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Thermochemical Data of Selected Phases in the FeO\textsubscript{x}–FeSO\textsubscript{4}–Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} System

Fisheh Tesfaye, In-Ho Jung, Min-Kyu Paek, Mykola Moroz, Daniel Lindberg and Leena Hupa

Abstract Several recent studies have shown the potential of oxy-fuel combustion to reduce NO\textsubscript{x}(gas) and SO\textsubscript{2}(gas) emissions. However, the mechanisms through which SO\textsubscript{2}(gas) reduction takes place has yet to be fully understood. Therefore, the development of oxy-sulfate thermodynamic database for a better understanding and control of SO\textsubscript{2}(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 FeO\textsubscript{x}–FeSO\textsubscript{4}–Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{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

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Introduction

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

In the present work, thermodynamic data of FeSO$_4$ and Fe$_2$(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.

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 Fe$_2$(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 (Fe$_2$(SO$_4$)$_3$) are illustrated in Fig. 1. Barany and Adami [5], Pankratc and Weller [6] and Majzlan et al. [7] measured the thermodynamic properties of Fe$_2$(SO$_4$)$_3$, and Moore and Kelly [8] measured the low temperature thermodynamic properties of FeSO$_4$. Using the susceptibility measurement technique, Frazer and Brow [9] and Kirfel et al. [10] measured magnetic data ($\mu_B$) for $\alpha$-FeSO$_4$ and $\beta$-FeSO$_4$ to be $4.1 \pm 0.4$ and $5.44 \pm 0.27$, respectively.

The anhydrous iron (III) sulfate (Fe$_2$(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]. Fe$_2$(SO$_4$)$_3$ is rare as a mineral, but it is an important compound for the 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 FeO$_x$–FeSO$_4$–Fe$_2$(SO$_4$)$_3$ system are presented and discussed in the subsequent sections.
Thermochemical Data of FeSO$_4$ and Fe$_2$(SO$_4$)$_3$

*Enthalpy of Formation ($\Delta H_f^\circ$) of FeSO$_4$*

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

FeCl$_2$(200H$_2$O) + H$_2$SO$_4$(200H$_2$O) $\rightarrow$ FeSO$_4$(200H$_2$O) + 2HCl(100H$_2$O). \hspace{1cm} (1)

In the NIST-JANAF thermochemical data [13], $\Delta_f H_f^\circ(298.15$ K, FeSO$_4$) values from the decomposition pressure of FeSO$_4$ reported by D’Ans [14], Greulich [15], and Neumann and Heinke [16] were also estimated by the second and third laws with an average value of $-925.1$ kJ mol$^{-1}$. $\Delta_f H_f^\circ(298.15$ K, FeSO$_4$) = $-928.85 \pm 8.4$ kJ mol$^{-1}$ and $\Delta_f H_f^\circ(0$ K) = $-919.33 \pm 8.4$ kJ mol$^{-1}$ are the values recommended by Chase [13].

*$\Delta H_f^\circ(Fe_2(SO_4)_3)$*

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, $\Delta_f H_f^\circ(298.15$ K, Fe$_2$(SO$_4$)$_3$) = $-2583 \pm 1.7$ kJ mol$^{-1}$ was estimated and presented in [13].

Fe$_2$O$_3$ + 3(H$_2$SO$_4$ · 14.85H$_2$O)(sol.) $\rightarrow$ Fe$_2$(SO$_4$)$_3$(cr) + 47.565H$_2$O(l). \hspace{1cm} (2)
The equilibrium pressures for decomposition of Fe₂(SO₄)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].

\[
\text{Fe}_2\text{(SO}_4\text{)}_3 = \text{Fe}_2\text{O}_3 + 3\text{SO}_3, \quad (3)
\]

\[
\text{SO}_3(\text{g}) = \text{SO}_2(\text{g}) + 0.5\text{O}_2. \quad (4)
\]

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 of each compound was evaluated. Based on the derived values for \(P(\text{SO}_3),\) \(\Delta H_r^\circ (298.15 \text{ K}, \text{Fe}_2\text{(SO}_4\text{)}_3)\) values were derived using the third law and presented in the NIST-JANAF thermochemical data [13]. These average values of the calculations give \(-2584.164 \text{ kJ mol}^{-1}.\) This value is higher only by \(-1 \text{ kJ mol}^{-1}\) than the value they obtained through the data of Barany and Adami [5].

