dependence of siderite solubility from pH and pCO_2 at 298.15 K

NAPSI = modified Nagra/PSI-database

The original Nagra/PSI-database contains a ferrous bicarbonate complex $Fe(HCO_3)^+$, whereas in the form presented here, the complexes $Fe(CO_3)^0$ and $Fe(CO_3)_2^{2-}$ were introduced. A closer inspection reveals that for total carbonate concentrations necessary to result in pH-values higher than 8.3 ionic strengths of higher than 0.05 M were calculated. At higher ionic strengths the extended Debye-Hückel equation is not valid anymore and thus SIT- or other approximations like the Pitzer-formalism would be necessary to calculate ionic activity corrections.

Given the experimental errors it was assumed for this data compilation, that ferrous iron speciates as Fe^{2+} and $Fe(CO_3)^0$. Pitzer parameters for the free ferrous iron can be adopted from other systems, described in this report, whereas Pitzer parameters for the interaction between ferrous iron and carbonate (or bicarbonate, resp.) are set zero. The rationale behind this is given by the very low total concentration of ferrous iron in a carbonate containing solution. As the Pitzer correction for activity coefficients essentially goes back to a summation of binary and ternary interactions with the molal concentrations of interacting ions as pre-factor, the contribution of ionic interactions between ferrous iron and carbonate (or bicarbonate, resp.) is negligible. The same holds true for possible interactions between the neutral ferrous carbonate complex and the main components of saline solutions.

The following figure depicts a calculation where the complex $Fe(CO_3)_2^{2-}$ is neglected. As could be expected the model is valid up to a pH of approximately 8.0, whereas the

observed increase in solubility due to the formation of the neglected complex cannot be represented.

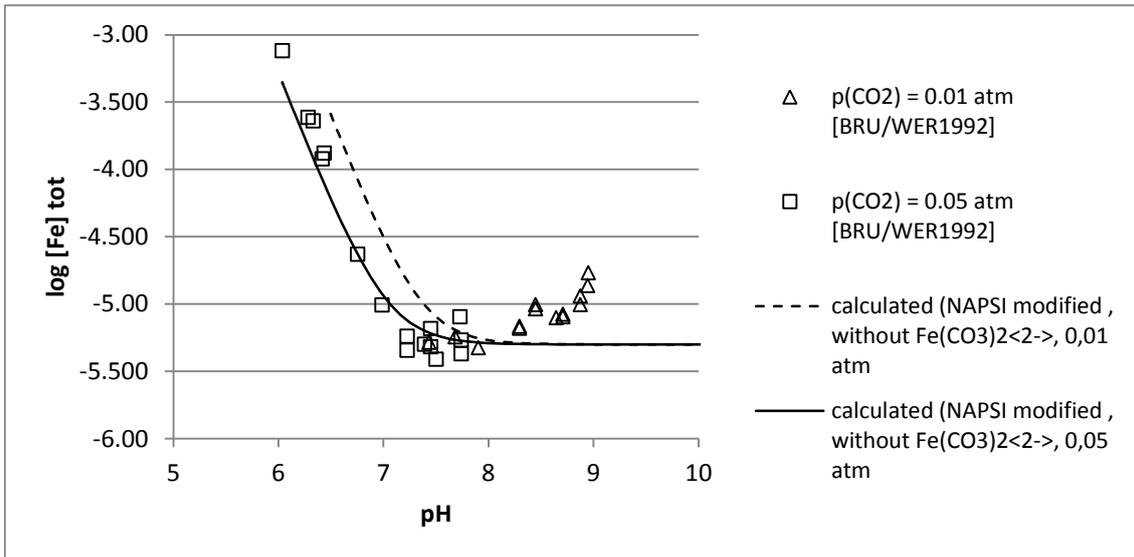


Fig. 9.2 Dependence of siderite solubility from pH and pCO₂ at 298.15 K

NAPSI = modified Nagra/PSI-database without Fe(CO₃)₂²⁻

As there are no data about the high-pH solubility in highly-saline solutions are available at the time being, no Pitzer parameters for Fe(CO₃)₂²⁻ can be calculated for such conditions, which is why for this compilation this complex is neglected.

The species FeCO₃(aq), however, must not be neglected. As is shown in the following figure, neglecting of this complex fails to represent the general correlation between pH and siderite solubility, given a particular pCO₂. This is not surprising, as higher pH leads to higher carbonate content in solution, thereby reducing the overall siderite solubility.

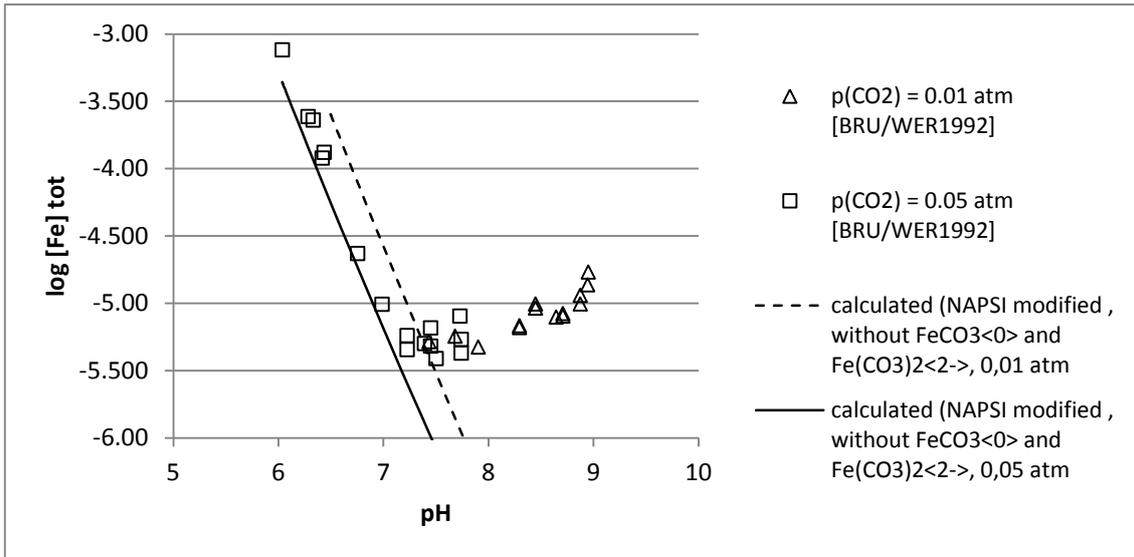


Fig. 9.3 Dependence of siderite solubility from pH and pCO₂ at 298.15 K

NAPSI = modified Nagra/PSI-database without FeCO₃(aq) and Fe(CO₃)₂²⁻

For thermodynamic data concerning FeCO₃(aq) we refer to a study conducted for ANDRA and the data of which went into the database THERMODDEM /BLA 2008, CHI 2004/. For the following reaction



the two principal data selected were logK = 5.69 /KIN 1998/ and $\Delta_r S = 89.6 \text{ J mol}^{-1} \text{ K}^{-1}$ /FOU 1984/.

From the stability constant the Standard Gibbs free energy of reaction can be calculated which together with the Standard entropy of reaction allows calculating the standard enthalpy of reaction. The latter quantity allows approximating the temperature dependence. In the THERMODDEM database this approximation is driven to temperatures as high as 300 °C. Given the fact that the respective formation reaction is not isocoumbic, this assumption seems questionable.

9.3 Solubility

Bénézech et al. did an extensive review on available literature and directly measured the temperature dependent solubility of siderite /BEN 2009/.

