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Thermochemical Data of Selected Phases in the FeO_x–$FeSO_4$–$Fe_2(SO_4)_3$ System

Fiseha 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_x(gas) and SO_2(gas) emissions. However, the mechanisms through which SO_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_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_x–$FeSO_4$–$Fe_2(SO_4)_3$ 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

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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 CaO–MgO–Al_2O_3–SiO_2–FeO–Fe_2O_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], Pankratz 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 (μ_B) for α-$FeSO_4$ and β-$FeSO_4$ to be 4.1 ± 0.4 and 5.44 ± 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.

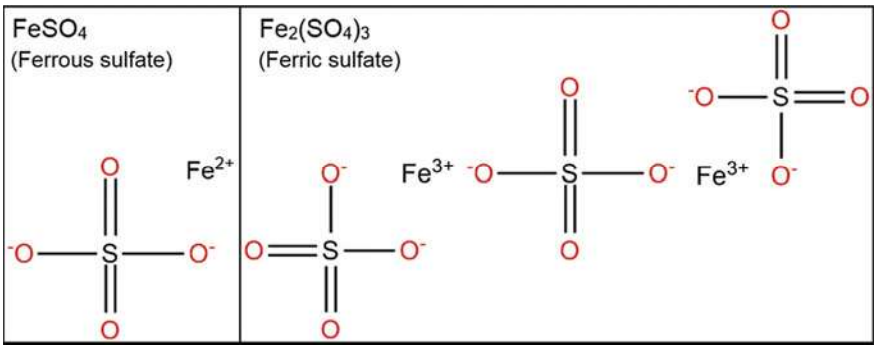

Fig. 1 Schematic diagram of the chemical structures of the ferrous and ferric sulfates, adopted from Chase [13]

Thermochemical Data of $FeSO_4$ and $Fe_2(SO_4)_3$

Enthalpy of Formation (ΔH_f°) 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 $\Delta_f H^\circ(298.15\ \text{K}, FeSO_4) = -924.66\ \text{kJ mol}^{-1}$.

$$FeCl_2(200H_2O) + H_2SO_4(200H_2O) = FeSO_4(200H_2O) + 2HCl(100H_2O). \quad (1)$$

In the NIST-JANAF thermochemical data [13], $\Delta H_f^\circ(298.15\ \text{K}, FeSO_4)$ 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 second and third laws with an average value of $-925.1\ \text{kJ mol}^{-1}$. $\Delta H_f^\circ(298.15\ \text{K}, FeSO_4) = -928.85 \pm 8.4\ \text{kJ mol}^{-1}$ and $\Delta H_f^\circ(0\ \text{K}) = -919.33 \pm 8.4\ \text{kJ mol}^{-1}$ 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, $\Delta H_f^\circ(298.15\ \text{K}, Fe_2(SO_4)_3) = -2583 \pm 1.7\ \text{kJ mol}^{-1}$ was estimated and presented in [13].

$$Fe_2O_3 + 3(H_2SO_4 \cdot 14.855H_2O)(\text{sol.}) = Fe_2(SO_4)_3(\text{cr}) + 47.565H_2O(\text{l}). \quad (2)$$

The equilibrium pressures for decomposition of $Fe_2(SO_4)_3$ 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].

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3, \tag{3}$$

$$SO_3(g) = SO_2(g) + 0.5O_2. \tag{4}$$

The measured pressure of the chemical equilibrium is the total pressures of $P(SO_3)$, $P(SO_2)$, and $P(O_2)$. In order to calculate the enthalpy change of Reaction (3), the partial pressures of $SO_3(g)$ from the total vapor pressure data at each temperature was evaluated. Based on the derived values for $P(SO_3)$, $\Delta H_r°(298.15\ K, Fe_2(SO_4)_3)$ 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 kJ mol^{-1}. This value is higher only by ~1 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 $\Delta H_f°(298.15\ K, Fe_2(SO_4)_3) = -2585.2 \pm 4.9$ kJ mol^{-1}, which is higher by ~2 kJ mol^{-1} than the value of Barany and Adami [5].