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

**Heat Capacity (\(C_p\)) and Entropy (\(S^\circ\))**

**FeSO₄**

The low-temperature \(C_p\) of the anhydrous FeSO₄ in the temperature range of 53–294.6 K was determined by Moore and Kelly [8] experimentally. Based on standard entropy at 50.12 K, they calculated, \(S^\circ(\text{FeSO}_4, 298.15 \text{ K}) = 107.57 \pm 0.84 \text{ J K}^{-1} \text{ mol}^{-1}.\) Since the report by Moore and Kelley [8] did not mention the magnetic entropy contribution, an attempt was made by Knacke et al. [25] to add magnetic entropy \(S_{\text{mag}}\) to \(S^\circ(\text{FeSO}_4, 298.15 \text{ K})\) and reevaluate the decomposition pressure data. They used the theoretical value of magnetic entropy \(S_{\text{mag}}\) for FeSO₄ \(\text{Rln(2S}_{\text{spin}}),\) where \(S_{\text{spin}}\) is the magnetic spin. Since the electrons in iron ions in FeSO₄ are in a high-spin configuration, they may have used \(S_{\text{spin}} = \frac{5}{2}\) which implies \(S_{\text{mag}} = \text{Rln5} = 13.4 \text{ J K}^{-1} \text{ mol}^{-1}.\) Therefore, the value \(S^\circ(298.15 \text{ K}) = (107.57 + 13.4) \text{ J K}^{-1} \text{ mol}^{-1}\) = 120.96 \text{ J K}^{-1} \text{ mol}^{-1}\) was adopted for FeSO₄. The \(C_p\) above 294.9 K was estimated by comparison with those for MnSO₄. In the calculations, the high-temperature \(C_p(\text{MnSO}_4), 870.3–1082.3 \text{ K},\) 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, \(J \text{ K}^{-1} \text{ g}^{-1},\) to be the same. The value of \(S^\circ(298.15 \text{ K})\) was estimated so that the second and third law \(\Delta H_r^\circ (298.15 \text{ K})\) values, derived from
decomposition pressure data, are in reasonable agreement. The value $S'(298.15\, K) = 120.957 \pm 1.3 \, J \, K^{-1} \, mol^{-1}$ was recommended in the NIST-JANAF thermochemical table [13].

Majzlan et al. [7] studied thermodynamic properties of the monoclinic Fe$_2$(SO$_4$)$_3$ by acid solution, adiabatic, and semi-adiabatic calorimetry methods. They reported $\Delta H_f'(298.15\, K, \, Fe_2(SO_4)_3) = -2585.2 \pm 4.9 \, kJ \, mol^{-1}$ obtained by an appropriate thermochemical cycle with enthalpies of solution of monoclinic Fe$_2$(SO$_4$)$_3$, $\alpha$-MgSO$_4$, $\gamma$-FeOOH, H$_2$O, and MgO in 5N HCl and at 298 K. They also compiled $C_p$ values from 0.5 to 400 K and represented the data in the temperature range of 273–395 K by Eq. (5).

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

**Melting and Decomposition Temperatures**

The decomposition temperature 1451 K for Fe$_2$(SO$_4$)$_3$ at which the total pressure of the gaseous products equals 1 atm, was calculated by [13] through the graphical extrapolation of the decomposition pressure data measured by Warner and Ingraham [27]. By a similar method, they also calculated $T_{decomp}(FeSO_4) = 944 \, K$ from the data of Greulich [15]. Reactions (3) and (6) are the decomposition reactions for which the vapor pressure experimental data are available.