For the dissolution reaction



They obtained a temperature function of the general form

$$\log_{10}K = a + bT + \frac{c}{T} + d\log_{10}T \quad (9.4)$$

Where T is the temperature in Kelvin, and $a = 175.568$, $b = 0.0139$, $c = -6738.483$, and $d = -67.898$. As can be seen in the following figure the solubility of siderite decreases with increasing temperature (in fact, from 25 to 250 °C by one order of magnitude).

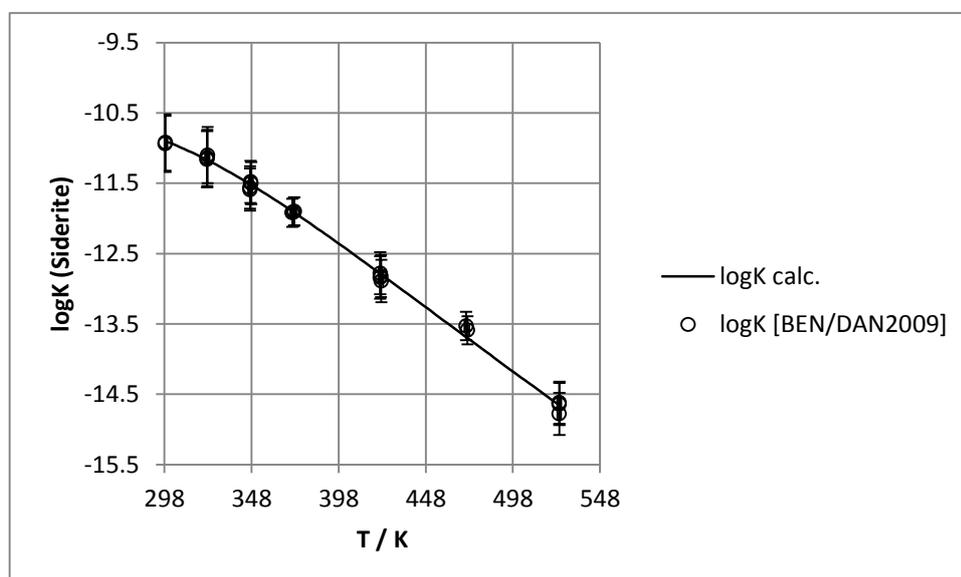


Fig. 9.4 Solubility constant of siderite as function of temperature

We regard this temperature function as principal source to subsequently calculate the standard enthalpy of formation $\Delta_f H^0$ (298.15 K), the standard entropy S^0 (298.15 K), and standard heat capacity C_p^0 (T). In /BEN 2009/ it is reported that following this calculation path and standard formation data given by /PAR 1995/, /SHO 1988/, /SHO 1997/ standard enthalpy of formation and heat capacity agrees well with earlier published data, whereas the standard entropy is somewhat higher.

9.4 High saline solutions

As the major contributions to the correction of activity coefficients for carbonate, bicarbonate, and ferrous iron stems from interactions with Na, K, Mg, Ca, Cl, and SO₄ it is a reasonable approximation to set Pitzer parameters for the interaction between ferrous iron and carbonate or bicarbonate to zero. Virtually no experimental data exist for the solubility of siderite in high-saline solutions at elevated temperatures, and a closer inspection would have been beyond the scope of the present study. However, the following example can serve to show what might be possible to calculate with the data of this report at hand.

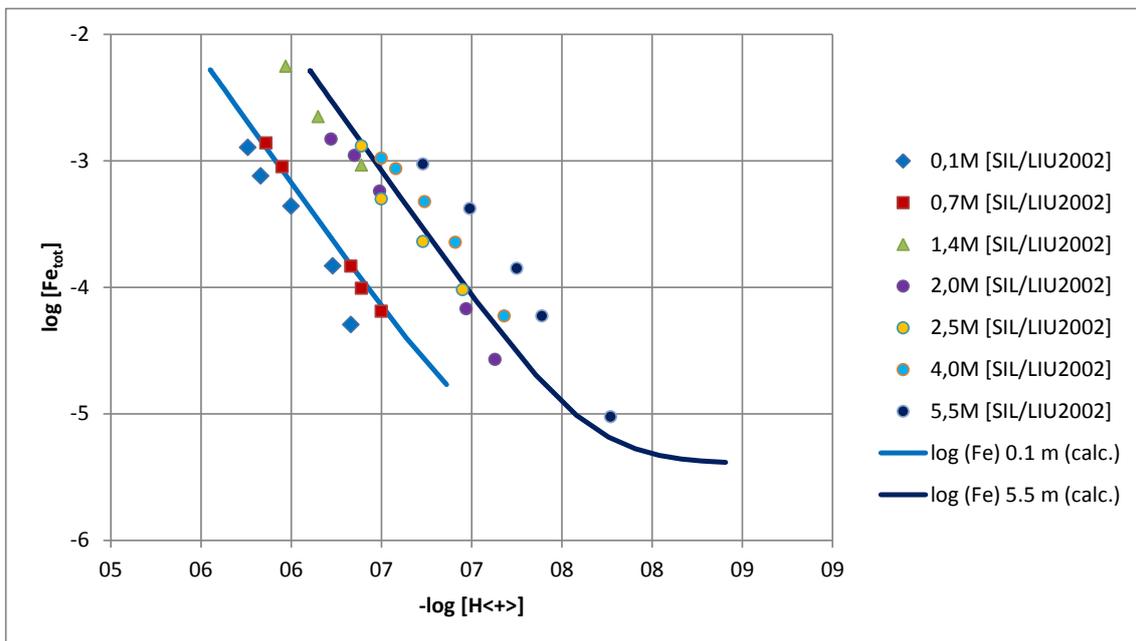


Fig. 9.5 Solubility of siderite in NaCl-solutions at 298.15 K

Silva et al. /SIL 2002/ determined the siderite solubility in NaCl solutions at a pCO₂ of 0.05 atm. Please note in the above figure that the x-axis is scaled in $-\log[H^+]$ which is the negative decadic logarithm of the molal hydrogen ion concentration, in /SIL 2002/ referred to as "pH"¹. Going from the lowest to the highest investigated NaCl-concentration (0.1 M → 5.5 M) we observe that the siderite solubility changes for about one order of magnitude. Second we note that at a given "pH" the siderite solubility in-

¹ In a first attempt the data by Silva and Liu were interpreted in terms of pH as indicated in their figure. It turned out that in our model calculations the relationship between siderite solubility and NaCl-concentrations was inverse to the observed one. Closer inspection of the publication revealed that the pH-electrode in the experiments of Silva and Liu was calibrated against hydrogen ion concentration.

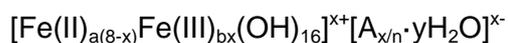
creases with increasing NaCl-concentration. This is a trend to be expected generally when dealing with mineral solubilities in high saline solutions. Considering the double logarithmic scaling the calculated solubilities do not match the experimental values very well. Unfortunately, Liu et al. do not state the accuracy of their ferrous iron analytics. However, they report the logarithmic iron concentration with a precision of three digits which appears too much.

Comparing the results for different $p\text{CO}_2$ and NaCl-concentration, it appears that the siderite solubility is much more sensitive to the first parameter.

10 Solid iron oxide phases

The nature and predominance of iron corrosion products in a salinary medium depends on the salinity, water content, pH and reducing/oxidizing strength. In this chapter, an overview of thermodynamic studies of iron oxides and their methods reported in the literature will be given for the sake of completeness. From this, reliable thermodynamic data were carefully selected and listed in Tab. 10.1.

