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to: SNL WIPP[1] Records Center, SNL WIPP Geochemistry
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subject: Thermodynamic quantities for Fe^{+2} - SO_4^{-2} - H^+ - H_2O system (Revision 0)

I. DRIVERS

SNL WIPP Geochemistry needs to add thermodynamic quantities of the Fe^{+2} - SO_4^{-2} system to enhance the completeness of the SNL WIPP TDB.[2] This memorandum addresses EPA issue 32, "Add Fe(II)-sulfate Pitzer parameters and solid phases to the WIPP thermodynamic database", listed in Letter from Tom Peake to Michael Gerle. 2022.06.30, Enclosure 1 (U. S. EPA, 2022).

In summary, the log Ks and PIPs of Reardon and Beckie (1987) are selected to be included in the SNL WIPP TDB without modification. Discussion below is provided to confirm the compatibility of the PIPs of Fe^{+2}/SO_4^{-2} and Fe^{+2}/HSO_4^- of Reardon and Beckie (1987) with the supporting PIPs in Harvie et al. (1984). The PIPs are compatible with each other within an acceptable difference (Figure IV-1, Excerpt IV-6). No derivation of new PIPs was performed in this memo.

II. CHEMICAL SYSTEM

The chemical system to be examined in this memo consists of the following chemicals: $FeSO_4$ - H_2SO_4 - H_2O. The four system components are Fe^{+2}, SO_4^{-2}, H^+, and H_2O. Interactions and reactions of SO_4^{-2} with other aqueous species relevant to brines of WIPP interest were reported in the SNL WIPP TDB per Harvie et al. (1984). Harvie et al. (1984) has been the basis brine model for SNL WIPP TDB.

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[1] SNL WIPP: Sandia National Laboratories at the Waste Isolation Pilot Plant (WIPP). WIPP is located ~26 miles southeast of Carlsbad, New Mexico, U.S.A., built 2,150 feet underground in the Salado Formation, a thick Permian evaporite deposit in the northern Delaware Basin.

[2] TDB: Thermodynamic Data Base

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Refer to Table III.1-1 (reactions and log Ks) and Table III.1-2 (PIPs) in GEOC-21-11 (Jang et al., 2021) for the other aqueous species whose interactions and reactions with SO_4^{-2} were reported in Harvie et al. (1984).

III. GOALS AND HYPHOTHESES

The goal of this memo is to evaluate the compatibility of PIPs relevant to the Fe^{+2} - SO_4^{-2} system derived by Reardon and Beckie (1987) with the PIPs of Harvie et al. (1984). To derive PIPs for the two species pairs and a triplet (Fe^{+2}/SO_4^{-2}, Fe^{+2}/HSO_4^-, $H^+/Fe^{+2}/HSO_4^-$), Reardon and Beckie (1987) made modifications on two supporting PIPs for species pairs of H^+/SO_4^{-2} and H^+/HSO_4^- of Harvie et al. (1984). Values reported in Reardon and Beckie (1987) are selected because the derivation of the PIPs therein was based on the isopiestic measurements of Oykova and Balarew (1974), and it is widely cited in the literature.[3]

The supporting PIPs listed in Harvie et al. (1984), i.e., PIPs for species pairs of H^+/SO_4^{-2} and H^+/HSO_4^-, are part of the basis brine model of the SNL WIPP TDB. SNL WIPP Geochemistry is not in the position to replace the PIPs in the current SNL WIPP TDB just for one system. Therefore, if the PIPs for Fe^{+2}/SO_4^{-2}, Fe^{+2}/HSO_4^-, and $H^+/Fe^{+2}/HSO_4^-$ of Reardon and Beckie (1987) are not compatible with PIPs for H^+/SO_4^{-2} and H^+/HSO_4^- of Harvie et al. (1984), the PIPs of Reardon and Beckie (1987) will be refitted to their selected isopiestic measurements, i.e., Oykova and Balarew (1974), to ensure the internal consistency of SNL WIPP TDB. Prior to accepting the PIPs modified and newly derived in Reardon and Beckie (1987), SNL WIPP Geochemistry needs to check to what extent the modified PIPs for H^+/SO_4^{-2} and H^+/HSO_4^- would create differences in the model delineation of the experimental data of Oykova and Balarew (1974).