$\text{FeSO}_4 \rightarrow \text{FeO} + \text{SO}_3.$ \quad (6)

The thermal decomposition of FeSO$_4$ $6H_2O$ 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 FeSO$_4$ between 798 and 983 K according to the following Reactions (7) and (8):

$$6\text{FeSO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{Fe}_2\text{O}_3 + 3\text{SO}_2(798–923\, K). \quad (7)$$

$$\text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{SO}_2 + 1.5\text{SO}_2(898–983\, K). \quad (8)$$

$$\text{Fe}_2(\text{SO}_4)_3 \rightarrow 2\text{FeSO}_4 + \text{SO}_2 + \text{O}_2. \quad (9)$$

$$\text{FeSO}_4 \rightarrow 0.5\text{Fe}_2\text{O}_3 + \text{SO}_2 + 0.25\text{SO}_2. \quad (10)$$

Gallagher et al. [29] studied the thermal decomposition of FeSO$_4$ $xH_2O$ using the conventional thermogravimetry, differential thermal analysis, and evolved gas analysis techniques. In an oxidizing atmosphere, they observed that FeSO$_4$ oxidizes as

$$2\text{FeSO}_4 + 0.5\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3(\text{SO}_4)_2. \quad (11)$$
\[
\text{Fe}_2\text{O}(\text{SO}_4)_{\text{3}} \rightarrow \text{Fe}_2\text{O}_3 + 2\text{SO}_2. \quad (873–948\text{K}) \quad (12)
\]

In the inert atmosphere

\[
2\text{FeSO}_4 \rightarrow \text{Fe}_2\text{O}_2\text{SO}_4 + \text{SO}_2, \quad (748–848 \text{ K}) \quad (13)
\]

\[
\text{Fe}_2\text{O}_2\text{SO}_4 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2 + 0.5\text{SO}_2. \quad (823–948\text{K}) \quad (14)
\]

Other proposed decomposition reactions under N\(_2\) (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 Fe\(_2\)(SO\(_4\))\(_3\) determined by different researchers and methods are compiled in Table 1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(T_{\text{trans/F}}/\text{K})</th>
<th>(T_{\text{decomp/F}}/\text{K})</th>
<th>Ref.</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-FeSO(_4) (\rightarrow) (\beta)-FeSO(_4)</td>
<td>623</td>
<td>–</td>
<td>[10]</td>
<td>High-pressure phase transition (at (P_{\text{total}} \approx 15\ \text{kbar})</td>
</tr>
<tr>
<td>Reaction (3): Fe(_2)(SO(_4))(_3) (\rightarrow) Fe(_2)O(_3) + 3SO(_3)</td>
<td>–</td>
<td>1461</td>
<td>[13]</td>
<td>Determined by the gas pressure measurements of [27]</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>1017</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>951</td>
<td>[30]</td>
<td>Heating rate 20 K min(^{-1})</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>1028</td>
<td>[31]</td>
<td>–</td>
</tr>
<tr>
<td>Reaction (7): 6FeSO(_4) (\rightarrow) 2Fe(_2)(SO(_4))(_3) + 2FeO(_3) + 5SO(_2)</td>
<td>–</td>
<td>798–923</td>
<td>891</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>960</td>
<td></td>
<td>Heating rate 20 K min(^{-1})</td>
</tr>
<tr>
<td>Reaction (8): Fe(_2)(SO(_4))(_3) (\rightarrow) Fe(_2)O(_3) + 5SO(_2) + 1.5SO(_2)</td>
<td>–</td>
<td>898–983</td>
<td>[28]</td>
<td>Inert atmosphere</td>
</tr>
<tr>
<td>Reaction (11): 2FeSO(_4) + 0.5SO(_2) (\rightarrow) Fe(_2)O(SO(_4))(_2)</td>
<td>–</td>
<td>870–948</td>
<td>873–948</td>
<td>[29]</td>
</tr>
<tr>
<td>Reaction (12): Fe(_2)O(SO(_4))(_2) (\rightarrow) Fe(_2)O(_3) + 2SO(_2)</td>
<td>–</td>
<td>870–948</td>
<td>873–948</td>
<td>[29]</td>
</tr>
<tr>
<td>Reaction (13): 2FeSO(_4) (\rightarrow) Fe(_2)O(_2)SO(_4) + SO(_2)</td>
<td>–</td>
<td>748–848</td>
<td>823–948</td>
<td>[29]</td>
</tr>
</tbody>
</table>
Gibbs Energy Data