Heat Capacity (C_P) and Entropy ($S°$)

$FeSO_4$

The low-temperature C_p of the anhydrous $FeSO_4$ 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, $S°(FeSO_4, 298.15\ K) = 107.57 \pm 0.84$ J K^{-1} 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_{mag}) to $S°(FeSO_4, 298.15\ K)$ and reevaluate the decomposition pressure data. They used the theoretical value of magnetic entropy (S_{mag}) for $FeSO_4$ $R\ln(2S_{spin})$, 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 $S_{spin} = 5/2$ which implies $S_{mag} = R\ln 5 = 13.4$ J K^{-1} mol^{-1}. Therefore, the value $S°(298.15\ K) = (107.57 + 13.4)$ J K^{-1} mol^{-1} $= 120.96$ J K^{-1} mol^{-1} was adopted for $FeSO_4$. The C_p above 294.9 K was estimated by comparison with those for $MnSO_4$. In the calculations, the high-temperature $C_p(MnSO_4)$, 870.3–1082.3 K, were taken from the experiments of Southard and Shomate [26].

$Fe_2(SO_4)_3$

The heat capacities were established by comparison with those for $FeSO_4$, assuming their average specific heats, J K^{-1} g^{-1}, to be the same. The value of $S°(298.15\ K)$ was estimated so that the second and third law $\Delta H_r°(298.15\ K)$ values, derived from

decomposition pressure data, are in reasonable agreement. The value $S°(298.15\ \mathrm{K}) = 120.957 \pm 1.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$ 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 $\Delta H_f°(298.15\ \mathrm{K},\ Fe_2(SO_4)_3) = -2585.2 \pm 4.9\ \mathrm{kJ\ mol^{-1}}$ obtained by an appropriate thermochemical cycle with enthalpies of solution of monoclinic $Fe_2(SO_4)_3$, α-$MgSO_4$, γ-FeOOH, H_2O, 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 of 273–395 K by Eq. (5).

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

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 $T_{\mathrm{decomp.}}(FeSO_4) = 944$ K from the data of Greulich [15]. Reactions (3) and (6) are the decomposition reactions for which the vapor pressure experimental data are available.

$$FeSO_4 \rightleftarrows FeO + SO_3. \quad (6)$$

The thermal decomposition of $FeSO_4 \cdot 6H_2O$ 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):

$$6FeSO_4 \rightarrow Fe_2(SO_4)_3 + 2Fe_2O_3 + 3SO_2 (798-923\ \mathrm{K}), \quad (7)$$

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_2 + 1.5O_2 (898-983\mathrm{K}). \quad (8)$$

$$Fe_2(SO_4)_3 \rightarrow 2FeSO_4 + SO_2 + O_2, \quad (9)$$

$$FeSO_4 \rightarrow 0.5Fe_2O_3 + SO_2 + 0.25O_2. \quad (10)$$

Gallagher et al. [29] studied the thermal decomposition of $FeSO_4 \cdot xH_2O$ using the conventional thermogravimetry, differential thermal analysis, and evolved gas analysis techniques. In an oxidizing atmosphere, they observed that $FeSO_4$ oxidizes as

$$2FeSO_4 + 0.5O_2 \rightarrow Fe_2O(SO_4)_2, \quad (11)$$

$$Fe_2O(SO_4)_2 \rightarrow Fe_2O_3 + 2SO_2. \quad (873-948K) \tag{12}$$

In the inert atmosphere

$$2FeSO_4 \rightarrow Fe_2O_2SO_4 + SO_2, (748-848\ K) \tag{13}$$

$$Fe_2O_2SO_4 \rightarrow Fe_2O_3 + SO_2 + 0.5O_2. \quad (823-948K) \tag{14}$$

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 1 Summary of the phase transition and decomposition temperatures of $FeSO_4$ and $Fe_2(SO_4)_3$

Reaction	$T_{trans.}$/K	$T_{decomp.}$/K	Ref.	Remark
α-$FeSO_4$ → β-$FeSO_4$	623	–	[10]	High-pressure phase transition (at $P_{tot} \approx 15$ kbar)
Reaction (3): $Fe_2(SO_4)_3$ → $Fe_2O_3 + 3SO_3$	–	1461	[13]	Determined by the gas pressure measurements of [27]
	–	1017	This work	
	–	951	[30]	Heating rate 20 K min^{-1}
	–	1028	[31]	–
	–	1024	[7]	–
Reaction (6): $FeSO_4$ → $FeO + SO_3$	–	944	[13]	–
Reaction (7): $6FeSO_4$ → $Fe_2(SO_4)_3 + 2Fe_2O_3 + 3SO_2$	– – –	798–923 891 960	[28] [30] [31]	Inert atmosphere Heating rate 20 K min^{-1} –
Reaction (8): $Fe_2(SO_4)_3$ → $Fe_2O_3 + 3SO_2 + 1.5O_2$		898–983	[28]	Inert atmosphere
Reaction (11): $2FeSO_4 + 0.5O_2$ → $Fe_2O(SO_4)_2$ Reaction (12): $Fe_2O(SO_4)_2$ → $Fe_2O_3 + 2SO_2$	–	870–948 873–948	[29]	Oxidizing atmosphere
Reaction (13): $2FeSO_4$ → $Fe_2O_2SO_4 + SO_2$ Reaction (14): $Fe_2O_2SO_4$ → $Fe_2O_3 + SO_2$	–	748–848 823–948	[29]	Inert atmosphere