Studies reported by Wang et al. /WAN 2001/ concerning the corrosion of mild steels in high concentrated brines of the WIPP (waste isolation pilot plant) under reducing conditions indicate the predominant of green rust as corrosion product. This compound can be described with the general formula



where A refers to Cl^- and SO_4^{2-} . The corrosion under anoxic conditions in artificial groundwater, on the other hand, leads to the formation of Fe(OH)_2 concomitant generation of hydrogen. Fe(OH)_2 forms magnetite (Fe_3O_4) by the Schikorr reaction /SMA 2002/ /SMA 2002b/:

$3\text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2 \text{H}_2\text{O} + \text{H}_2 \text{ (g)}$ (10.1) According to several studies concerning corrosion products formed at reactive barriers of zero-valent iron /ROH 2000/ /BLO 1997/ /PHI 2000/ /GU 1999/ /MAC 1999/ /FUR 2002/ the following iron compounds can be selected as possible authigenic minerals: Magnetite, Green Rust, Mackinawite (Fe_{1+x}S : $x = 0 - 0.11$), Calcite, Aragonite, Siderite (FeCO_3), Goethite ($\alpha\text{-FeOOH}$) and Lepidocrocite ($\gamma\text{-FeOOH}$). Following the generalized reaction scheme presented by King and Stroes-Gascoyne /KIN 2000/, the initial formation of Fe(OH)_2 under neutral and slightly alkaline condition continues with the conversion to different Green Rust products, Goethite, Lepidocrocite, Maghemite ($\gamma\text{-Fe}_2\text{O}_3$), Hematite ($\alpha\text{-Fe}_2\text{O}_3$) in an initial aerobic condition. Magnetite is the predominant product formed under anaerobic conditions and converts slowly to Maghemite.

For the magnetite, the revision reported by Chivot /CHI 2004/ recommended values of $\Delta_f G^0 = -1013.73 \text{ kJ mol}^{-1}$, $\Delta_f H^0 = -1115.548 \text{ kJ mol}^{-1}$, $S^0 = 152.5 \text{ J K}^{-1} \text{ mol}^{-1}$ as taken from the report by Haas et al. /HAA 1988/. These values do not differ largely from data published by Ziemak et al. /ZIE 1995/ and Hemingway /HEM 1990/. The value of $\Delta_f G^0 = -1013.73 \text{ kJ mol}^{-1}$ was internally calculated by taking $S_{\text{Fe}}^0 = 27.319 \text{ J K}^{-1} \text{ mol}^{-1}$ and

$S^0_{O_2} = 205.152 \text{ J K}^{-1} \text{ mol}^{-1}$. Thus, the temperature function for the heat capacity was extracted from the reports of /SAX 1993/ and /BEV 1996/ (see Tab. **10.1**). A difference lower than $\pm 4 \%$ is observed between both functions.

For Hematite, Chivot /CHI 2004/ recommended thermodynamic values reported by Hemingway /HEM 1990/: $\Delta_f G^0 = -744.249 \text{ kJ mol}^{-1}$, $\Delta_f H^0 = -826.230 \text{ kJ mol}^{-1}$ and $S^0 = 103.85 \text{ J K}^{-1} \text{ mol}^{-1}$. These values do not present large discrepancies compared with those read in the data compilations reported by Wagman et al. /WAG 1982/ and Chase /CHA 1998/. The temperature function of C_p^0 reported by Chivot /CHI 2004/ was obtained by regression of that reported originally by Hemingway /HEM 1990/ to the parameters a,b,c, d and h, as given in Tab. 10.1.

The report by Chivot /CHI 2004/ considers thermodynamic data from the work of Diakonov /DIA 1998/ as recommendable. He reported two data sets referring to ordered and disordered types of Maghemite (see Tab. **10.1**). Majzlan et al. /MAJ 2003/ have measured the heat capacity of magnetite, goethite and lepidocrocite by a combination of adiabatic, semi-adiabatic and differential scanning calorimetry. For Magnetite, they calculated an entropy $S^0 = 93.0 \pm 0.2 \text{ JK}^{-1} \text{ mol}^{-1}$ and a Maier-Kelly polynomial $C_p^0 [\text{JK}^{-1} \text{ mol}^{-1}]$ with $a = 106.8$, $b = 0.06509$ and $d = -1.886 \times 10^6$.

For Goethite, reliable data were reported by Diakonov et al. /DIA 1994/. These data were derived from calorimetric studies of the dehydration reaction of Goethite to Hematite: $2 \text{ FeOOH} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$. They measured a reaction enthalpy $\Delta_r H^0 = 13.7 \pm 2.4 \text{ kJ mol}^{-1}$, which is in good agreement with a former value measured by Ferrier /FER 1966/ $\Delta_r H^0 = 13.7 \pm 2.4 \text{ kJ mol}^{-1}$ and by Korobeinikova et al. /KOR 1975/ $\Delta_r H^0 = 13.7 \pm 4 \text{ kJ mol}^{-1}$. Diakonov et al. /DIA 1994/ derived a temperature function of the heat capacity of goethite from data reported by King and Weller /KIN 1970/ and Korobeinikova /KOR 1975/: $C_p^0(T) [\text{J K}^{-1} \text{ mol}^{-1}] = 100.671 - 0.83486 \times 10^{-2} T - 0.21199 \times 10^{-7} T^2$. The thermodynamic data reported by Wagman et al. /WAG 1982/ differs largely from that reported in /PAR 1995/ and /DIA 1994/ and were not further considered. Majzlan et al. /MAJ 2003/ calculated an entropy $S^0 = 59.7 \pm 0.2 \text{ JK}^{-1} \text{ mol}^{-1}$ and a Maier-Kelly polynomial $C_p^0 [\text{JK}^{-1} \text{ mol}^{-1}]$ with $a = 1.246$, $b = 0.2332$ and $d = 3.139 \times 10^5$.

There are scarce reported thermochemical data for polymorph oxy-hydroxide Akaganeite ($\beta\text{-FeOOH}$); however, a study of stability of different oxide phases as a function of their size published by Navrotsky et al. /NAV 2008/ has demonstrated that such a phase may render the stable phase by formation of oxide nanoparticles. Laberty

and Navrotsky /LIB 1998/ has reported an enthalpy of formation $\Delta_f H^0 = -561.3 \pm 2.4 \text{ kJ mol}^{-1}$. Mazeina et al. /MAZ 2006/, on the other hand, reported $\Delta_f H^0 = -554.7 \pm 1.9 \text{ kJ mol}^{-1}$. Lang /LAN 2005/ obtained a value of $S^0 = 53.8 \pm 3.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta_f S^0 = -246.2 \pm 3.3 \text{ J K}^{-1} \text{ mol}^{-1}$. Thus, a value of $\Delta_f G^0 = -481 \pm 1.9 \text{ kJ mol}^{-1}$ was internally calculated. Snow et al. /SNO 2011/ has determined the heat capacity of Akaganeite at temperatures from 0.7 to 302 K. With these data, they were able to make a reliable calculation of the entropy of this polymorph species by $81.8 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$. Heat capacity data reported by Snow et al. /SNO 2011/ were regressed with a function (3.6) and the parameters are presented in Tab. 10.1.