The solid gas reactions below 1100 K were studied using the EMF technique by Skeaff and Espelund [32], Hsieh and Chang [33], Musbah and Chan [34], Kobe and Couch [35], Rosenqvist and Hofseth [36], Schaefer [37], in a continuously flowing gas atmosphere, using the vapor pressure measurements technique by Warner and Ingraham [27] and using the DTA technique by Alcock et al. [40]. Gibbs energies of reactions determined by the different methods are summarized in Table 2. These EMF experiments may not correspond to equilibrium with the gas phase, which can contain other gaseous species such as SO₃, SO₂ and O₂, but rather to a fixed potential of SO₂; i.e. the other gaseous species do not form fast enough to significantly change the composition of the flowing SO₂. If the equilibrium with the gas phase were attained, it would be almost pure SO₂ over the range of $P_{O_2}$ from $10^{-4}$ to $10^{-14}$ atm. At higher oxygen potentials, amounts of SO₃ and O₂ become substantial, while at lower $P_{O_2}$ the partial pressure of S₂ starts to increase. The composition of the gas flowing out of the EMF furnaces was estimated by Shishin et al. [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.

Jacob and Iyengar [39] studied the Fe₂SO₃ + Fe₄(SO₄)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

<table>
<thead>
<tr>
<th>Equilibrium reaction</th>
<th>$\Delta G_f^\circ$ (kJ mol$^{-1}$)</th>
<th>$T/K$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂(SO₄)₃ ⇌ Fe₂O₃ + 3SO₂ + 1.5O₂</td>
<td>970.05 – 0.724 $\cdot$ T</td>
<td>673–1073</td>
<td>[44]</td>
</tr>
<tr>
<td>772.32 – 0.724 $\cdot$ T</td>
<td>920–1020</td>
<td>[32]</td>
<td></td>
</tr>
<tr>
<td>$870.23$/$45$ – 0.8245 $\cdot$ T ($\pm 1.4$)</td>
<td>800–1000</td>
<td>[39]</td>
<td></td>
</tr>
<tr>
<td>704.61 – 0.697 $\cdot$ T</td>
<td>878–955</td>
<td>[40]</td>
<td></td>
</tr>
<tr>
<td>802.86 – 0.762 $\cdot$ T</td>
<td>906–995</td>
<td>[27]</td>
<td></td>
</tr>
<tr>
<td>753.09$8$ – 0.744 $\cdot$ T</td>
<td>900–1000</td>
<td>[27]*</td>
<td></td>
</tr>
<tr>
<td>730.5 – 0.688 $\cdot$ T</td>
<td>800–900</td>
<td>[43]</td>
<td></td>
</tr>
<tr>
<td>Fe₂(SO₄)₃ ⇌ Fe₂O₃ + 3SO₃</td>
<td>576.895 – 0.546 $\cdot$ T ($\pm 0.5$)</td>
<td>800–1000</td>
<td>[39]</td>
</tr>
<tr>
<td>557.42 – 0.558 $\cdot$ T</td>
<td>900–1000</td>
<td>[27]*</td>
<td></td>
</tr>
<tr>
<td>Fe₂(SO₄)₃ ⇌ 2FeSO₄ + SO₂ + O₂</td>
<td>395.64 – 0.352 $\cdot$ T</td>
<td>703–904</td>
<td>[32]</td>
</tr>
<tr>
<td>FeSO₄ ⇌ 0.5Fe₂O₃ + SO₂ + 1/4O₂</td>
<td>258.74 – 0.202 $\cdot$ T</td>
<td>773–903</td>
<td>[44]</td>
</tr>
<tr>
<td>FeSO₄ ⇌ 0.5Fe₂O₃ + SO₂ + 1/4O₂</td>
<td>203.47 – 0.202 $\cdot$ T</td>
<td>779–900</td>
<td>[32]</td>
</tr>
</tbody>
</table>

*Re-calculated from the experimental data of Warner and Ingraham [27]
system. The determined Gibbs energies of reactions involving the gases SO₃, SO₂, O₂ are compiled in Table 2.

