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Published in:
Materials Processing Fundamentals 2019

DOI:
[10.1007/978-3-030-05728-2_21](https://doi.org/10.1007/978-3-030-05728-2_21)

Published: 01/01/2019

Document Version
Accepted author manuscript

Document License
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[Link to publication](#)

Please cite the original version:

Tesfaye, F., Jung, I.-H., Paek, M.-K., Moroz, M., Lindberg, D., & Hupa, L. (2019). Thermochemical Data of Selected Phases in the FeO_x–FeSO₄–Fe₂(SO₄)₃ System. In G. Lambotte, J. Lee, A. Allanore, & S. Wagstaff (Eds.), *Materials Processing Fundamentals 2019* (pp. 227–240). Springer. https://doi.org/10.1007/978-3-030-05728-2_21

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Thermochemical Data of Selected Phases in the $\text{FeO}_x\text{-FeSO}_4\text{-Fe}_2(\text{SO}_4)_3$ System

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Abstract

Several recent studies have shown the potential of oxy-fuel combustion to reduce $\text{NO}_x(\text{gas})$ and $\text{SO}_2(\text{gas})$ emissions. However, the mechanisms through which $\text{SO}_2(\text{gas})$ reduction takes place has yet to be fully understood. Therefore, development of oxy-sulfate thermodynamic database for a better understanding and control of $\text{SO}_2(\text{gas})$ emission during oxy-fuel combustion processes is essential. The focus of this research is on the thermodynamic modelling of the iron oxide - sulfate system with the FactSage 7.2 software package. Thermodynamic properties of selected phases in the $\text{FeO}_x\text{-FeSO}_4\text{-Fe}_2(\text{SO}_4)_3$ system were critically reviewed, compiled and assessed over a wide temperature range (298–2000 K) to obtain accurate thermodynamic description of the system at different temperatures. New C_p -functions, which include the recent experimental data, were optimized. The obtained results are presented and discussed.

Keywords: Sulfate, Sulfur dioxide, Decomposition reaction, Thermochemical data

1 Introduction

Today, oxy-fuel combustion is considered as one of the major technologies for $\text{CO}_2(\text{gas})$ capture in power plants. A number of recent studies have also shown its potential to reduce $\text{NO}_x(\text{gas})$ and $\text{SO}_2(\text{gas})$ emissions. To control and optimize the emission reduction mechanisms, development of oxy-sulfate thermodynamic database for the oxy-fuel combustion processes is essential. Therefore, the focus of this research is on the thermodynamic modelling of the $\text{FeO}_x\text{-FeSO}_4\text{-Fe}_2(\text{SO}_4)_3$ system with the FactSage 7.2 software package as a part of the larger database of the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-FeO-Fe}_2\text{O}_3\text{-sulfate}$ system.

In the present work, thermodynamic data of FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ were compiled and critically assessed below 2000 K to obtain accurate thermodynamic parameters. All calculations were carried out using the FactSage 7.2 thermochemical software [1], including the pure substances and self-developed databases.

1.1 Phase Relations in the Ternary Fe-S-O system

Recently, the relatively well known Fe-O and Fe-S systems were reevaluated by Hidayat et al. [2] and Walder and Pelton [3], respectively. The ternary Fe-S-O system was investigated by Shishin et al. [4]. In this system, only two stable ternary compounds, FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ were reported. At ambient pressure conditions, both ternary phases decompose below 1500 K to form the gas and oxide phases before melting [4]. Chemical structures of the anhydrous ferrous sulfate (FeSO_4) and ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) are illustrated in Fig. 1. Barany and Adami [5], Pankratz and Weller [6] and Majzlan et al. [7] measured the thermodynamic properties of $\text{Fe}_2(\text{SO}_4)_3$, and Moore and Kelly [8] measured the low temperature thermodynamic properties of FeSO_4 . Using the susceptibility measurement technique, Frazer & Brow [9] and Kirfel et al. [10] measured magnetic data (μ_B) for $\alpha\text{-FeSO}_4$ and $\beta\text{-FeSO}_4$ to be 4.1 ± 0.4 and 5.44 ± 0.27 , respectively.