Therefore, the hypothesis to be tested is as follows: The model using thermodynamic quantities derived by Reardon and Beckie (1987) would not generate significant differences when compared to the model using parameters in Harvie et al. (1984).

Reardon and Beckie (1987) revised the PIPs for the species pairs of H^+/SO_4^{-2} and H^+/HSO_4^- to determine the PIPs for the species pairs of Fe^{+2}/SO_4^{-2} and Fe^{+2}/HSO_4^-. They used the isopiestic measurements of Oykova and Balarew (1974). However, $[H^+]$[4] is lower than $[SO_4^{-2}]$ and $[HSO_4^-]$ in

[3] Readers are welcomed to suggest additional literature as deemed important. SNL WIPP Geochemistry so far located the following additional papers, but their thermodynamic quantities, log Ks and PIPs, are not reviewed in this memo: Christov (2004); Christov and Moller (2004); Charykova et al. (2010, I); Charykova et al. (2010, II); Kobylin et al. (2007); Kobylin et al. (2011). SNL WIPP Geochemistry assumes that their thermodynamic quantities would be non-identifiable compared to Harvie et al. (1984) and Reardon and Beckie (1987). SNL WIPP Geochemistry can issue Memoranda similar to this one upon requests in writing through SNL WIPP Management.

[4] [..] means the concentration of .. hereafter.

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their experiment where the isopiestic measurements were performed on the mixture of $FeSO_4$ - H_2O.[5] Therefore, the PIPs derived in Reardon and Beckie (1987) for the species pairs of Fe^{+2}/SO_4^{-2} and Fe^{+2}/HSO_4^- using the isopiestic measurements of Oykova and Balarew (1974) would be insensitive to the modification made by Reardon and Beckie (1987) on the PIPs for the supporting species pairs of H^+/SO_4^{-2} and H^+/HSO_4^-.

Reardon and Beckie (1987) also presented regression equations to calculate log Ks (I=0) of $FeSO_4.H_2O$(s) (Szomolnokite) and $FeSO_4.7H_2O$(s) (Melanterite) as a function of temperature. The regression equations were based on the solubility measurements of Bullough et al. (1952) for $FeSO_4.H_2O$(s) (Szomolnokite) and Linke and Seidell (1958) for $FeSO_4.7H_2O$(s) (Melanterite) (Reardon and Beckie, 1987). We provide log Ks of $FeSO_4.H_2O$(s) (Szomolnokite) and $FeSO_4.7H_2O$(s) (Melanterite) calculated using the equations of Reardon and Beckie (1987) in Section IV.2.

IV. REVIEW OF REARDON AND BECKIE (1987)

In Excerpt IV-1A, Reardon and Beckie (1987) stated that their modification to the PIPs for species pairs of H^+/SO_4^{-2} and H^+/HSO_4^- would produce insignificant difference. In Excerpt IV-1B, the modifications were presented. In Excerpt IV-1C and D, the new PIPs for the two species pairs and a triplet (Fe^{+2}/SO_4^{-2}, Fe^{+2}/HSO_4^-, and $H^+/Fe^{+2}/HSO_4^-$) are presented.

[5] The measurements therein were not amended with experimental uncertainty.

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Excerpt IV-1. Captured from pages 2360, 2361, and 2362 of Reardon and Beckie (1987).

A

from 0 to 70°C are presented in Table 5. The small differences between our values at 25°C and those of HARVIE *et al.* (1984) produce no substantive difference in the quality of the fit of the experimental data. For programming simplicity, the following expressions are

B

Table 5 Results of the reevaluation of the temperature dependency of the interaction parameters in the H_2SO_4-H_2O system from the work of Pitzer *et al.* (1977). The tabulated values are those to be used when the higher order electrostatic interaction terms are included in the Pitzer formulation. Regression equations describing the temperature dependency are given in the text. The final column records the 25°C values reported by Harvie *et al.* (1984).

