

Dehydration of iron(II) sulfate heptahydrate

Tong Wang, Kenneth A. Debelak*, John A. Roth

Department of Chemical Engineering, Vanderbilt University, Nashville, TN 37235, USA

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Abstract

We studied the dehydration behavior of iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) as part of NASA's in situ resource utilization program for the recovery of water on Mars. We examined the effect of the variables important in using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The temperatures at which waters of hydration are removed and the enthalpy values for the various dehydration steps were measured using DSC. For the dehydration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, a particle size $<45 \mu\text{m}$, a heating rate of $2.5^\circ\text{C}/\text{min}$, an open DSC pan, and a horizontal baseline correction produced experimental values for the enthalpies of each dehydration step and overall dehydration of 145.7, 180.4, 64.8 and 390.9 kJ/mol, respectively, which were in -8.8 , 1.2 , 3.35 and -2.47% , respectively, of those estimated from standard heats of formation and literature heat capacities. Generally, lower heating rates and smaller particle sizes are better for resolving the dehydration steps. The horizontal baseline corrections give better results when there is little or no peak overlap.

As discussed above, proper selection of DSC and TGA operating parameters and baseline analysis technique is required to obtain accurate thermal results.

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1. Introduction

The Mars exploration program is a science-driven program that seeks to understand whether Mars was, or can be, a habitable world. To support exploration on Mars, in situ resources must be recovered. This work is part of NASA's In Situ Resource Recovery Program. Water is especially important both in supporting manned exploration and understanding the history of Mars. The present knowledge of the chemistry and mineralogy of the Martian surface rocks and soils is limited. Data were obtained by the two Viking Landers and the mobile alpha proton X-ray spectrometer (AXPS) on board the rover of the Mars pathfinder. The chemical analysis of Martian soil has been reported in several publications [1–4]. More data on the chemical composition of Martian soils come from the mobile alpha proton X-ray spectrometer on board the rover of the Mars pathfinder [5]. These data indicate that silicates are predominate in the Martian soil.

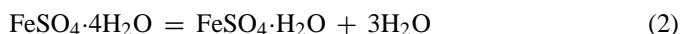
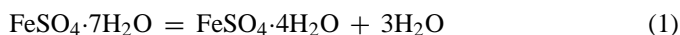
Iron (ranging from 16 to 19% Fe as Fe_2O_3) is in abundance as well as sulfur and chlorine. Viking also revealed that the soils are highly magnetic, possibly resulting from 1 to 7 wt% of a strongly magnetic component like hematite (Fe_2O_3) dispersed as a pigment throughout the surface particles [6]. The mineralogical composition is also dominated by the silicate minerals, which may include weathered, igneous silicates including pyroxenes, feldspars, magnetite, glass of igneous composition and smectite clays of various compositions [4]. Data [7] obtained by the gamma-ray spectrometer on the Mars Odyssey probe have identified two regions near the poles that are enriched in hydrogen. In the upper layer, hydrogen is present in the form of physically or chemically bound water. The upper layer may be mixed with a middle layer, since ice is not stable in the middle layer. In the deeper layer, ice may be the only phase in which hydrogen is present. Hydrated species could be present on the upper and middle layer of Mars. The Martian soils could contain large quantities of hydrated compounds such as iron(II) sulfate heptahydrate. This is inferred from a high concentration [4] (nearly 12%) of sulfate salts and the iron in the Martian surface. The most recent data from the Mars Exploration Rovers Spirit and Opportunity provide convincing evidence of water interacting with the rocks in the Gusev plains and Meridiani Planum on Mars [8–13].

* Corresponding author at: Vanderbilt University, VU Station B 351604, 2301 Vanderbilt Place, Nashville, TN 37235-1604, USA. Tel.: +1 615 322 2088; fax: +1 615 343 7951.

E-mail address: kenneth.a.debelak@vanderbilt.edu (K.A. Debelak).