The anhydrous iron (III) sulfate ($\text{Fe}_2(\text{SO}_4)_3$) crystallizes in two modifications, monoclinic and trigonal. The stability relationship between the two phases is not clear. Only the trigonal polymorph has been reported in nature, under the name mikasaite. Mikasaite is formed by precipitation from hot gases escaping fractures in coal beds [7]. $\text{Fe}_2(\text{SO}_4)_3$ is rare as a mineral, but it is an important compound for development of a thermodynamic database for a number of natural hydrated iron sulfates [11] and oxy-fuel combustion applications. More details on the thermodynamic properties of the phases in the $\text{FeO}_x\text{-FeSO}_4\text{-Fe}_2(\text{SO}_4)_3$ system are presented and discussed in the subsequent sections.

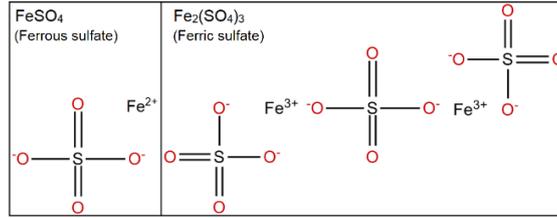
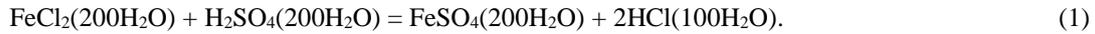


Fig. 1 Schematic diagram of the chemical structures of the ferrous and ferric sulfates, adopted from [12]

2 Thermochemical Data of FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$

2.1 Enthalpy of Formation (ΔH_f°) of FeSO_4

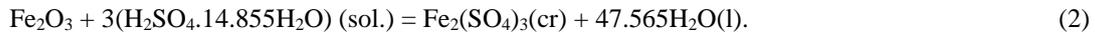
Thomsen [13] measured the enthalpy of reaction (1). In the NIST-JANAF thermochemical table [12], this enthalpy of reaction (1) was used to estimate $\Delta_f H^\circ(298.15 \text{ K}, \text{FeSO}_4) = -924.66 \text{ kJ}\cdot\text{mol}^{-1}$.



In the NIST-JANAF thermochemical data [12], $\Delta_f H^\circ(298.15 \text{ K}, \text{FeSO}_4)$ values from the decomposition pressure of FeSO_4 reported by D'Ans [14], Greulich [15], and Neumann and Heintke [16] were also estimated by the 2nd and 3rd laws with an average value of $-925.1 \text{ kJ}\cdot\text{mol}^{-1}$. $\Delta_f H^\circ(298.15 \text{ K}, \text{FeSO}_4) = -928.85 \pm 8.4 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H^\circ(0 \text{ K}) = -919.33 \pm 8.4 \text{ kJ}\cdot\text{mol}^{-1}$ are the values recommended by [12].

2.2 $\Delta_f H^\circ(\text{Fe}_2(\text{SO}_4)_3)$

Based on the data reported for the chemical reaction (2) by Barany and Adami [5] and using enthalpies of formations of the other components involved in the reaction, $\Delta_f H^\circ(298.15 \text{ K}, \text{Fe}_2(\text{SO}_4)_3) = -2583 \pm 1.7 \text{ kJ}\cdot\text{mol}^{-1}$ was estimated and presented in [12].



The equilibrium pressures for decomposition of $\text{Fe}_2(\text{SO}_4)_3$ have been determined by several investigators [16-23] at different temperatures via chemical reactions (3) and (4). The data were critically reviewed by Kellogg [24].