T°C	0	15	25	35	45	55	70	25
$\beta^{(2)}_{M\text{-}SO_4}$	0.0398	0.0280	0.0217	0.0159	0.0101	0.0044	-0.0039	0.0298
$C^{\phi}_{M\text{-}SO_4}$	0.0217	0.0341	0.0411	0.0475	0.0534	0.0589	0.0666	0.0438
$\beta^{(0)}_{M\text{-}HSO_4}$	0.2278	0.2164	0.2106	0.2054	0.2006	0.1962	0.1900	0.2065
$\beta^{(1)}_{M\text{-}HSO_4}$	0.6879	0.5919	0.5320	0.4804	0.4364	0.3972	0.3452	0.5556

C

Table 2 Pitzer parameters and their standard errors for $FeSO_4$ from activity coefficient data. The entries for $\beta^{(2)}$ are the average and standard deviation of other bivalent metal sulphate data tabulated by Pitzer (1979).

Parameter	Value	St. Error
$\beta^{(0)}$	0.2568	0.019
$\beta^{(1)}$	3.063	0.016
$\beta^{(2)}$	-42.0	9.2
C^{ϕ}	0.0209	0.009

D

Table 6 Pitzer parameters for Fe-HSO_4 interaction at 25°C determined from ferrous sulphate heptahydrate solubility data in H_2SO_4 solutions.

Parameter	Value	St. Error
$\beta^{(0)}_{Fe\text{-}HSO_4}$	0.4273	0.014
$\beta^{(1)}_{Fe\text{-}HSO_4}$	3.48	0.602
$\psi_{H\text{-}Fe\text{-}HSO_4}$	0.0143	0.0043

The solubility constants for $FeSO_4.H_2O(s)$ (Szomolnokite) and $FeSO_4.7H_2O(s)$ (Melanterite) were presented in Reardon and Beckie (1987) as functions of temperature (Excerpt IV-2 and Excerpt IV-3).

Excerpt IV-2. Log K of $FeSO_4.7H_2O$ (Melanterite) in Reardon and Beckie (1987) in the abstract and page 2359.

to determine log K_{sp} values for melanterite over the temperature range of 0 to 55°C:

$$\log K_{sp} = 1.447 - 0.004153T - \frac{214949}{T^2} \quad (20)$$

Excerpt IV-3. Log K of $FeSO_4.H_2O$ (Szomolnokite) in Reardon and Beckie (1987) in the abstract and page 2362.

$$\log K_{sp} = 25.211 - 0.063405T - \frac{641220}{T^2}. \quad (28)$$

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IV.1. Pitzer interaction parameters (PIPs)

Reactions and the log Ks and the PIPs reported in Harvie et al. (1984) and Reardon and Beckie (1987) (Excerpt IV-1, Excerpt IV-2) are summarized in Table IV-1 (reactions and log Ks) and Table IV-2 (PIPs). In Table IV-2, the different PIPs for the supporting species pairs of interest, i.e., H^+/SO_4^{-2} and H^+/HSO_4^-, are compared in black and green fonts.

Table IV-1. Reactions and log Ks at 25 °C and I = 0 used for the compatibility check between Harvie et al. (1984) and Reardon and Beckie (1987).

Reactions	Log K	Source
Aqueous reactions		
$H^+ + OH^- = H_2O$	13.99	Harvie et al. (1984)
$HSO_4^- = SO_4^{-2} + H^+$	-1.97	Harvie et al. (1984), Shock and Helgeson (1988)
$FeOH^+ + H^+ = Fe^{+2} + H_2O$	9.31	Jang et al. (2021) and reference(s) therein
$Fe(OH)_2(aq) + 2H^+ = Fe^{+2} + 2H_2O$	20.84	Jang et al. (2021) and reference(s) therein
$Fe(OH)_3^- + 3H^+ = Fe^{+2} + 3H_2O$	31.00	Jang et al. (2021) and reference(s) therein
$Fe(OH)_4^{-2} + 4H^+ = Fe^{+2} + 4H_2O$	46.00	Jang et al. (2021) and reference(s) therein
Solid reactions		
$Fe(OH)_2(s)$ (Ferrous Iron Hydroxide) $+ 2H^+ = Fe^{+2} + 2H_2O$	12.89	Kim et al. (2017)
$FeSO_4.H_2O(s)$ (Szomolnokite) $= Fe^{+2} + SO4^{-2} + H_2O$	-0.90	Reardon and Beckie (1987)
$FeSO_4.7H_2O(s)$ (Melanterite) $= Fe^{+2} + SO4^{-2} + 7H_2O$	-2.20	Reardon and Beckie (1987)

Table IV-2. PIPs at 25 °C for Fe^{+2} - SO_4^{-2} in Reardon and Beckie (1987) compared with Harvie et al. (1984) in green fonts.