For Lepidocrocite (γ -FeOOH), Chivot /CHI 2004/ has recommended the use of the thermodynamic data reported by Diakonov /DIA 1998b/, who carried out a critical analysis of published heat capacity data published by Korobeinikova /KOR 1975/, calorimetric measurements reported by Fricke and Zerrweck /FRI 1937/, Korobeinikova /KOR 1975/ and Korobeinikova et al. /KOR 1975/ and solubility and potentiometric measurements performed by Hashimoto and Misawa /HAS 1973/, Doyle /DOY 1968/ and Mohr et al. /MOH 1972/. From this study, values of $\Delta_f G^0 = -486 \pm 2.5 \text{ kJ mol}^{-1}$, $\Delta_f H^0 = -556.4 \pm 2.0$, $S^0 = 62.5 \text{ JK}^{-1} \text{ mol}^{-1}$ result. The temperature dependency for the heat capacity: $C_p^0 = 65.205 + 0.067665 T - 0.81564 \times 10^{-6} T^2$ was obtained from regression of experimental data from Korobeinikova /KOR 1975/. Calorimetric measurements were carried out by Majzlan et al. /MAJ 2003/, who reported values of $S^0 = 65.1 \pm 0.2 \text{ JK}^{-1} \text{ mol}^{-1}$ and a Maier-Kelley temperature function for the heat capacity: $C_p^0 = 59.76 + 0.06052 T - 7.729 \times 10^{-5} T^2$.

Thermodynamic properties of green rust one at 25 °C were reported by Refait et al. /REF 1999/, Refait and Génin /REF 1993/ and Drissi et al. /DRI 1995/. According to these authors, $\Delta_f G^0 = -2145.0 \pm 7 \text{ kJ mol}^{-1}$ for $\text{Fe}_3^{\text{II}}\text{Fe}^{\text{III}}(\text{OH})_8\text{Cl}$, $\Delta_f G^0 = -3588.0 \pm 11 \text{ kJ mol}^{-1}$ for $\text{Fe}_3^{\text{II}}\text{Fe}^{\text{III}}(\text{OH})_{12}\text{CO}_3$ and $\Delta_f G^0 = -3785.0 \pm 12 \text{ kJ mol}^{-1}$ for $\text{Fe}_3^{\text{II}}\text{Fe}^{\text{III}}(\text{OH})_{12}\text{SO}_4$. For sulfate-containing green rust one, Ayala-Luis et al. /AYA 2008/ has measured a value of $\Delta_f G^0 = -3819.43 \text{ kJ mol}^{-1} + y \times [\Delta_f G^0(\text{H}_2\text{O}_{(l)})]$, where y is the number of interlayer water molecules per formula unit.

The solubility constant of the pure-iron end-member of hibbingite, of a general formulae $(\text{Fe}^{\text{II}}, \text{Mg})_2(\text{OH})_3\text{Cl}$, was found by Nemer et al. /NEM 2011/ to be $\log K = 17.12 \pm 0.15$ ($\text{Fe}_2(\text{OH})_3\text{Cl} + 3 \text{ H}^+ \rightarrow 2 \text{ Fe}^{2+} + \text{Cl}^- + 3 \text{ H}_2\text{O}$). Using auxiliary data from Tab. A.1 and

$\Delta_f G^\circ(\text{Cl}^-) = -131.2 \text{ kJ mol}^{-1}$, a value of $\Delta_f G^\circ(\text{Fe}_2(\text{OH})_3\text{Cl}) = -928.02 \text{ kJ mol}^{-1}$ can be calculated.

Tab. 10.1 Selected thermodynamic data for the System Fe-H₂O. $C_p^0(T) = a + b \times T + c \times T^2 + d \times T^{-2} + h \times T^{-0.5}$

Species	$\Delta_f G^0$ [kJ mol ⁻¹]	$\Delta_f H^0$ [kJ mol ⁻¹]	S^0 [J K ⁻¹ mol ⁻¹]	C_p^0 [J K ⁻¹ mol ⁻¹]	$C_p^0(T) / T > 298,15 \text{ K}$ [J K ⁻¹ mol ⁻¹]					Ref.
					a	b	c	d	h	
Magnetite (Fe ₃ O ₄)	-1013.73 ⁽²⁾	-1115.548	150.64	152.50						/HAA 1988/
	-1015.23 ⁽³⁾	-1118.38	146.15	150.73						/ZIE 1995/
	-1012.566 ⁽²⁾	-1115.726	146.14	150.87	91.091	4.682E-2	2.220E-4	1.738E-6	4.922E2	/HEM 1990/ /SAX 1993/ ⁽¹⁾
Hematite (α -Fe ₂ O ₃)	-744.249 ⁽²⁾	-826.230	87.40	103.85	2659.108	-2.521	1.367E-3	2.073E-5	-3.645E4	/BEV 1996/
	-742.20 ⁽²⁾	-824.20	87.40	103.85	994.7099	0.79812	7.055E-6	4.027E-4	1.3262E4	/HEM 1990/
	-743.52 ⁽²⁾	825.50±1.3	87.40	103.763						/WAG 1982/ /CHA 1998/
Maguemite (γ -Fe ₂ O ₃)	-723.9±6.4 ⁽²⁾	-805.8±5.71	87.4±101	110.3±41						/DIA 1998/
	-725.1±6.42 ⁽²⁾	-805.8±5.72	91.4±102	104.0±2.52	106.8	0.06509		1.8860E6		/MAJ 2003/
(1) ordered			93.0±0.2							
Goethite (α -FeOOH)	-492.1±1.5 ⁽²⁾	-562.9±1.5	60.38±0.63	74.33±0.4	100.671	-8.348E-3	-	-2.119E7		/DIA 1994/
			59.7±0.2		1.246	0.2332		3.139E5		/MAJ 2003/
Akaganeite (β -FeOOH)	-481.7±1.9 ⁽²⁾	-554.7±1.9	53.8±3.3							/NAV 2008/
			81.8±2		-37.521	0.70607	-9.177E-4	3.134E-4		/SNO 2011/
Lepidocrocite (γ -FeOOH)	-486.3±2.5 ⁽²⁾	-556.4±2.0	62.5±5.0	76.2±1.5	59.76	0.06052		-7.729E5		/DIA 1998b/ /MAJ 2003/
			65.1±0.2							
Green rust (Cl-)	-2145.0±0.7 ⁽⁴⁾									/REF 1993/
(SO ₄)	-3785.0±12 ⁽⁴⁾									/REF 1999/
(CO ₃)	-3819.43 ⁽⁴⁾									/AYA 2008/
	-3588.0±0.1 ⁽⁴⁾									/DRI 1995/

⁽¹⁾ Adapted from other temperature function; ⁽²⁾ internally calculated; ⁽³⁾ adopted from /BAR 1989/; ⁽⁴⁾ potentiometric titration

11 Solid iron sulfide phases

There are three ferrous compounds that can be formed in the Fe-S-H₂O system: Pyrite (FeS₂), its polymorph Marcasite, the crystalline Troilite (FeS) and its amorphous form. For Pyrite, thermodynamic data can be adopted from the NIST-JANAF Thermochemical Tables /CHA 1998/: $\Delta_f H^\circ = -171.54 \pm 2.1 \text{ kJ mol}^{-1}$, $S^\circ = 52.916 \pm 0.13 \text{ J K}^{-1} \text{ mol}^{-1}$. The heat capacity reported in /CHA 1998/ was based in experimental data reported by Grønvold and Westrum /GRO 1962/ /GRO 1976/. Data were regressed with equation (3.6) and the coefficients are shown in Tab. 10.1. Marcansite, with an orthorombic structure is a metastable polymorph of cubic pyrite below 673 K. The transformation reaction to pyrite is however kinetically slow at low temperature, explaining its persistence in the nature /KJE 1975/. Thermodynamic data for Marcansite were taken from the selection presented in /CHA 1998/ and are listed in Tab. 10.1.