Recent evidence from Mars Global Surveyor Mars Orbiter Cam show new gully deposits, formed since August 1999, which exhibit attributes expected from displacement aided by a fluid with the properties of liquid water. The observations suggest that liquid water flowed on the surface of Mars during the past decade [14]. The discovery of jarosite at Meridiani Planum has generated interest in the study of sulfates which may exist on the surface of Mars. As Frost et al. [15] have pointed out, this discovery provides evidence of pre-existing or existing water. Frost and co-workers [16–19] have used several spectroscopic techniques including NIR, Raman, optical and EPR to study and build a spectroscopic data base on iron(II) and iron(III) containing sulfates to aid in the identification of these compounds on Mars.

Based on the current knowledge of the composition of Martian soils [20], nearly 20% of the Martian surface contains iron minerals. Although no hydrated compounds have been specifically identified, it is believed that Mars was once wet. Consequently, hydrated inorganics might currently exist on Mars. Accordingly, we studied the dehydration of a hydrated iron compound, iron(II) sulfate heptahydrate [$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$]. Iron(II) sulfate heptahydrate is composed of blue-green, monoclinic and odorless crystals or granules [21]. Thermal dehydration of iron(II) sulfate heptahydrate has been studied by a number of investigators. Diev [22] considered that the true structure of heptahydrate is $(\text{FeSO}_4 \cdot \text{H}_2\text{O}) \cdot 6\text{H}_2\text{O}$. Heptahydrate can be easily dehydrated to the monohydrate in 5–7 min and to FeSO_4 in 120 min by heating isothermally at 200 °C. Rodionov et al. [23] studied the dehydration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in air. Their results showed melting of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in its own crystalline water and simultaneous dehydration in the temperature range 40–100 °C simultaneously forming $\text{Fe}(\text{OH})\text{SO}_4$ and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$. With further heating treatment in the temperature range 300–400 °C, $\text{Fe}(\text{OH})\text{SO}_4$ and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ lost H_2O and formed FeSO_4 . Kanari et al. [24] investigated the dehydration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in nitrogen, and indicated the mechanism of the thermal dehydration of iron(II) sulfate heptahydrate to the anhydrous form occurred according to the following equations:



Results indicated that the dehydration rate was almost independent of the flow rate of nitrogen. The conversion of tetrahydrated to monohydrated iron(II) sulfate was more temperature sensitive than that of heptahydrated to tetrahydrated iron(II) sulfate.

Swamy and Prasad [25] determined the heat of dehydration of the monohydrate from DTA curves was 50.2 kJ/mol. Sharma et al. [26] obtained micro-Raman spectra of iron(II) sulfate hydrates. They identified low temperature spectra interpreted as being characteristic of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ hydrates.

The objective of this study is to determine the temperatures at which waters of hydration are removed and to determine the

enthalpy for each dehydration step. The thermodynamic values for various dehydration steps were also estimated using standard heats of formation for the hydrated compounds and heat capacities.

2. Materials and methods

2.1. Materials

Iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was supplied from J.T. Baker Chemical Co. The other materials were purchased from Fisher Scientific Co. High purity (99.99%) nitrogen was obtained from J & M Cylinder Gases, Inc.

2.2. Apparatus

The iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was heated in nitrogen atmosphere at different heating rates. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to study the dehydration using a TA instruments model Q600 SDT and a TA instruments DSC 2920. The dehydration studies were performed with a sample size of 15 mg, in a nitrogen environment with a flow rate of 50 cc/min. The heating rates were 2.5, 5 and 10 °C/min.

3. Results and discussion

3.1. Dehydration study of iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)

Fig. 1 shows the dehydration process versus temperature at different heating rates.

There are three plateaus indicative of a three-step process for the dehydration of iron(II) sulfate heptahydrate. A mass loss of 19% between 70 and 90 °C at a heating rate of 2.5 °C/min is substantively representative of the first dehydration step with a loss of three water molecules. A mass loss of 20% between 140 and 200 °C is substantively the second dehydration step