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

Results and Discussion

The \( C_p(SO_3) \) functions obtained through the reactions \( \text{MeO} + \text{SO}_3 = \text{MeSO}_4 \) (Me = Ca, Mg, Mn) were calculated by applying the Neumann–Kopp’s rule described in Alcock et al. [41]. 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 \( \text{FeSO}_4 \) were calculated between 273 and 400 K by comparison with those experimental data reported for \( \text{Fe}_2\text{(SO}_4\text{)}_3 \), assuming their average

![Image of Cp versus T diagram of FeSO₄](image-url)

**Fig. 2** \( C_p \) versus \( T \) diagram of FeSO₄
specific heats, $c_p (J \, K^{-1} \, g^{-1})$, to be the same. We have also calculated the experimental $C_p(FeSO_4)$ values reported by Moore and Kelly [8] for the temperature range 273–295 K. By combining these all $C_p$ values with the $C_p(FeSO_4)$ obtained through the derived $C_p(SO_3)$ from the reaction MnSO₄ = MnO + SO₃ using the data of Barin Sadakane et al. [42], optimal $C_p(FeSO_4)$ was calculated at each temperature, in the temperature range of 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 $C_p(Fe_2(SO_4)_3)$ and the results are illustrated in Fig. 3. The optimized $C_p$ polynomials for $Fe(SO_4)_3$ in the temperature range 273–2000 K is expressed by Eq. (17).

$$C_p(FeSO_4, 273–500 \, K) = 118.67 + (0.047) \cdot T - (24.903) \cdot 10^5 \cdot T^{-2}$$
- $(5.943) \cdot 10^{-6} \cdot T^2$,  \hspace{1cm} (15)

$$C_p(FeSO_4, 500–2000 \, 1muK) = 108.213 + (0.0612) \cdot T - (12.842) \cdot 10^5 \cdot T^{-2}$$
- $(10.980) \cdot 10^{-6} \cdot T^2$,  \hspace{1cm} (16)

$$C_p(Fe_2(SO_4)_3, 273–2000 \, K) = 305.363 + (0.136) \cdot T - (62.0743) \cdot 10^5 \cdot T^{-2}$$
- $(20.7454) \cdot 10^{-6} \cdot T^2$.  \hspace{1cm} (17)
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 [13].

Recently, Majzlan et al. [7] determined the change in enthalpies of formations of $\text{Fe}_2(\text{SO}_4)_3$ in the temperature range of 273–395 K. This value is higher by about $-2.2 \text{ kJ mol}^{-1}$ than the value recommended by NIST-JANAF [13]. In this work, we adopted the value $\Delta H_f^\circ(298.15 \text{ K, Fe}_2(\text{SO}_4)_3) = -(2585.2 \pm 4.9) \text{ kJ mol}^{-1}$ reported by Majzlan et al. [7], which was obtained through rigorous experimental studies.

By applying our new database for $\text{FeO}_x-\text{Fe}_2\text{O}_3-\text{Fe}_2(\text{SO}_4)_3$, $\Delta G_f^\circ(T)$ 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 of 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 2. Except for the values reported by Sadakane et al. [43] and Alcock et al. [40], the literature values are in agreement with our calculation.

![Fig. 4 $\Delta G_f^\circ$ versus $T$ 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]](image)
**Potential Phase Diagrams**

Based on the results obtained for FeSO₄ and Fe₂(SO₄)₃, in this work, and the literature data for the other phases, chemical potential phase diagram has been calculated for the Fe–O₂–SO₂ system between 580 and 1250 K.

The potential phase diagram of $\log_{10} P(\text{O}_2)$ versus $T$ shown in Fig. 5 was calculated at $P(\text{SO}_2) = 1$ atm and $P_{\text{Total}} = 2$ 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.

By graphical extrapolation of the decomposition pressure data measured by Warner and Ingraham [27], we calculated $T_{\text{decomp}}(\text{Fe}_2(\text{SO}_4)_3) = 1017$ 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 [13] using the same source of experimental data. This large deviation indicates that there were most likely calculation errors in the NIST-JANAF thermochemical data [13]. Our calculations are in agreement with the results reported by [7, 31] and presented in Table 2.

**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 essen-
tial. 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 FeOx–FeSO₄–Fe₂(SO₄)₃ system were critically reviewed, compiled and assessed over a wide temperature range of 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 the reactions FeSO₄ $\rightarrow$ FeO + SO₃(g) and Fe₂(SO₄)₃ $\rightarrow$ Fe₂O₃ + 3SO₃(g), respectively, at ambient pressure condition.

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