Five well characterized compounds appears in natural specimens in the range FeS to Fe₇S₈ /GRO 1992/. Minerals within this composition range are named Pyrrhotite. The name Troilite is reserved for the stoichiometric composition FeS. For Troilite, thermodynamic data were taken as selected in NIST-JANAF Tables /CHA 1998/: $\Delta_f H^\circ = -107.17 \pm 0.8 \text{ kJ mol}^{-1}$, $S^\circ = 60.321 \pm 0.04 \text{ J K}^{-1} \text{ mol}^{-1}$. Grønvold and Stølen /GRO 1992/ reported values of $\Delta_f H^\circ = -102.59 \text{ kJ mol}^{-1}$, $\Delta_f G^\circ = -102.87 \text{ kJ mol}^{-1}$ and $\Delta_f S^\circ = 0.94119 \text{ J K}^{-1} \text{ mol}^{-1}$, referring to a work of Cemic and Kleppa /CEM 1988/. Heat capacity data of Troilite reported in /GRO 1992/ were regressed by eq. (3.6) and the coefficients are shown in Tab. 10.1. For Pyrrhotite (Fe₇S₈), thermodynamic data and heat capacity values were taken from the work of Grønvold and Stølen /GRO 1992/ (see Tab. 10.1).

Tab. 11.1 Selected thermodynamic data for the System Fe-S-H₂O. $C_p^0(T) = a + b \times T + c \times T^2 + d \times T^{-2} + h \times T^{-0.5}$

Species	$\Delta_f G^0$ [kJ mol ⁻¹]	$\Delta_f H^0$ [kJ mol ⁻¹]	S^0 [J K ⁻¹ mol ⁻¹]	C_p^0 [J K ⁻¹ mol ⁻¹]	$C_p^0(T) / T > 298,15 \text{ K}$ [J K ⁻¹ mol ⁻¹]					Ref.
					a	b	c	d	h	
Pyrite		-171.54±2.1	52.916±0.13		142.400	-0.04241	1.846E-5	-225.075	-1196.08	/CHA 1998/
Marcansite (FeS ₂)		-167.36±2.1	53.865±0.13		144.357	-0.04793	2.385E-5	-224.980	-1205.13	/CHA 1998/
Pyrrhotite (Fe ₇ S ₈)	-98.861 ^(§)	-97.447		103.054	-0.06508	1.007E-4	-150.004	-737.245	/GRO 1992/	
Troilite (FeS)	-102.87 ^(§)	-102.59	60.321±0.04	-287.508	-0.08867	9.227E-4	-149.993	4883.334	/GRO 1992/ /CHA 1998/	

8

(*) Adapted from other temperature function; (§) internally calculated

12 Conclusions

A review of all available literature was conducted to derive a set of Pitzer parameters suitable of calculating ferrous iron activity coefficients in high saline solutions of Na^+ , K^+ - Cl^- , SO_4^{2-} - H_2O . The review focussed on solubility and vapour pressure data.

For chloride systems the existing set of Pitzer parameters could be extended to about 100 °C. The new parameter set is based on both solubility- and – more importantly – vapour pressure data. It is possible to calculate the polythermal solubility of three ferrous chloride hydrates.

For aqueous ferrous sulphate systems a general paucity of thermodynamic was ascertained. Even with more types of thermodynamic data and including recent reviews the validity of Pitzer parameters for temperatures higher than 25 °C is questionable. Own experiments yielded uncertain results because aqueous ferrous sulphate systems exhibit an exceedingly sluggish attainment of equilibrium. For future work it is therefore recommended to develop other methods based on either the direct measurement of vapour pressure or electrochemical potentials.

In corrosion experiments, Amakinite and Hibbingite were not detected as corrosion products. Instead hematite, Maghemite, green rust, and akageneite were identified, for which thermodynamic data are recommended. Explicit consideration of ionic interactions between ferrous iron and hydroxide in terms of Pitzer parameters is not necessary as long as moderate pH values up to ~8 are considered.

In addition to the original scope of the project we also looked at the system $\text{Fe(II)-CO}_3\text{-H}_2\text{O}$. Thermodynamic data for siderite and for a relevant species are recommended. For the solubility of siderite in high-saline solution only a single publication could be sourced which indicated that no Pitzer parameters for the interaction between ferrous iron and carbonate are necessary. The recommended speciation model is valid for pH values up to 8 only.

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A Appendix

A.1 Selected auxiliary data

Tab. A.1 Selected auxiliary data used for the calculation of thermodynamic properties of iron compounds at 25 °C

Temperature functions for the heat capacity are displayed in Tab. 8.8.

Species	$\Delta_f G^0$ [kJ mol ⁻¹]	$\Delta_f H^0$ [kJ mol ⁻¹]	S^0 [J K ⁻¹ mol ⁻¹]	C_p^0 [J K ⁻¹ mol ⁻¹]	Reference
Fe(cr)	0	0	27.28 ±0.13	24.98	[PHI 1988]
Fe ²⁺ (aq)	-90.536(*)	-90.000 ±0.5	-101.6 ±3.7		[PAR 1995]
H ₂ O(l)	-237.140 ±0.041 (*)	-285.830 ±0.040	69.950 ±0.030	75.351 ±0.080	[NEA 1995]
H ₂ (g)	0	0	130.680 ±0.003	28.836 ±0.002	[NEA 1995]
OH ⁻ (aq)	-157.220 ±0.072(*)	-230.015 ±0.040	-10.900 ±0.200		[NEA 1995]
O ₂ (g)	0	0	205.152 ±0.005	29.378 ±0.003	[NEA 1995]
Cl ⁻	-131.217 ±0.117(*)	-167.080 ±0.1000	56.6 ±0.2000		[NEA 1995]
SO ₄ ²⁻	-744.004 ±0.418(*)	-909.340 ±0.4000	18.5 ±0.4000		[NEA 1995]
Fe ₃ O ₄ (cr)	-1013,728 (*)	-1115.548	150.640	152.5	[SAX 1993]
Fe(OH) ₂ (cr)	-491.96	-574.04	87.864	97.069	[CHA 1998]

(*) Internally calculated data

The entropy for the formation reaction $\Delta_f S^0(T_0)$ for some compounds can be calculated taking absolute entropy values in Tab. A.1, see the following table.