The measured pressure of the chemical equilibrium is the total pressures of $P(\text{SO}_3)$, $P(\text{SO}_2)$, and $P(\text{O}_2)$. In order to calculate the enthalpy change of reaction (3), the partial pressures of $\text{SO}_3(\text{g})$ from the total vapor pressure data at each temperature was evaluated. Based on the derived values for $P(\text{SO}_3)$, $\Delta_f H^\circ(298.15 \text{ K}, \text{Fe}_2(\text{SO}_4)_3)$ values were derived using the 3rd law and presented in the NIST-JANAF thermochemical data [12]. These average values of the calculations give $-2584.164 \text{ kJ}\cdot\text{mol}^{-1}$. This value is higher only by $\sim 1 \text{ kJ}\cdot\text{mol}^{-1}$ than the value they obtained through the data of Barany and Adami [5].

After experimental studies in the temperature range 273-395 K, Majzlan et al. [7] determined $\Delta_f H^\circ(298.15 \text{ K}, \text{Fe}_2(\text{SO}_4)_3) = -2585.2 \pm 4.9 \text{ kJ}\cdot\text{mol}^{-1}$, which is higher by $\sim 2 \text{ kJ}\cdot\text{mol}^{-1}$ than the value of Barany and Adami [5].

2.3 Heat Capacity (C_p) and Entropy (S°)

FeSO_4

The low temperature C_p of the anhydrous FeSO_4 in the temperature range 53 - 294.6 K were determined by Moore and Kelly [8] experimentally. Based on standard entropy at 50.12 K, they calculated, $S^\circ(\text{FeSO}_4, 298.15\text{K}) = 107.57 \pm 0.84 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Since the report by Moore and Kelley [8] did not mention the magnetic entropy contribution, an attempt was made by [25] to add magnetic entropy (S_{mag}) to $S^\circ(\text{FeSO}_4, 298.15\text{K})$ and reevaluate the decomposition pressure data. They used the theoretical value of magnetic entropy (S_{mag}) for FeSO_4 $R \ln(2S_{\text{spin}})$, where S_{spin} is the magnetic spin. Since, the electrons in the iron ions in FeSO_4 are in a high-spin configuration they may have used $S_{\text{spin}} = 5/2$ which implies $S_{\text{mag}} = R \ln 5 = 13.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Therefore, the value $S^\circ(298.15 \text{ K}) = (107.57 + 13.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 120.96 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ was adopted for FeSO_4 . The C_p above 294.9 K were estimated by comparison with those for MnSO_4 . In the calculations, the high-temperature $C_p(\text{MnSO}_4)$, 870.3-1082.3 K, were taken from the experiments of Southard and Shomate [26].

Fe₂(SO₄)₃

The heat capacities were established by comparison with those for FeSO₄, assuming their average specific heats, J·K⁻¹·g⁻¹, to be the same. The value of S°(298.15K) was estimated so that the 2nd and 3rd law ΔH_f°(298.15 K) values, derived from decomposition pressure data, are in reasonable agreement. The value S°(298.15 K) = 120.957 ± 1.3 J·K⁻¹·mol⁻¹ was recommended in the NIST-JANAF thermochemical table [12].

Majzlan et al. [7] studied thermodynamic properties of the monoclinic Fe₂(SO₄)₃ by acid solution, adiabatic, and semi-adiabatic calorimetry methods. They reported ΔH_f°(298.15K, Fe₂(SO₄)₃) = -2585.2±4.9 kJ·mol⁻¹ obtained by an appropriate thermochemical cycle with enthalpies of solution of monoclinic Fe₂(SO₄)₃, α-MgSO₄, γ-FeOOH, H₂O, and MgO in 5NHCl and at 298 K. They also compiled C_p values from 0.5 to 400 K and represented the data in the temperature range 273 to 395 K by Eq. (5).

$$C_p/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 213 + 0.312\cdot(T) - 2.959\cdot 10^6\cdot(T)^{-2} \quad (273 - 395\text{K}) \quad (5)$$