i	*j*	α_1/α_2 [6]	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^ϕ	Source
H^+	SO_4^{-2}	2.0/12.0	0.0298	0.0	0.0	0.0438	Harvie et al. (1984)
			0.0217	0.0	0.0	0.0411	Reardon and Beckie (1987)
H^+	HSO_4^-	2.0/12.0	0.2065	0.5556	0.0	0.0	Harvie et al. (1984)
			0.2106	0.5320	0.0	0.0	Reardon and Beckie (1987)
Fe^{+2}	SO_4^{-2}	1.4/12.0	0.2568±0.019	3.063±0.016	-42.0±9.2	0.0209±0.009	Reardon and Beckie (1987)
Fe^{+2}	HSO_4^-	2.0/12.0	0.4273±0.014	3.48±0.602	0	0	Reardon and Beckie (1987)
i	***j***		$\theta_{cc'}$ **or** $\theta_{aa'}$				**Source**
SO_4^{-2}	OH^-		-0.013				Harvie et al. (1984)
			0.0 [7]				Reardon and Beckie (1987)
i	***j***	***k***	$\psi_{cc'a}$ **or** $\psi_{aa'c}$				**Source**
H^+	Fe^{+2}	HSO_4^-	0.0143±0.0043				Reardon and Beckie (1987)

It was noted earlier that the PIPs for supporting species pairs of H^+/SO_4^{-2} and H^+/HSO_4^- were modified in Reardon and Beckie (1987) from those in Harvie et al. (1984) (see numbers in green and black fonts in Table IV-2). The modification was made while Reardon and Beckie (1987) refitted the

[6] α_1 and α_2 are pre-set constants used in the Pitzer activity coefficient equation. α_1 and α_2 apply for only cation-anion binary pair. α_2 is not applied when $\beta^{(2)}$ is zero or not used. Unit for α_1 and α_2 is $kg^{1/2} \cdot mol^{-1/2}$ (Pitzer, 1991). For 2-2 electrolytes, α_1 = 1.4 and α_2 = 12.0 as adopted by Pitzer (1991, p 102). When a monovalent ions is involved in the pairs, α_1 = 2.0 and α_2 = 12.0.
[7] Not mentioned in Reardon and Beckie (1987), which is equivalent to setting to zero.

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isopiestic measurements of Oykova and Balarew (1974) (Excerpt IV-4). Reardon and Beckie (1987) revised the measurements prior to refitting based on the insights compiled in the literature since Oykova and Balarew (1974).[8] The re-processed measurements of Oykova and Balarew (1974) by Reardon and Beckie (1987) are captured in Excerpt IV-5 and transcribed into Table IV-3. The difference is the use of different reference mean molal activity coefficients, i.e., $\Gamma_{\pm}$ and $\gamma_{\pm}$ in Excerpt IV-4 and Excerpt IV-5, respectively. Both symbols represent the same quantity, i.e., the mean molal activity coefficient value of $FeSO_4$. Oykova and Balarew (1974) used 0.150 while Reardon and Beckie (1987) used 0.161. Note that the same isopiestic measurements can be interpreted into different mean molal activity coefficients based on the choice of the reference value.

Therefore, in this memo, the re-processed values in Excerpt IV-5, i.e., those in Table IV-3, will be used to evaluate the compatibility of PIPs of Reardon and Beckie (1987) with those in Harvie et al. (1984).

Excerpt IV-4. Table 1 in page 1211 of Oykova and Balarew (1974). The fourth column header Γ should be $\Gamma_{\pm}$ to be consistent with Equation (1) in page 1212 of Oykova and Balarew (1974), and the $\Gamma_{\pm} = 0.150$ at 0.1 m $FeSO_4$ in parentheses is an assumed values based on Robinson and Stokes (1970).