Tab. A.2 Calculated formation entropies for some selected compounds

Species	Reaction	$\Delta_f S^0$ [J K ⁻¹ mol ⁻¹]
OH ⁻	$\frac{1}{2} O_2 + \frac{1}{2} H_2 + e^- \rightarrow OH^-$	-244.156
H ₂ O	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	-136.306
Fe ₃ O ₄	$3 Fe + 2 O_2 \rightarrow Fe_3O_4$	-341.504
Fe(OH) ₂	$Fe + O_2 + H_2 \rightarrow Fe(OH)_2$	-275.248

A.2 Primary experimental data

Tab. A.3 Water activity data for the determination of binary parameters in the system FeCl₂-H₂O

T [°C]	m _{salt} [mol/kg]	Δm _{salt} [mol/kg]	(1)	Δ(1)	a _w (exp)	φ (exp)	Δφ(exp)	φ(calc)
/SUS 1976/ / (1) p _{H2O} [Torr]								
40	1		52.38		0.9459	1.0293		1.0285
40	2		48.12		0.8690	1.2994		1.2996
40	3		43.15		0.7792	1.5386		1.5361
40	4		38.28		0.6913	1.7079		1.7143
40	4.84		34.27		0.6189	1.8345		1.8127
50	1		87.70		0.9469	1.0089		1.0054
50	2		80.85		0.8730	1.2568		1.2551
50	3		72.80		0.7860	1.4847		1.4772
50	4		64.94		0.7012	1.6420		1.6465
50	4.84		58.50		0.6316	1.7563		1.7414
60	1		141.8		0.9482	0.9842		0.9825
60	2		131.2		0.8773	1.2109		1.2113
60	3		118.8		0.7944	1.4196		1.4196
60	4		106.4		0.7115	1.5746		1.5808
60	4.84		96.6		0.6460	1.6707		1.6729
70	1		222.1		0.9495	0.9585		0.9594
70	2		206.1		0.8811	1.1709		1.1680
70	3		187.4		0.8012	1.3672		1.3631
70	4		168.7		0.7212	1.5117		1.5170
70	4.84		153.8		0.6575	1.6028		1.6067
85	1		412.7		0.9514	0.9217		0.9245
85	2		385.0		0.8875	1.1036		1.1037
85	3		352.0		0.8115	1.2884		1.2803
85	4		319.0		0.7354	1.4216		1.4242
85	4.84		292.0		0.6732	1.5130		1.5115
100	1		725.0		0.9537	0.8769		0.8889
100	2		679.4		0.8937	1.0394		1.0399
100	3		625.5		0.8228	1.2027		1.1992
100	4		570.8		0.7509	1.3254		1.3343
100	4.84		525.0		0.6906	1.4151		1.4203

Tab. A.4 Solubility data for the determination of binary parameters in the system FeCl₂-H₂O

T [°C]	m_{salt} [mol/kg]	solid phase
/SCH 1928/		
1.55	3.9923	FeCl ₂ .6H ₂ O
4.05	4.1555	FeCl ₂ .6H ₂ O
5.05	4.1832	FeCl ₂ .6H ₂ O
7.05	4.3045	FeCl ₂ .6H ₂ O
8.05	4.5742	FeCl ₂ .6H ₂ O
12.35	4.7539	FeCl ₂ .6H ₂ O
12.35	4.7539	FeCl ₂ .4H ₂ O
16.05	4.8355	FeCl ₂ .4H ₂ O
20.55	4.9598	FeCl ₂ .4H ₂ O
25.05	5.0866	FeCl ₂ .4H ₂ O
28.55	5.1295	FeCl ₂ .4H ₂ O
36.55	5.3479	FeCl ₂ .4H ₂ O
42.55	5.4599	FeCl ₂ .4H ₂ O
52.05	5.8553	FeCl ₂ .4H ₂ O
56.05	6.0495	FeCl ₂ .4H ₂ O
60.05	6.1738	FeCl ₂ .4H ₂ O
63.05	6.3002	FeCl ₂ .4H ₂ O
68.55	6.5866	FeCl ₂ .4H ₂ O
70.55	6.6668	FeCl ₂ .4H ₂ O
73.05	6.8848	FeCl ₂ .4H ₂ O
76.55	7.1095	FeCl ₂ .4H ₂ O
76.55	7.1095	FeCl ₂ .2H ₂ O
82.05	7.1381	FeCl ₂ .2H ₂ O
86.05	7.1956	FeCl ₂ .2H ₂ O
90.55	7.2535	FeCl ₂ .2H ₂ O
96.05	7.3706	FeCl ₂ .2H ₂ O
117.55	8.0167	FeCl ₂ .2H ₂ O
/CHO 1985/		
20.5	4.8334	FeCl ₂ .4H ₂ O
26.65	5.0166	FeCl ₂ .4H ₂ O
27.98	5.0314	FeCl ₂ .4H ₂ O
36.57	5.2531	FeCl ₂ .4H ₂ O
42.87	5.4893	FeCl ₂ .4H ₂ O
50.15	5.7460	FeCl ₂ .4H ₂ O
51.49	5.7649	FeCl ₂ .4H ₂ O
60.02	6.1964	FeCl ₂ .4H ₂ O
60.88	6.2014	FeCl ₂ .4H ₂ O
69.77	6.6721	FeCl ₂ .4H ₂ O
72.26	6.8462	FeCl ₂ .4H ₂ O
73.07	6.8462	FeCl ₂ .4H ₂ O

Tab. A.4 (contd.) Solubility data for the determination of binary parameters in the system FeCl₂-H₂O

T [°C]	m_{salt} [mol/kg]	solid phase
/SCH 1952/		
0	3.9211	FeCl ₂ .6H ₂ O
20	4.9389	FeCl ₂ .4H ₂ O
40	5.4149	FeCl ₂ .4H ₂ O
60	6.1738	FeCl ₂ .4H ₂ O
100	7.4896	FeCl ₂ .4H ₂ O
/SCH 1949/		
20	4.9389	FeCl ₂ .4H ₂ O
/LUZ 1949/		
35	5,1747	FeCl ₂ .4H ₂ O
/BUR 1975/		
25	4.9411	FeCl ₂ .4H ₂ O
40	5.3882	FeCl ₂ .4H ₂ O
/LEG 1967/		
0	3.9668	FeCl ₂ .6H ₂ O
40	5.5589	FeCl ₂ .4H ₂ O
0	3.9668	FeCl ₂ .6H ₂ O
40	5.5589	FeCl ₂ .4H ₂ O
/ZDA 1974/		
0	3.9744	FeCl ₂ .6H ₂ O
15	4.7946	FeCl ₂ .4H ₂ O
/ATB 1996/		
30	5.1877	FeCl ₂ .4H ₂ O
40	5.5394	FeCl ₂ .4H ₂ O

Tab. A.5 Water activity data for the determination of binary parameters in the system $\text{FeSO}_4\text{-H}_2\text{O}$

T [°C]	m_{salt} [mol/kg]	Δm_{salt} [mol/kg]	(1)	$\Delta(1)$	$a_w(\text{exp})$	$\phi(\text{exp})$	$\Delta\phi(\text{exp})$
/OYK 1974/							
25	0.1				0.9980	0.5556	
25	0.2				0.9963	0.5144	
25	0.3				0.9945	0.5102	
25	0.4				0.9927	0.5084	
25	0.5				0.9907	0.5186	
25	0.6				0.9888	0.5210	
25	0.7				0.9868	0.5269	
25	0.8				0.9848	0.5314	
25	0.9				0.9826	0.5413	
25	1.0				0.9805	0.5466	
25	1.1				0.9782	0.5561	
25	1.2				0.9760	0.5619	
25	1.3				0.9735	0.5734	
25	1.4				0.9710	0.5834	
25	1.5				0.9682	0.5979	
25	1.6				0.9651	0.6162	
25	1.7				0.9618	0.6359	
25	1.8				0.9583	0.6568	
25	1.9				0.9542	0.6848	
25	1.9641				0.9514	0.7040	
/NIK 1989/							
25	0.1	0.00020			0.9977	0.6391	0.139
25	0.2	0.00040			0.9959	0.5701	0.069
25	0.3	0.00060			0.9944	0.5195	0.046
25	0.4	0.00080			0.9931	0.4804	0.035
25	0.5	0.00100			0.9917	0.4626	0.028
25	0.6	0.00120			0.9904	0.4462	0.023
25	0.7	0.00140			0.9891	0.4345	0.020
25	0.8	0.00160			0.9877	0.4294	0.017
25	0.9	0.00180			0.9864	0.4223	0.015
25	1.0	0.00200			0.9852	0.4138	0.014
25	1.2	0.00240			0.9830	0.3966	0.012
25	1.4	0.00280			0.9804	0.3924	0.010
25	1.6	0.00320			0.9756	0.4285	0.009
25	1.8	0.00360			0.9653	0.5445	0.008
/MOO 2004/							
25	1.4013	0.0001				0.5868	0.0012
25	1.4033	0.0001				0.5860	0.0012
25	1.4983	0.0001				0.5943	0.0008
25	1.4994	0.0001				0.5939	0.0008