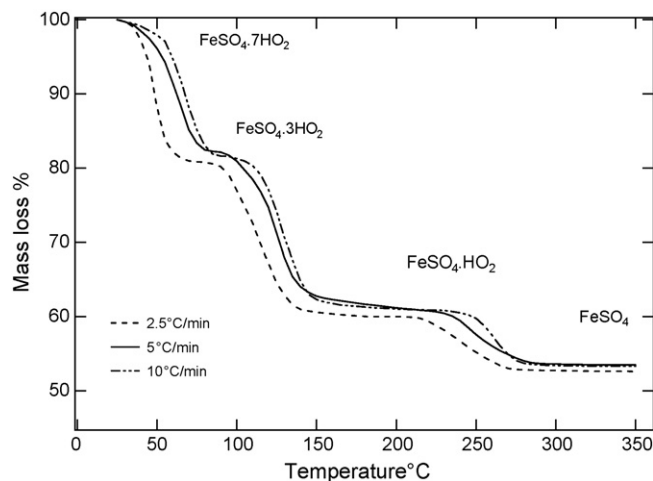


Fig. 1. TGA results of the iron(II) sulfate heptahydrate at different heating rates. 15 mg sample size, and 50 cc/min nitrogen flow rate.

Table 1
Heats of formation and heat capacities for various compounds

Compound	Standard $\Delta H_f^{25^\circ\text{C}}$ (kJ/mol) [27,29]	Molar heat capacity at constant pressure (J/mol K) (28)
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	−3012.6	401.2
$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$	−2129.2	265.85
$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	−1242.69	135.4
FeSO_4	−932.2	91.96
H_2O (l)	−258.84	75.30
H_2O (g)	−241.83	33.58

with the loss of three water molecules. The mass loss of 7% between 270 and 350 °C is the third dehydration step. These results indicate that iron(II) sulfate heptahydrate dehydration gives off water in the following relative molar sequence: 3-3-1, consistent with the results of other investigators [22–26]. The results at different heating rates show that a slower heating rate shifts the dehydration step to a lower temperatures range.

The enthalpy values for the various dehydration steps were estimated from thermodynamic data and compared with the experimental results. The heats required for the various dehydration steps were estimated using the heats of formation and heat capacities of water and the various hydrates of iron(II) sulfate. The heats of formation and molar heat capacity of the compounds are shown in Table 1.

The total estimated enthalpy change in going from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to FeSO_4 using the data in Table 1 is 400.8 kJ/mol. This value includes the enthalpy of vaporization for water. The enthalpy to transition from one hydrated species to another is 159.8, 178.3 and 62.7 kJ/mol corresponding to the three dehydration steps in Eqs. (1–3).

The experimental enthalpy of dehydration for each step was estimated at the temperature peak on the DSC heating curve. Fig. 2 shows the DSC heating curve for iron(II) sulfate heptahydrate at a heating rate of 10 °C/min.

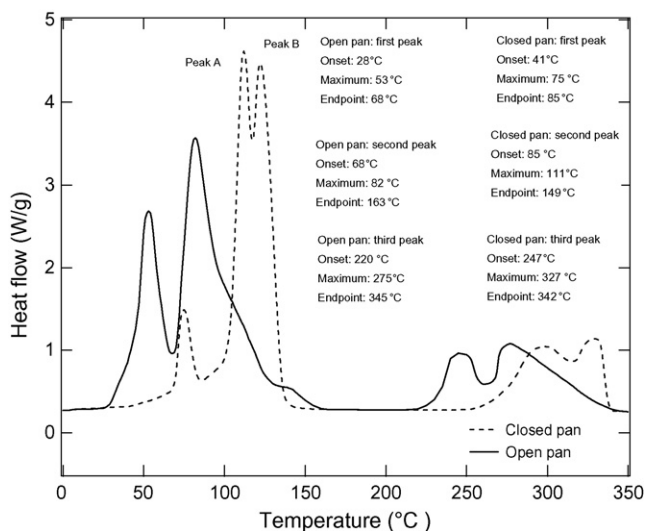


Fig. 2. DSC heating curve for iron(II) sulfate heptahydrate using closed pan and open pan with a heating rate of 10 °C/min; 15 mg sample size, and 50 cc/min nitrogen flow rate.