2.4 Melting and Decomposition Temperatures

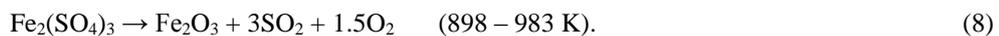
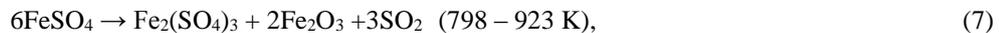
The decomposition temperature 1451 K for Fe₂(SO₄)₃ at which the total pressure of the gaseous products equals 1 atm, was calculated by [12] through the graphical extrapolation of the decomposition pressure data measured by Warner and Ingraham [27]. By a similar method they also calculated T_{decomp.}(FeSO₄) = 944 K from the data of Greulich [15]. Reactions (3) and (6) are the decomposition reactions for which the vapor pressure experimental data are available.

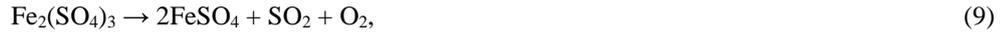


Table I. Summary of the phase transition and decomposition temperatures of FeSO₄ and Fe₂(SO₄)₃

Reaction	T _{trans./K}	T _{decomp./K}	Ref.	Remark
α-FeSO ₄ → β-FeSO ₄	623	-	[10]	High-pressure phase transition (at P _{tot} ≈ 15 kbar)
Reaction (3): Fe ₂ (SO ₄) ₃ → Fe ₂ O ₃ + 3SO ₃	-	1461	[12]	Determined by the gas pressure measurements of [27]
	-	1017	This work	
	-	951	[30]	Heating rate 20K·min ⁻¹
	-	1028	[31]	-
	-	1024	[7]	-
Reaction (6): FeSO ₄ → FeO + SO ₃	-	944	[12]	-
Reaction (7): 6FeSO ₄ → Fe ₂ (SO ₄) ₃ + 2Fe ₂ O ₃ + 3SO ₂	-	798- 923	[28]	Inert atmosphere
	-	891	[30]	Heating rate 20K·min ⁻¹
	-	960	[31]	-
Reaction (8): Fe ₂ (SO ₄) ₃ → Fe ₂ O ₃ + 3SO ₂ + 1.5O ₂	-	898 – 983	[28]	Inert atmosphere
Reaction (11): 2FeSO ₄ + 0.5O ₂ → Fe ₂ O(SO ₄) ₂	-	870-948	[29]	Oxidizing atmosphere
Reaction (12): Fe ₂ O(SO ₄) ₂ → Fe ₂ O ₃ + 2SO ₂		873-948		
Reaction (13): 2FeSO ₄ → Fe ₂ O ₂ SO ₄ + SO ₂	-	748 – 848	[29]	Inert atmosphere
Reaction (14): Fe ₂ O ₂ SO ₄ → Fe ₂ O ₃ + SO ₂		823 – 948		

The thermal decomposition of FeSO₄·6H₂O was studied by Masset et al. [28] applying the mass spectroscopy coupled with DTA/TG thermal analysis technique under inert atmosphere. After the dehydration, they reported to have observed two decomposition steps for FeSO₄ between 798 and 983 K according to the following reactions (7) and (8):





Gallagher et al. [29] studied the thermal decomposition of $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$ using the conventional thermogravimetry, differential thermal analysis, and evolved gas analysis techniques. In an oxidizing atmosphere, they observed that FeSO_4 oxidizes as



In the inert atmosphere:



Other proposed decomposition reactions under $\text{N}_2(\text{gas})$ protective atmosphere are for reaction (7), 891 K [30] (heating rate 20 K/min) and 960 K [31], and for reaction (3), 951 K [30] (heating rate 20 K/min) and 1028 K [31].

A comparative summary of the decomposition temperatures of FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ determined by different researchers and methods are compiled in Table I.