Tab. A.5 (contd.) **Tab. A.5** Water activity data for the determination of binary parameters in the system $\text{FeSO}_4\text{-H}_2\text{O}$

T [°C]	m_{salt} [mol/kg]	Δm_{salt} [mol/kg]	(1)	$\Delta(1)$	$a_{\text{w}}(\text{exp})$	$\phi(\text{exp})$	$\Delta\phi(\text{exp})$
/APE 1993/ / (1) = $p_{\text{H}_2\text{O}}$ [kPa]							
7.57	1.282		0.773		0.7418	6.465	
7.72	1.287		0.787		0.7475	6.275	
7.93	1.295		0.800		0.7491	6.194	
8.01	1.297		0.807		0.7515	6.112	
9.11	1.336		0.920		0.7952	4.761	
11.03	1.404		1.117		0.8491	3.233	
12.95	1.474		1.340		0.8975	2.035	
15.31	1.563		1.613		0.9272	1.343	
16.96	1.627		1.813		0.9381	1.091	
18.94	1.705		2.073		0.9471	0.885	
20.20	1.756		2.300		0.9717	0.454	
20.97	1.788		2.360		0.9508	0.783	
22.10	1.834		2.533		0.9524	0.738	
23.30	1.885		2.800		0.9790	0.313	
23.45	1.891		2.826		0.9791	0.309	
25.26	1.969		3.180		0.9887	0.160	
27.24	2.055		3.450		0.9545	0.629	
29.07	2.137		3.693		0.9186	1.103	
31.81	2.263		4.413		0.9386	0.777	
/DIE 1937/ / (1) = $p_{\text{H}_2\text{O}}$ [mm Hg]							
18.6	1.692		15.52		0.9656	0.5745	
20.3	1.760		17.07		0.9555	0.7170	
23.2	1.880		20.35		0.9543	0.6902	
25.0	1.957		22.65		0.9535	0.6746	
27.4	2.062		26.03		0.9512	0.6739	
29.7	2.166		29.72		0.9505	0.6509	
31.9	2.267		33.73		0.9516	0.6069	
/OJK 1982/ / (1) = $p_{\text{H}_2\text{O}}$ [mm Hg]							
25.00	1.957		22.589		0.9510	0.7129	
/OJK 1978/ / (1) = $p_{\text{H}_2\text{O}}$ [mm Hg]							
25.00	1.957		22.592		0.9511	0.7110	
/RUD 1972/ / (1) = $p_{\text{H}_2\text{O}}$ [mm Hg]							
50.00	3.194		91.5		0.7434	2.577	

Tab. A.5 (contd.) **Tab. A.5** Water activity data for the determination of binary parameters in the system $\text{FeSO}_4\text{-H}_2\text{O}$

T [°C]	m_{salt} [mol/kg]	Δm_{salt} [mol/kg]	(1)	Δ(1)
This Work / (1) = m _{NaCl} [mol/kg] reference solution				
40	0.7987	0.0028	0.4062	0.0015
40	0.8001	0.0028	0.4062	0.0015
40	0.8001	0.0028	0.4062	0.0015
40	0.8002	0.0028	0.4062	0.0015
40	1.558	0.005	0.8571	0.0028
40	1.558	0.005	0.8571	0.0028
40	1.558	0.005	0.8571	0.0028
40	1.556	0.005	0.8571	0.0028
40	1.726	0.006	0.987	0.004
40	1.727	0.006	0.987	0.004
40	1.726	0.006	0.987	0.004
40	1.7268	0.0056	0.987	0.004
40	0.5215	0.0028	0.2688	0.0022
40	0.5196	0.0028	0.2688	0.0022
40	0.5196	0.0028	0.2688	0.0022
40	0.5191	0.0028	0.2688	0.0022
40	1.0197	0.0065	0.528	0.004
40	1.022	0.007	0.528	0.004
40	1.023	0.007	0.528	0.004
40	1.026	0.007	0.528	0.004
40	1.301	0.007	0.688	0.005
40	1.297	0.007	0.688	0.005
40	1.294	0.007	0.688	0.005
40	1.297	0.007	0.688	0.005

Tab. A.5 (contd.) **Tab. A.5** Water activity data for the determination of binary parameters in the system $\text{FeSO}_4\text{-H}_2\text{O}$

T [°C]	m_{salt} [mol/kg]	Δm_{salt} [mol/kg]	(1)	$\Delta(1)$
This Work / (1) = m_{NaCl} [mol/kg] reference solution				
60	1.059	0.012	0.505	0.004
60	1.055	0.012	0.505	0.004
60	1.051	0.012	0.505	0.004
60	1.047	0.012	0.505	0.004
60	1.356	0.024	0.647	0.012
60	1.348	0.024	0.647	0.012
60	1.332	0.024	0.647	0.012
60	1.335	0.024	0.647	0.012
60	1.381	0.023	0.675	0.008
60	1.379	0.023	0.675	0.008
60	1.377	0.023	0.675	0.008
60	1.358	0.023	0.675	0.008
60	1.99	0.06	0.976	0.025
60	1.96	0.06	0.976	0.025
60	1.92	0.06	0.976	0.025
60	1.94	0.06	0.976	0.025
60	1.91	0.08	0.989	0.030
60	1.85	0.08	0.989	0.030
60	1.84	0.07	0.989	0.030
60	1.84	0.07	0.989	0.030
60	1.56	0.04	0.814	0.027
60	1.54	0.04	0.814	0.027
60	1.52	0.04	0.814	0.027
60	1.52	0.04	0.814	0.027
60	1.61	0.05	0.813	0.024
60	1.61	0.05	0.813	0.024
60	1.59	0.05	0.813	0.024
60	1.56	0.05	0.813	0.024
60	0.79	0.04	0.389	0.014
60	0.79	0.04	0.389	0.014
60	0.76	0.04	0.389	0.014
60	0.75	0.04	0.389	0.014
60	0.79	0.05	0.392	0.021
60	0.79	0.05	0.392	0.021
60	0.75	0.05	0.392	0.021

Tab. A.5 (contd.) **Tab. A.5** Water activity data for the determination of binary parameters in the system FeSO₄-H₂O