A sample was heated in a closed DSC pan with a pinhole. A duplicate sample was heated in an open DSC pan. The onset, end point and the maximum temperature are labeled. Horizontal baselines were used to determine the enthalpy from the area under each curve for each step. The total enthalpy to dehydrate from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to FeSO_4 for the closed DSC pan experiment is 366.8 kJ/mol. The enthalpies for reactions (1), (2) and (3) are 102.6, 205.5 and 58.7 kJ/mol, respectively. The closed pan experimental total enthalpy is 8.5% lower than the enthalpy estimated using the standard heats of formation and heat capacities (see Table 1) at a heating rate of 10 °C/min. The dehydration enthalpy for the first step is 35.8% lower, 15.3% greater for the second step and 2.5% lower for the third step than the estimated enthalpy values using Table 1 data. The first peak in the DSC heating curve occurs during the removal of the first three water molecules. This dehydration from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ took place at temperature below 100 °C. The water, which is at atmospheric pressure, is not completely vaporized during this first step of the dehydration process. However, the estimated enthalpy in this step includes the enthalpy of water vaporization. The estimated enthalpy for this step is 96.5 kJ/mol if the enthalpy for the vaporization of water is excluded. The experimental result, 102.6 kJ/mol, is between the two.

The second step of dehydration from $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ to $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ took place over a temperature range from 85 to 149 °C. Water generated by this dehydration step is vaporized. Simultaneously, water from the first dehydration step is vaporized as the temperature rises to 100 °C or greater. The second peak in the DSC heating curve represents the removal of the three water molecules and the vaporization. The estimated value of enthalpy for reaction step (2) is 227.3 kJ/mol, if the enthalpy for the vaporization of six water molecules is included. The DSC experimental result for the second step, 205.5 kJ/mol is 9.6% lower than the estimated thermal value if one assumes that six water molecules are vaporized.

The third step of dehydration from $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ to FeSO_4 took place over a temperature range from 247 to 342 °C. One-water molecular is removed during this dehydration. The enthalpy of third peak of DSC heating curve corresponds to the total enthalpy of dehydration of water and vaporization of water for step (3).

The DSC heating curve for iron(II) sulfate heptahydrate using an open DSC pan at a heating rate of 10 °C/min is also shown in Fig. 2. Horizontal baselines were used to determine the enthalpy for each step. The enthalpies to transition from one hydrate to another are 138.7, 181.5 and 62.8 kJ/mol. The total enthalpy to transition from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to FeSO_4 is 383.4 kJ/mol. The experimental value for the enthalpy of dehydration for the first step is 13.2% lower, 1.8% greater for the second step, 0.2% greater for the third step and 4.4% lower for the total enthalpy than the values estimated by the standard heats of formation and molar heat capacities from Table 1 data. Again, the water is not completely vaporized during this first step of the dehydration process. The estimated enthalpy in this step does include the enthalpy of water vaporization. If the enthalpy for the vaporization of water is excluded, the estimated enthalpy for this step is 96.5 kJ/mol. The open pan experimental result, 138.7 kJ/mol, is closer to the estimated value of 159.8 kJ/mol, than the closed pan

Table 2
Effect of open pan and closed pan operation and baseline analysis method; heating rate is 10 °C/min

Experimental condition	Enthalpy of 1st step (kJ/mol)	Enthalpy of 2nd step (kJ/mol)	Enthalpy of 3rd step (kJ/mol)	Total enthalpy (kJ/mol)
Enthalpy from thermal data [27,28]	159.8	178.3	62.7	400.8
DSC data using closed pan (analysis with horizontal baseline)	102.6	205.5	58.7	366.8
% Difference compared with estimated value	−35.8	15.3	−2.5	−8.5
DSC data using open pan (analysis with horizontal baseline)	138.7	181.5	62.8	383.4
% Difference compared with estimated value	−13.2	1.8	0.2	−4.4
DSC data using closed pan (analysis with sigmoidal baseline)	86.9	171.3	58.0	316.3
% Difference compared with estimated value	−45.6	−3.9	−7.5	−21.1
DSC data using open pan (analysis with sigmoidal baseline)	103.2	121.7	61.1	286.0
% Difference compared with estimated value	−35.4	−31.8	−2.5	−28.6

Table 3
Dehydration enthalpy of iron(II) sulfate heptahydrate with varying particle size; heating rate of 2.5 °C/min, 15 mg sample and 50 cc/min nitrogen flow rate

Enthalpy	Particle size						Estimated ^b
	>149 μm	Δ% ^a	90–63 μm	Δ% ^a	<45 μm	Δ% ^a	
Δ <i>H</i> of 1st step (kJ/mol)	138.0 ± 4	−13.6	143 ± 2	−11	145.7 ± 3	−8.8	159.8
Δ <i>H</i> 2nd step (kJ/mol)	175.1 ± 15	−1.85	175.8 ± 3	−1.4	180.4 ± 5	1.2	178.3
Δ <i>H</i> of 3rd step (kJ/mol)	55.8 ± 3	−11	58.8 ± 1	−6.2	64.8 ± 1	3.35	62.7
Total enthalpy (kJ/mol)	362.4 ± 18	−7	376.9 ± 6	−5.9	390.9 ± 4	−2.47	400.8

^a % Difference compared with values estimated from standard heats of formation and heat capacities [27,28,29].