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 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_{O2} from 10^{-4} to 10^{-14} atm. At higher oxygen potentials, amounts of SO_3 and O_2 become substantial, while at lower P_{O2} the partial pressure of S_2 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 Fe_2O_3 + $Fe_2(SO_4)_3$ 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

Table 2 A comparative summary of Gibbs energies of reactions determined by different authors

Equilibrium reaction	ΔG_f°(kJ mol^{-1})	T/K	Ref.
$Fe_2(SO_4)_3 \rightleftarrows Fe_2O_3 + 3SO_2 + 1.5O_2$	970.05–0.724 · T	673–1073	[44]
	772.32–0.724 · T	920–1020	[32]
	870.235–0.8245 · T (±1.4)	800–1000	[39]
	704.61–0.697 · T	878–955	[40]
	802.86–0.762 · T	906–995	[27]
	753.098–0.744 · T	900–1000	[27]*
	730.5–0.688 · T	800–900	[43]
$Fe_2(SO_4)_3 \rightleftarrows Fe_2O_3 + 3SO_3$	576.895–0.546.1 · T (±0.5)	800–1000	[39]
	557.42–0.558 · T	900–1000	[27]*
$Fe_2(SO_4)_3 \rightleftarrows 2FeSO_4 + SO_2 + O_2$	395.64–0.352 · T	703–904	[32]
$FeSO_4 \rightleftarrows 0.5Fe_2O_3 + SO_2 + 1/4O_2$	258.74–0.202 · T	773–903	[44]
$FeSO_4 \rightleftarrows 0.5Fe_2O_3 + SO_2 + 1/4O_2$	203.47–0.202 · T	779–900	[32]

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

system. The determined Gibbs energies of reactions involving the gases SO_3, SO_2, O_2 are compiled in Table 2.

Combining the high-temperature change in enthalpy of reaction $Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_2(g) + 1.5O_2(g)$ reported by Jacob and Iyengar [39] with the pure substances enthalpy data of FactSage 7.2 for $SO_2(g)$ and Fe_2O_3, we have calculated $\Delta H_f^\circ(Fe_2(SO_4)_3) = -2586.55$ 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 $Fe_2(SO_4)_3$ from the vapor pressure measurements to be $\Delta H^\circ_{\text{decomp.}} = 566.51$ kJ mol^{-1}.

Results and Discussion

The $C_p(SO_3)$ functions obtained through the reactions $MeO + SO_3 = MeSO_4$ (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 $C_p(FeSO_4)$ values were calculated according to Reaction (6). The results are illustrated in Fig. 2.

The heat capacities of $FeSO_4$ were calculated between 273 and 400 K by comparison with those experimental data reported for $Fe_2(SO_4)_3$, assuming their average