Table 1

Molality, water activity, osmotic coefficients and activity coefficients of ferrosulfate in binary solutions

M	a_w	φ	Γ
0.1	0.9980	0.5757	(0.150)
0.2	0.9963	0.5118	0.1008
0.3	0.9945	0.5118	0.0822
0.4	0.9927	0.5118	0.0713
0.5	0.9907	0.5246	0.0648
0.6	0.9888	0.5118	0.0586
0.7	0.9868	0.5209	0.0548
0.8	0.9848	0.5278	0.0518
0.9	0.9826	0.5402	0.0496
1.0	0.9805	0.5566	0.0481
1.1	0.9782	0.5583	0.0460
1.2	0.9760	0.5651	0 0446
1.3	0.9735	0 5757	0.0435
1.4	0.9710	0.5849	0.0426
1.5	0.9682	0.5971	0.0419
1.6	0.9651	0.6197	0.0418
1.7	0.9618	0.6360	0.0416
1.8	0.9583	0.6575	0.0416
1.9	0.9542	0.6868	0.0421
1.9641	0.9514	0.7035	0.0425

[8] Refer to the left column in page 2356 of Reardon and Beckie (1987).

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Excerpt IV-5. Table 1 of Reardon and Beckie (1987), where the experimental data of Oykova and Balarew (1974) are processed using $\gamma_{\pm} = 0.161 \pm 0.010$ at 0.1 m $FeSO_4$. Oykova and Balarew (1974) used $\gamma_{\pm} = 0.150$. See discussion in the left column in page 2356 of Reardon and Beckie (1987). The molality, ϕ, and $\gamma_{\pm}$ are transcribed in Table IV-3.

Table 1 Osmotic coefficients (ϕ) and mean molal activity coefficients for $FeSO_4$ solutions from 0.1 to 2.0 molal concentration calculated from the isopiestic measurements of Oykova and Balarew (1974).

m	ϕ	$\gamma_{\pm}$	m	ϕ	$\gamma_{\pm}$
0.1	0.556	0.161	1.1	0.557	0.052
0.2	0.515	0.115	1.2	0.562	0.051
0.3	0.511	0.093	1.3	0.574	0.050
0.4	0.509	0.081	1.4	0.584	0.049
0.5	0.519	0.073	1.5	0.598	0.048
0.6	0.521	0.067	1.6	0.617	0.047
0.7	0.527	0.062	1.7	0.636	0.047
0.8	0.532	0.059	1.8	0.657	0.047
0.9	0.542	0.056	1.9	0.685	0.048
1.0	0.547	0.054	2.0	0.705	0.049

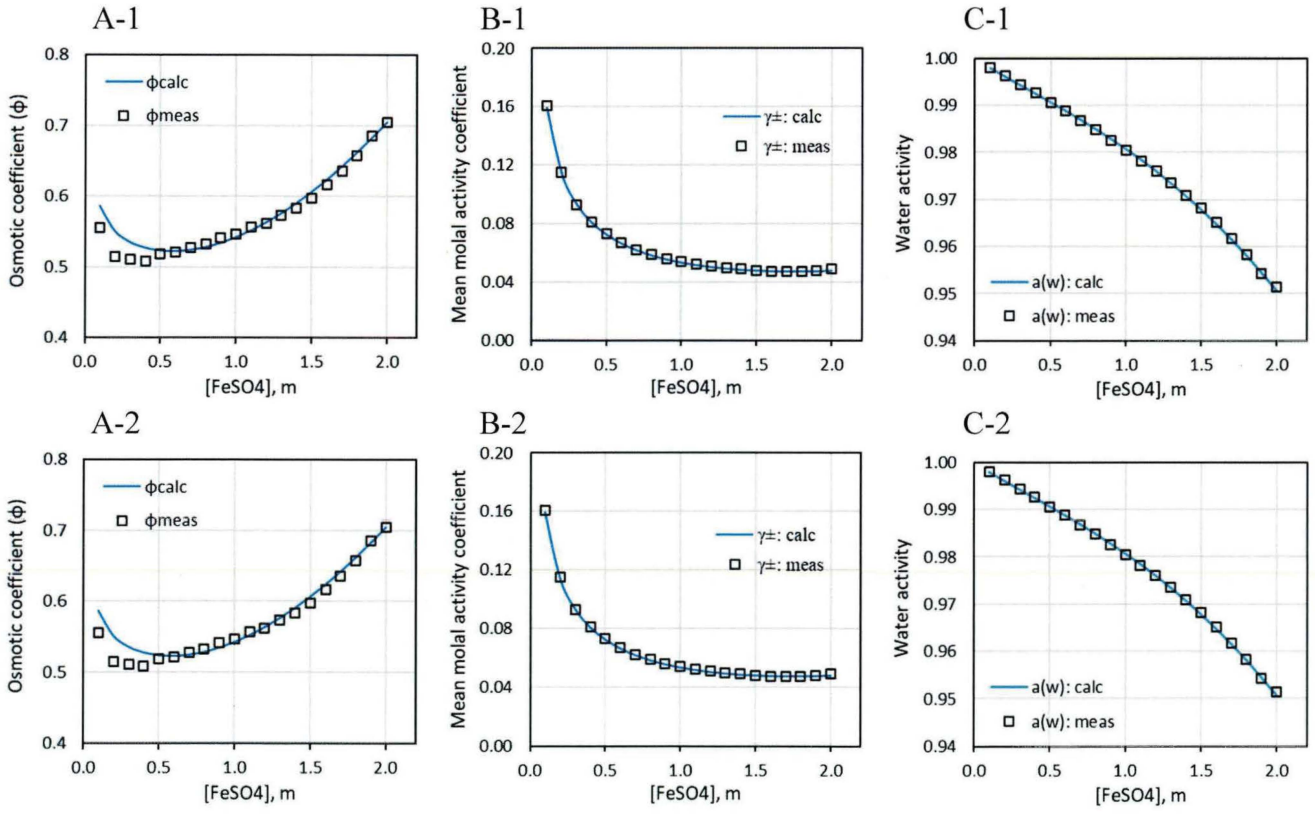
Table IV-3. Transcription of Table 1 of Reardon and Beckie (1987).