2.5 Gibbs Energy Data

The solid-gas reactions below 1100 K were studied using the EMF technique by [32-39], in a continuously flowing gas atmosphere, using the vapor pressure measurements technique by [27] and using the DTA technique by [40]. Gibbs energies of reactions determined by the different methods are summarized in Table II. These EMF experiments may not correspond to equilibrium with the gas phase, which can contain other gaseous species such as SO_3 , SO_2 and O_2 , but rather to a fixed potential of SO_2 , i.e. the other gaseous species do not form fast enough to significantly change the composition of the flowing SO_2 . If the equilibrium with the gas phase were attained, it would be almost pure SO_2 over the range of P_{O_2} from 10^{-4} to 10^{-14} atm. At higher oxygen potentials, amounts of SO_3 and O_2 become substantial, while at lower P_{O_2} the partial pressure of S_2 starts to increase. The composition of the gas flowing out of the EMF furnaces was estimated by [4] which indicated that large amounts of condensed phases in EMF cells would have to react in order to produce the gas phase of equilibrium composition, which is not what happened in the experiments.

Table II. A comparative summary of Gibbs energies of reactions determined by different authors

Equilibrium reaction	$\Delta G_f^\circ (\text{kJ} \cdot \text{mol}^{-1})$	T / K	Ref.
$\text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons \text{Fe}_2\text{O}_3 + 3\text{SO}_2 + 1.5\text{O}_2$	$970.05 - 0.724 \cdot T$	673–1073	[41]
	$772.32 - 0.724 \cdot T$	920–1020	[32]
	$870.235 - 0.8245 \cdot T$ (± 1.4)	800–1000	[39]
	$704.61 - 0.697 \cdot T$	878–955	[40]
	$802.86 - 0.762 \cdot T$	906–995	[27]
	$753.098 - 0.744 \cdot T$	900–1000	[27]*
	$730.5 - 0.688 \cdot T$	800–900	[42]
$\text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons \text{Fe}_2\text{O}_3 + 3\text{SO}_3$	$576.895 - 0.546 \cdot T$ (± 0.5)	800–1000	[39]
	$557.42 - 0.558 \cdot T$	900–1000	[27]*
$\text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons 2\text{FeSO}_4 + \text{SO}_2 + \text{O}_2$	$395.64 - 0.352 \cdot T$	703–904	[32]
$\text{FeSO}_4 \rightleftharpoons 0.5\text{Fe}_2\text{O}_3 + \text{SO}_2 + 1/4\text{O}_2$	$258.74 - 0.202 \cdot T$	773–903	[41]
$\text{FeSO}_4 \rightleftharpoons 0.5\text{Fe}_2\text{O}_3 + \text{SO}_2 + 1/4\text{O}_2$	$203.47 - 0.202 \cdot T$	779–900	[32]

*Re-calculated from the experimental data of Warner and Ingraham [27].

Jacob and Iyengar [39] studied the $\text{Fe}_2\text{O}_3 + \text{Fe}_2(\text{SO}_4)_3$ phase equilibria by the EMF method. They measured EMF values between 800 and 1000 K. Based on their results, they have concluded that oxysulfates do not form below 1100 K in the Fe-S-O system. The determined Gibbs energies of reactions involving the gases SO_3 , SO_2 , O_2 are compiled in Table II.

Combining the high-temperature change in enthalpy of reaction $\text{Fe}_2(\text{SO}_4)_3 = \text{Fe}_2\text{O}_3 + 3\text{SO}_2(\text{g}) + 1.5\text{O}_2(\text{g})$ reported by Jacob and Iyengar [39] with the pure substances enthalpy data of FactSage 7.2 for $\text{SO}_2(\text{g})$ and Fe_2O_3 , we have calculated $\Delta H_f^\circ(\text{Fe}_2(\text{SO}_4)_3) = -2586.55 \text{ kJ}\cdot\text{mol}^{-1}$. This value is higher only by $-1.35 \text{ kJ}\cdot\text{mol}^{-1}$ than that of Majzlan et al. [7]. Warner and Ingraham [27] have also determined the enthalpy of decomposition of $\text{Fe}_2(\text{SO}_4)_3$ from the vapor pressure measurements to be $\Delta H^\circ_{\text{decomp.}} = 566.51 \text{ kJ}\cdot\text{mol}^{-1}$.