^b Estimated from standard heats of formation and heat capacities [27,28,29] in Table 1.

experimental value. The peak of dehydration and vaporization overlap completely when open pan DSC was used. The open pan DSC method did not resolve the second peak in the heating curve into a dehydration peak and water vaporization peak whereas the closed pan method did. However, the experimental enthalpy values using the open pan are closer to the estimated values using the standard thermodynamic data given in Table 1.

A second baseline method using three sigmoidal baselines was also used to determine the enthalpy from the area under each DSC curve. The peak areas were less when using a sigmoidal baseline correction since the peaks do not return to the baseline. A summary of results is provided in Table 2. Comparison of both the total enthalpy and the enthalpy for the individual steps shows that the analysis with horizontal baseline is closer to the estimated enthalpies than the analysis with sigmoidal baseline, especially for the open DSC pan, where the total enthalpy measured experimentally is 383.4 kJ/mol a difference of only 4.4% from the estimated value.

Three iron(II) sulfate heptahydrate samples of different particle size were heated in the DSC using an open pan. All experiments were analyzed using a heating rate of 2.5 °C/min. The particle sizes used were >149 μm, 90–63 μm and <45 μm. The results provided in Table 3 are the average of three runs and include the standard deviation. Our data show that the enthalpy measured experimentally for the small particle size was greater for all steps when compared to the large particle size. The reason might be that the crystal size of samples is affecting heat transfer during the DSC analysis. The heat transfer may not be uniform for particles of different sizes. Dehydration might occur at different bulk temperatures for the different particle sizes. In addition the larger size crystals might not dehydrate completely during the first and second dehydration steps which take place

over a narrow temperature range. The experimental DSC heating curve for the smallest particle size was found to give better resolution.

4. Conclusions

For the dehydration of FeSO₄·7H₂O, a particle size <45 μm, a heating rate of 2.5 °C/min, an open DSC pan, and a horizontal baseline correction produced experimental values for the enthalpies of each dehydration step and overall dehydration which were in good agreement with those estimated from standard heats of formation and heat capacities. Generally, lower heating rates and smaller particle sizes are better for resolving the dehydration steps. The horizontal baseline corrections give better results when there is little or no peak overlap. The sigmoidal baseline correction is better suited for dehydrations studies where there is peak overlap. Duval and Lecomte [30] showed that the resolution of successive dehydration steps could be achieved by increasing the water vapor pressure in the purge gas stream. The increased vapor pressure has the effect of suppressing the dehydration step, moving it to a higher temperature. TA instruments [31] report that a DSC pan with pinhole achieves similar results. The water from the first stage of dehydration remains in the head space above the sample suppressing the second stage.

TGA/DSC dehydration experiments require proper selection of the heating rate, particle size, open pan or closed pan, and baseline corrections methods to correctly determine accurate thermal data, none of which are obvious a priori. The enthalpies determined from standard heats of formation and heat capacities provide data for comparison with experimental data obtained in the TGA/DSC experiments. Experimentally

determined enthalpies of reaction for each dehydration step and total enthalpy obtained under different heating rates, choices of open/closed pan and baseline correction method can be compared with the estimated values. By comparing the experimental and estimated enthalpies, the optimal choice of experimental operating parameters and conditions can be made. To experimentally determine thermal data for these solid hydrated compounds using DSC/TGA, the kinetic rates of the dehydration steps, heat transfer rates to the solid particles and baseline characteristics of the instrument all can impact the determination of thermodynamic data. For the recovery of water on Mars, knowing the energy demand for the dehydration of a hydrated species is necessary to design process systems of minimum mass and energy demand.

Acknowledgment

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