$[FeSO_4]$, m	Osmotic coefficient, ϕ	Mean molal activity coefficient of $FeSO_4$, $\gamma_{\pm}$	File name
0.1	0.556	0.161	feso4_01.3i
0.2	0.515	0.115	feso4_02.3i
0.3	0.511	0.093	feso4_03.3i
0.4	0.509	0.081	feso4_04.3i
0.5	0.519	0.073	feso4_05.3i
0.6	0.521	0.067	feso4_06.3i
0.7	0.527	0.062	feso4_07.3i
0.8	0.532	0.059	feso4_08.3i
0.9	0.542	0.056	feso4_09.3i
1.0	0.547	0.054	feso4_10.3i
1.1	0.557	0.052	feso4_11.3i
1.2	0.562	0.051	feso4_12.3i
1.3	0.574	0.050	feso4_13.3i
1.4	0.584	0.049	feso4_14.3i
1.5	0.598	0.048	feso4_15.3i
1.6	0.617	0.047	feso4_16.3i
1.7	0.636	0.047	feso4_17.3i
1.8	0.657	0.047	feso4_18.3i
1.9	0.685	0.048	feso4_19.3i
2.0	0.705	0.049	feso4_20.3i

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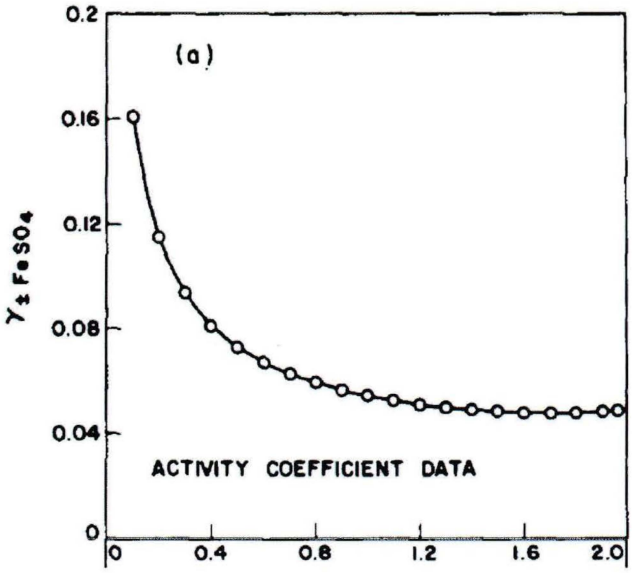
Twenty EQ3NR input files were prepared and executed using (i) the reactions and their log Ks in Table IV-1 and PIPs of Reardon and Beckie (1987) only in Table IV-2, and (ii) the same reactions but with the PIPs for the species pairs of H^+/SO_4^{-2} and H^+/HSO_4^- replaced with Harvie et al. (1984) (the values in green fonts in Table IV-2). Results of the two calculations of osmotic coefficients, mean molal activity coefficients, and water activities are presented in Figure IV-1, where the calculation of (i) shown in panels A-1, B-1, and C-1; and the calculation of (ii) shown in panels A-2, B-2, and C-2. The curves in Figure IV-1B-1, B-2 show excellent agreement with that depicted in Excerpt IV-6, where the Reardon and Beckie (1987) calculation is captured.