3 Results and Discussion

The $C_p(\text{SO}_3)$ -functions obtained through the reactions $\text{MeO} + \text{SO}_3 = \text{MeSO}_4$ ($\text{Me} = \text{Ca}, \text{Mg}, \text{Mn}$) were calculated by applying the Neumann-Kopp's rule described in [43]. With the obtained C_p values, the corresponding $C_p(\text{FeSO}_4)$ values were calculated according to reaction (6). The results are illustrated in Fig. 2.

The heat capacities of FeSO_4 were calculated between 273 – 400 K by comparison with those experimental data reported for $\text{Fe}_2(\text{SO}_4)_3$, assuming their average specific heats, $c_p(\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1})$, to be the same. We have also calculated the experimental $C_p(\text{FeSO}_4)$ values reported by Moore and Kelly [8] for the temperature range 273 – 295 K. By combining these all C_p values with the $C_p(\text{FeSO}_4)$ obtained through the derived $C_p(\text{SO}_3)$ from the reaction $\text{MnSO}_4 = \text{MnO} + \text{SO}_3$ using the data of Barin [44], optimal $C_p(\text{FeSO}_4)$ was calculated at each temperature, in the temperature range 273 – 2000 K. By using the normal format for C_p -polynomials, we fitted all the data together in two temperature ranges, 273 – 500 K (Eq. 15) and 500 – 2000 K (Eq. 16). Likewise, we have calculated $C_p(\text{Fe}_2(\text{SO}_4)_3)$ and the results are illustrated in Fig. 3. The optimized C_p -polynomials for $\text{Fe}_2(\text{SO}_4)_3$ in the temperature range 273 – 2000 K is expressed by Eq. (17).

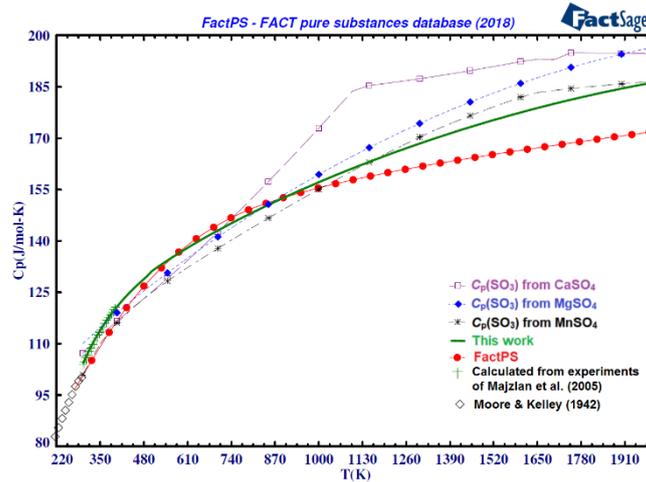


Fig. 2. C_p vs. T diagram of FeSO_4

$$C_p(\text{FeSO}_4, 273-500 \text{ K}) = 118.67 + (0.047)\cdot T - (24.903)\cdot 10^5\cdot T^{-2} - (5.943)\cdot 10^{-6}\cdot T^2, \quad (15)$$

$$C_p(\text{FeSO}_4, 500-2000 \text{ K}) = 108.213 + (0.0612)\cdot T - (12.842)\cdot 10^5\cdot T^{-2} - (10.980)\cdot 10^{-6}\cdot T^2, \quad (16)$$

$$C_p(\text{Fe}_2(\text{SO}_4)_3, 273-2000 \text{ K}) = 305.363 + (0.136)\cdot T - (62.0743)\cdot 10^5\cdot T^{-2} - (20.7454)\cdot 10^{-6}\cdot T^2. \quad (17)$$