T [°C]	m _{salt} [mol/kg]	Δm _{salt} [mol/kg]	(1)	Δ(1)
This Work / (1) = m _{NaCl} [mol/kg] reference solution				
60	0.74	0.05	0.392	0.021
60	0.530	0.024	0.273	0.011
60	0.526	0.024	0.273	0.011
60	0.510	0.023	0.273	0.011
60	0.507	0.023	0.273	0.011
60	0.535	0.033	0.273	0.016
60	0.531	0.032	0.273	0.016
60	0.506	0.031	0.273	0.016
60	0.503	0.031	0.273	0.016
90	1.233	0.017	0.476	0.010
90	1.222	0.017	0.476	0.010
90	1.225	0.017	0.476	0.010
90	1.216	0.017	0.476	0.010
90	2.10	0.04	0.97	0.13
90	2.13	0.04	0.97	0.13
90	2.14	0.04	0.97	0.13
90	2.10	0.04	0.97	0.13
90	1.46	0.05	0.625	0.017
90	1.46	0.05	0.625	0.017
90	1.47	0.05	0.625	0.017
90	1.42	0.05	0.625	0.017
90	2.00	0.04	0.932	0.028
90	2.00	0.04	0.932	0.028
90	2.00	0.04	0.932	0.028
90	1.96	0.04	0.932	0.028
90	1.52	0.04	0.654	0.006
90	1.50	0.04	0.654	0.006
90	1.49	0.04	0.654	0.006
90	0.633	0.013	0.277	0.018
90	0.645	0.013	0.277	0.018
90	0.641	0.013	0.277	0.018
90	0.633	0.013	0.277	0.018
90	1.012	0.023	0.440	0.017
90	1.025	0.023	0.440	0.017
90	1.034	0.023	0.440	0.017
90	1.014	0.023	0.440	0.017

Tab. A.6 Solubility data for the determination of binary parameters in the system $\text{FeSO}_4\text{-H}_2\text{O}$

T [°C]	m_{salt} [mol/kg]	solid phase
/BUL 1952/		
0	1.956	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
25	2.992	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
45	3.489	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
55	3.290	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
60	2.445	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
80	1.393	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
100	1.956	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
/BEL 1948/		
10	1.360	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
15	1.554	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
20	1.739	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
25	1.964	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
30	2.159	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
35	2.383	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
40	2.650	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
45	2.937	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Tab. A.6 (contd.) Solubility data for the determination of binary parameters in the system $\text{FeSO}_4\text{-H}_2\text{O}$

T [°C]	m_{salt} [mol/kg]	solid phase
/BEL 1948/		
0	1.042	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
5	1.203	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
0	1.058	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
25	1.864	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/KOB 1956/		
0	1.072	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
27	2.045	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
40	2.650	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
60	3.639	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
100	1.911	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
/CAM 1930/		
0	1.129	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
25	2.021	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
75	3.082	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
/SCH 1910/		
30	2.183	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/MCL 1933/		
0	1.065	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
25	1.928	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/BEN 1929/		
97	1.602	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
/OCC 1925/		
25	1.964	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/BUR 1975/		
25	1.943	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
40	2.663	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
60	3.490	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
/LEG 1967/		
0	1.060	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
40	2.656	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/ZDA 1974/		
0	1.036	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
15	1.578	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
25	1.972	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Tab. A.6 (contd.) Solubility data for the determination of binary parameters in the system $\text{FeSO}_4\text{-H}_2\text{O}$

T [°C]	m_{salt} [mol/kg]	solid phase
/FRA 1907/		
0.00	1.030	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
10.00	1.350	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
15.25	1.571	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
20.13	1.748	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
25.02	1.949	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
30.03	2.168	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
35.07	2.427	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
40.05	2.646	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
45.18	2.918	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
50.21	3.199	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
52.00	3.305	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
54.03	3.428	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
60.01	3.617	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
65.00	3.659	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
68.02	3.444	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
70.04	3.692	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
77.00	3.022	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
80.41	2.869	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
85.02	2.663	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
90.13	2.453	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
/DAN 1960/		
50	3.210	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/WIR 1913a/		
25	1.949	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/OJK 1978/		
25	1.96	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/AGD 1926/		
1	1.054	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
9.6	1.359	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
21	1.784	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
25	1.966	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
34	2.384	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
43	2.829	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
54	3.471	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
80	2.864	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Tab. A.6 (contd.) Solubility data for the determination of binary parameters in the system $\text{FeSO}_4\text{-H}_2\text{O}$

T [°C]	m_{salt} [mol/kg]	solid phase
/ETA 1894/		
-1	0.984	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
5	1.171	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
24	1.933	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
34	2.349	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
52	3.170	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
60	3.768	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
67	3.984	$\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$
77	4.001	$\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$
86	4.001	$\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$
94	3.817	$\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$
102	3.498	$\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$
112	2.560	$\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$
130	1.377	$\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$
152	0.169	$\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$
/MUL 1860/		
0	0.520	<i>unknown</i>
0	0.533	<i>unknown</i>
0	0.513	<i>unknown</i>
16.5	1.435	<i>unknown</i>
33	2.423	<i>unknown</i>
42.5	2.943	<i>unknown</i>
63	4.259	<i>unknown</i>
75.5	4.207	<i>unknown</i>
83.5	4.035	<i>unknown</i>
98	3.002	<i>unknown</i>
98	3.081	<i>unknown</i>
98	3.041	<i>unknown</i>
99	2.929	<i>unknown</i>
/TOB 1855/		
0	1.040	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
10	1.310	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
12	1.402	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
20	1.712	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
21	1.804	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
30	2.146	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
37	2.403	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
45	2.824	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
55	3.094	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
70	3.719	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Tab. A.6 (contd.) Solubility data for the determination of binary parameters in the system $\text{FeSO}_4\text{-H}_2\text{O}$

T [°C]	m_{salt} [mol/kg]	solid phase
/NOV 1953/		
25	1.938	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
60	3.535	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
/KUL 1968/		
40	2.647	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/KON 1996b/		
25	2.015	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
90	2.927	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
/BLI 1958/		
25	1.998	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/BAL 1973/		
25	1.922	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/MU 2006/		
25	2.183	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/GOR 1953/		
20	1.671	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/DRU 1960/		
25	2.093	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
40	2.707	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/LEG 1966/		
20	1.754	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/BUR 1982a/		
44.85	2.943	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
54.85	3.442	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
59.85	3.432	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
59.85	3.786	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
/BUR 1982b/		
49.85	3.175	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
54.85	3.475	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/BUR 1980/		
19.85	1.735	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
39.85	2.662	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/BAL 1975/		
25	1.786	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
/NOV 1989/		
60	3.366	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
75	2.761	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$

Tab. A.6 (contd.) Solubility data for the determination of binary parameters in the system $\text{FeSO}_4\text{-H}_2\text{O}$

T [°C]	m_{salt} [mol/kg]	solid phase
This Work		
44.8	2.898	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
49.8	3.213	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
49.8	3.205	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
55.0	3.425	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
58.0	3.511	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
58.0	3.507	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
59.9	3.558	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
59.9	3.549	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
59.9	3.527	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
63.1	3.665	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
63.1	3.636	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
63.1	3.662	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
<i>63.1</i>	<i>3.058</i>	<i>$\text{FeSO}_4 \cdot \text{H}_2\text{O}$</i>
<i>66.1</i>	<i>3.127</i>	<i>$\text{FeSO}_4 \cdot 4\text{H}_2\text{O} + \text{FeSO}_4 \cdot \text{H}_2\text{O}$</i>
<i>66.1</i>	<i>3.121</i>	<i>$\text{FeSO}_4 \cdot 4\text{H}_2\text{O} + \text{FeSO}_4 \cdot \text{H}_2\text{O}$</i>
<i>66.1</i>	<i>3.108</i>	<i>$\text{FeSO}_4 \cdot 4\text{H}_2\text{O} + \text{FeSO}_4 \cdot \text{H}_2\text{O}$</i>
<i>70.0</i>	<i>3.126</i>	<i>$\text{FeSO}_4 \cdot \text{H}_2\text{O}$</i>
75.0	2.639	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
75.0	2.593	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
80.0	2.600	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
80.0	2.550	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
85.0	2.354	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
85.0	2.355	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
89.8	2.065	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
89.8	2.078	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$

Data in italic were classified as outliers

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