Figure IV-1. Calculated vs. measured osmotic coefficients in A; mean molal activity coefficient in B; and water activity in C using the PIPs of Reardon and Beckie (1987) only (A-1, B-1, and C-1); in combination of PIPs of Harvie et al. (1984) (A-2, B-2, and C-2). The $FeSO_4$ solutions up to 2.0 m are of circumneutral pH, thus, the differences in PIPs for the species pairs H^+/SO_4^{-2}, H^+/HSO_4^-, and SO_4^{-2}/OH^- (Table IV-2) would not be conspicuous.



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Excerpt IV-6. Measurements (Oykova and Balarew, 1974) compared with the prediction of Reardon and Beckie (1987) for the mean molal activity coefficient of $FeSO_4$ ($\Gamma_{\pm}$ or $\gamma_{\pm}$) = 0.161.



The results in Figure IV-1 were reproduced by run control coordinator (RCC) using (i) EQ3/6 Version 8.0a (Wolery and Jarek, 2003) officially installed and documented, and (ii) the qualified SNL WIPP TDB (data0.fm1; Xiong, 2011).

The RCC updated the qualified SNL WIPP TDB using the PIPs in black font text blocks in Table IV-2 to create an interim TDB. Using the interim TDB, RCC ran the input files in Table IV-3 through the officially installed/documented EQ3/6 Version 8.0a (Wolery and Jarek, 2003).

The RCC updated the interim TDB above using the PIPs for species pairs for H^+/SO_4^{-2} and H^+/HSO_4^- are those in green font in Table IV-2 to create another interim TDB. Using the updated interim TDB, RCC ran the input files in Table IV-3 through the officially installed/documented EQ3/6 Version 8.0a (Wolery and Jarek, 2003).

The reproduction results are archived in "CVS/CVSLIB/WIPP_EXTERNAL/feso4".

IV.2. Solubility constants for $FeSO_4.7H_2O$(s) (Melanterite) and $FeSO_4.H_2O$(s) (Szomolnokite)

SNL WIPP Geochemistry will accept the solubility constants for $FeSO_4.7H_2O$(s) (Melanterite) and $FeSO_4.H_2O$(s) (Szomolnokite). The values are calculated by the equations in Reardon and Beckie (1987). The equations are captured in Excerpt IV-2 and Excerpt IV-3.

The calculated log K of $FeSO_4.7H_2O$(s) (Melanterite) is -2.20927 ≡ -2.20 by truncation of the underlined numbers. $FeSO_4.7H_2O$(s) (Melanterite) is expected to be highly soluble. Its solubility is

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1.96 m at 25 °C (Excerpt IV-7). Therefore, it would not form in conditions where the ΣFe is controlled by $Fe(OH)_2(s)$, $Fe_2Cl(OH)_3(s)$ (Hibbingite), $FeCO_3(s)$ (Siderite), and/or $Fe_2CO_3(OH)_2(s)$ (Chukanovite) (Kim et al., 2017), especially when ΣSO4 concentration is limited by $CaSO_4(s)$ (Anhydrite) or $CaSO_4.2H_2O(s)$ (Gypsum). The activity correction using the PIPs in Table IV-2 would not affect this claim.

The log K of $FeSO_4.H_2O(s)$ (Szomolnokite) can be calculated to be -0.90656 ≡ -0.90 by truncation of the underlined numbers. Note that it is stable at temperature higher than 60 °C and H_2SO_4 concentration higher than 3 m (Reardon and Beckie, 1987; Excerpt IV-7), making it less relevant to WIPP Geochemistry along with the ΣFe controlled by $Fe(OH)_2(s)$, $Fe_2Cl(OH)_3(s)$ (Hibbingite), $FeCO_3(s)$ (Siderite), and/or $Fe_2CO_3(OH)_2(s)$ (Chukanovite) (Kim et al., 2017).

The log Ks are listed in Table IV-1.

Excerpt IV-7. Table 4 of Reardon and Beckie (1987) captured from pages 2359 therein.