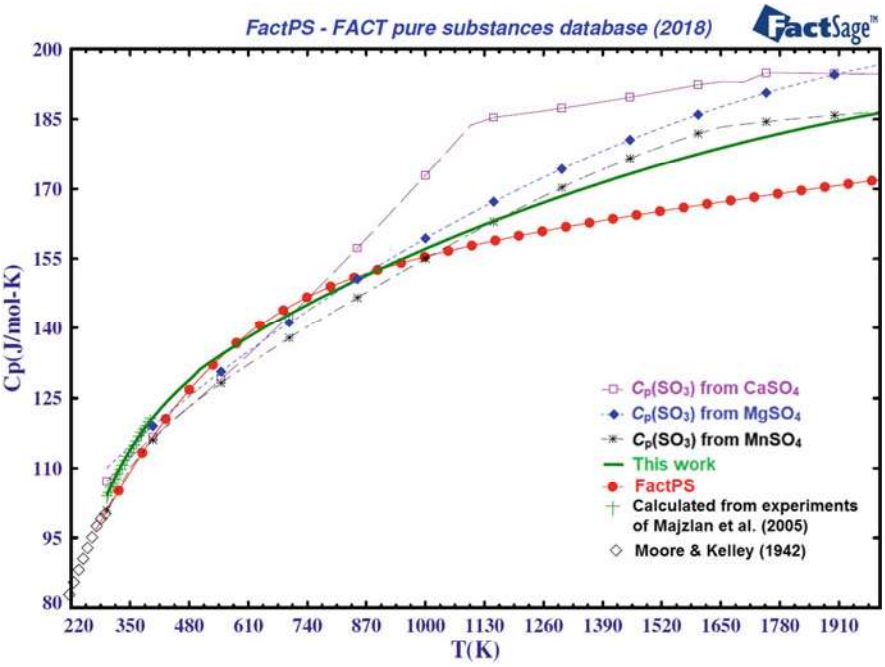

Fig. 2 C_p versus T diagram of $FeSO_4$

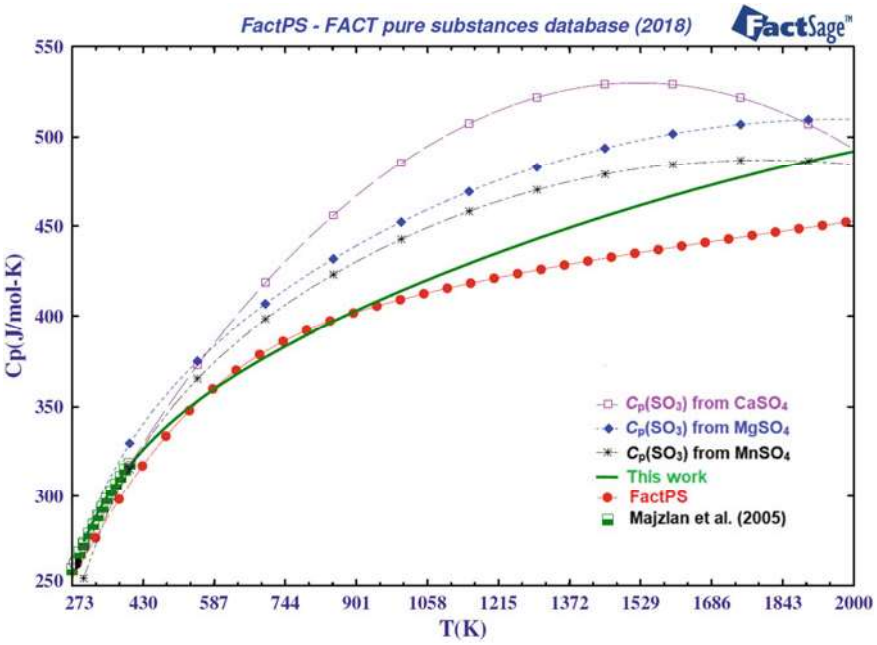

Fig. 3 C_p versus T diagram of $Fe_2(SO_4)_3$

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 $MnSO_4 = MnO + SO_3$ 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 $C_p(Fe(SO_4)_3)$ 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).

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

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

$$C_p(Fe_2(SO_4)_3, 273{-}2000K) = 305.363 + (0.136)\cdot T - (62.0743)\cdot 10^5 \cdot T^{-2} - (20.7454)\cdot 10^{-6}\cdot T^2. \quad (17)$$

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 $Fe_2(SO_4)_3$) in the temperature range of 273–395 K. This value is higher by about -2.2 kJ·mol^{-1} than the value recommended by NIST-JANAF [13]. In this work, we adopted the value $\Delta H_f^\circ(298.15\ \text{K}, Fe_2(SO_4)_3) = -(2585.2 \pm 4.9)$ kJ mol^{-1} reported by Majzlan et al. [7], which was obtained through rigorous experimental studies.

By applying our new database for FeO_x–$FeSO_4$–$Fe_2(SO_4)_3$, $\Delta G_r^\circ(T)$ for an equilibrium reaction $Fe_2O_3 + 3SO_2 + 1.5O_2 \rightleftarrows Fe_2(SO_4)_3$ 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.