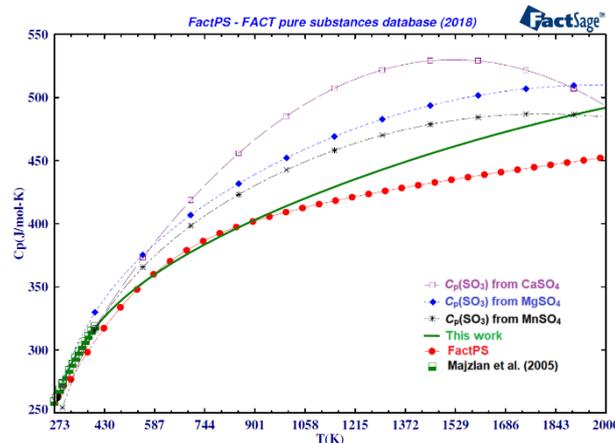


Fig. 3 C_p vs. T diagram of $\text{Fe}_2(\text{SO}_4)_3$

As shown in Fig. 2, at high-temperatures the C_p values are remarkably higher than the values currently used in the FactSage 7.2 database, which is based on the NIST-JANAF thermochemical data [12].

Recently, Majzlan et al. [7] determined the change in enthalpies of formations of $\text{Fe}_2(\text{SO}_4)_3$ in the temperature range 273-395 K. This value is higher by about $-2.2 \text{ kJ}\cdot\text{mol}^{-1}$ than the value recommended by NIST-JANAF [12]. In this work, we adopted the value $\Delta H_f^\circ(298.15\text{K}, \text{Fe}_2(\text{SO}_4)_3) = -(2585.2 \pm 4.9) \text{ kJ}\cdot\text{mol}^{-1}$ reported by Majzlan et al. [7], which was obtained through rigorous experimental studies.

By applying our new database for $\text{FeO}_x\text{-FeSO}_4\text{-Fe}_2(\text{SO}_4)_3$, $\Delta G_r^\circ(T)$ for an equilibrium reaction $\text{Fe}_2\text{O}_3 + 3\text{SO}_2 + 1.5\text{O}_2 \rightleftharpoons \text{Fe}_2(\text{SO}_4)_3$ was calculated in the temperature range 760–1000 K, in which all the available experimental literature data fall. The obtained result is illustrated in Fig. 4 together with the selected experimental literature data presented in Table II. Except the values reported by Sadakane et al. [42] and Alcock et al. [40], the literature values are in agreement with our calculation.

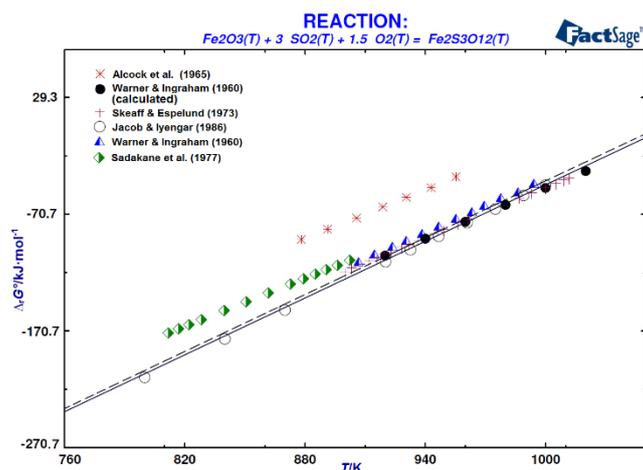


Fig. 4 ΔG_r° vs. T diagram for the ferric sulfate formation reaction together with the literature experimental data. The solid line is calculated with the database developed in this work and the dashed line is calculated using the pure substances database in the commercial version of FactSage 7.2 [1]

3.1 Potential Phase Diagrams

Based on the results obtained for FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$, in this work, and the literature data for the other phases, chemical potential phase diagram has been calculated for the $\text{Fe-O}_2\text{-SO}_2$ system between 580 and 1250 K.