Table 4 Results of equilibria calculations to determine the solubility products of the ferrous sulphate mono and heptahydrate as a function of temperature. Solubility measurements for the heptahydrate (melanterite) were taken from the smoothed values reported by Linke and Seidell (1958) whereas measurements for the monohydrate (szomolnokite) are those reported by Bullough *et al.* (1952).

T°C	m	I	a_w	$\gamma_\pm$	log K_{sp}
Melanterite					
0	1.04	4.1	0.980	0.0537	-2.570
5	1.20	4.8	0.976	0.0519	-2.486
10	1.37	5.5	0.971	0.0505	-2.409
15	1.54	6.2	0.966	0.0494	-2.339
20	1.73	6.9	0.960	0.0486	-2.275
25	1.96	7.8	0.952	0.0480	-2.205
30	2.16	8.6	0.944	0.0475	-2.153
35	2.40	9.6	0.934	0.0474	-2.096
40	2.64	10.5	0.923	0.0476	-2.048
45	2.90	11.6	0.909	0.0482	-1.999
50	3.18	12.7	0.893	0.0493	-1.954
55	3.48	13.9	0.874	0.0510	-1.911
Szomolnokite					
60	3.35	13.4	0.885	0.0451	-1.695
65	3.10	12.4	0.903	0.0386	-1.889
70	2.92	11.7	0.915	0.0339	-2.048
85	2.36	9.4	0.947	0.0238	-2.526
95	1.90	7.6	0.966	0.0196	-2.874
100	1.67	6.7	0.974	0.0183	-3.044

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V. SUMMARY

As illustrated in Figure IV-1 and compared with Excerpt IV-6, the use of PIPs for the supporting species pairs of H^+/SO_4^{-2} and H^+/HSO_4^- of Harvie et al. (1984) instead of those given by Reardon and Beckie (1987) did not result in significant differences. The difference was smaller than the dimension of the symbols in Figure IV-1. This observation can be attributed to the low $[H^+]$ in the Oykova and Balarew (1974) experiment, i.e., minimized influence of the interactions of the two species pairs and a triplet (H^+/SO_4^{-2}, H^+/HSO_4^-, and $H^+/Fe^{+2}/HSO_4^-$) on the calculation of osmotic coefficient, mean molal activity coefficient, and the water activity.

Therefore, the hypothesis posed in Section III is proved. That is, the PIPs for Fe^{+2}/SO_4^{-2}, Fe^{+2}/HSO_4^-, and $H^+/Fe^{+2}/HSO_4^-$ of Reardon and Beckie (1987) are compatible with the SNL WIPP TDB, and can be used in the compliance-decision-making calculations. Since the original data of Oykova and Balarew (1974) are not provided with uncertainties, the statistical validity of the PIPs cannot be evaluated. SNL WIPP Geochemistry selected the PIPs for H^+/SO_4^{-2} and H^+/HSO_4^- of Harvie et al. (1984), and we won't judge the accuracy of the PIPs for the species pairs of H^+/SO_4^{-2} and H^+/HSO_4^- in Reardon and Beckie (1987). SNL WIPP Geochemistry considers them non-identifiable from each other.

Calculated ΣFe using the log Ks of $FeSO_4.H_2O(s)$ (Szomolnokite) and $FeSO_4.7H_2O(s)$ (Melanterite) under ΣSO4 limited by $CaSO_4(s)$ (Anhydrite) and/or $CaSO_4.2H_2O(s)$ (Gypsum) would not be achieved in conditions where the dissolved ΣFe is controlled by other reactive Fe solids, e.g., $Fe(OH)_2(s)$, $Fe_2Cl(OH)_3(s)$ (Hibbingite), $FeCO_3(s)$ (Siderite), and/or $Fe_2CO_3(OH)_2(s)$ (Chukanovite).

VI. FUTURE WORK

SNL WIPP Geochemistry plans to revisit Kim et al. (2017) and, consequently, Sections IV.1 to IV.5 of GEOC-21-11 (Jang et al., 2021) to refine the model and issue addendum to both if necessary for CRA-2029. No changes in the thermodynamic quantities reported in Kim et al. (2017) and the Sections of GEOC-21-11 (Jang et al., 2021) is hypothesized for now considering the precision of the measurements reported therein.

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