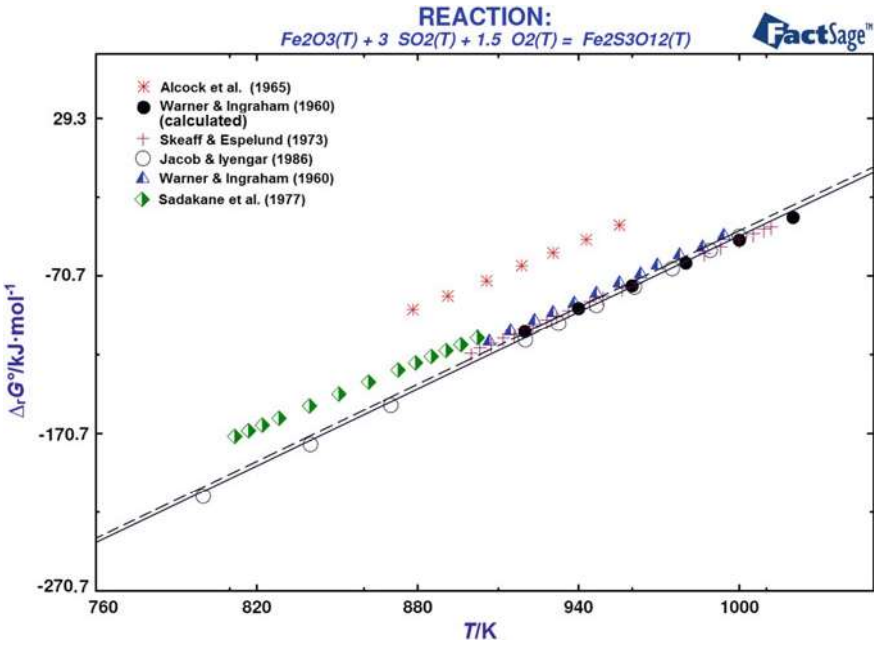

Fig. 4 ΔG_r° versus T diagram for the ferric sulfate formation reaction together with the literature experimental data. The solid line is calculated with the database developed in this work and the dashed line is calculated using the pure substances database in the commercial version of FactSage 7.2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

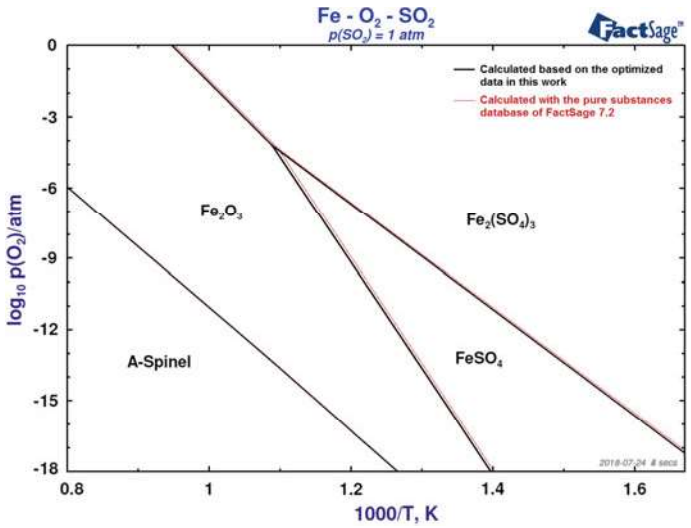

Fig. 5 Calculated potential phase diagram of Fe–O_2–SO_2 at $P(SO_2) = 1$ atm

Potential Phase Diagrams

Based on the results obtained for $FeSO_4$ and $Fe_2(SO_4)_3$, in this work, and the literature data for the other phases, chemical potential phase diagram has been calculated for the Fe–O_2–SO_2 system between 580 and 1250 K.

The potential phase diagram of $\log_{10}P(O_2)$ versus T shown in Fig. 5 was calculated at $P(SO_2) = 1$ atm and $P_{Total} = 2$ 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 $T_{decomp.}(Fe_2(SO_4)_3) = 1017$ 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 SO_2 (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–$FeSO_4$–$Fe_2(SO_4)_3$ 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 $FeSO_4$ and $Fe_2(SO_4)_3$, 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 $FeSO_4$ and 1017 K for the decomposition of $Fe_2(SO_4)_3$ according to the reactions $FeSO_4 \rightarrow FeO + SO_3(g)$ and $Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3(g)$, respectively, at ambient pressure condition.

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