The potential phase diagram of $\log_{10}P(\text{O}_2)$ vs. T shown in Fig. 5 was calculated at $P(\text{SO}_2)=1 \text{ atm}$ and $P_{\text{Total}}= 2 \text{ atm}$. The results obtained are in good agreement with those of Shishin et al.'s [4], hence they may have also used a total pressure close to 2 atm in their calculations.

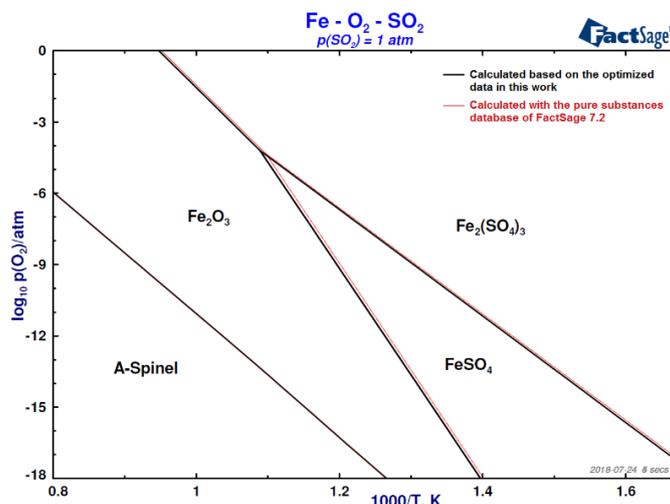


Fig. 5. Calculated potential phase diagram of $\text{Fe-O}_2\text{-SO}_2$ at $P(\text{SO}_2)=1 \text{ atm}$

By graphical extrapolation of the decomposition pressure data measured by Warner and Ingraham [27], we calculated $T_{\text{decomp}}(\text{Fe}_2(\text{SO}_4)_3) = 1017 \text{ K}$ at which the total pressure of the gaseous products equals one

atmosphere. This value is 434 K lower than the value reported in the NIST-JANAF thermochemical data [12] using the same source of experimental data. This large deviation indicates that there were most likely calculation errors in the NIST-JANAF thermochemical data [12]. Our calculations are in agreement with the results reported by [7,31] and presented in Table II.

4 Summary and Conclusions

The development of an oxy-sulfate thermodynamic database for a better understanding and control of SO₂(gas) emission during oxy-fuel combustion processes is essential. Therefore, the focus of this research was on the thermodynamic modelling of the iron oxide - sulfate system with the FactSage 7.2 software package. Thermodynamic properties of selected phases in the FeO_x-FeSO₄-Fe₂(SO₄)₃ system were critically reviewed, compiled and assessed over a wide temperature range 298–2000 K to obtain accurate thermodynamic parameters. The obtained results were generally in agreement with the literature values in the low-temperature conditions and deviate in the high-temperature conditions. New high temperature C_p-functions, which include the recent experimental data, were optimized. Regarding the decomposition temperatures of FeSO₄ and Fe₂(SO₄)₃ large deviation were observed among the literature values. This warrants that there is a need for new experiments to accurately determine the decomposition temperatures. According to our assessment of the available literature values, we recommend 944 K for the decomposition of FeSO₄ and 1017 K for the decomposition of Fe₂(SO₄)₃ according to reactions $\text{FeSO}_4 \rightarrow \text{FeO} + \text{SO}_3(\text{g})$ and $\text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{SO}_3(\text{g})$, respectively, at ambient pressure condition.

Acknowledgements

The authors are grateful to the Academy of Finland for financial support. This work was made under the project "Thermodynamic investigation of complex inorganic material systems for improved renewable energy and metals production processes" (Decision number 311537) as part of the activities of the Johan Gadolin Process Chemistry Center at Åbo Akademi University. This work is also a part of the project clean and efficient utilization of demanding fuels (CLUE), with support from the industrial partners: ANDRITZ, Fortum, International Paper, UPM-Kymmene Corporation, and Valmet Technologies Oy.

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