

### A Study of Corrosive Reactions with the TG/MS: Using Pure H<sub>2</sub>S to Sulfuret TiO<sub>2</sub>

#### Abstract

The sulfurization of Titanium Dioxide (TiO<sub>2</sub>) by pure Hydrogen Sulfide (H<sub>2</sub>S) was successfully monitored using a simultaneous Thermogravimetry (TG) and Mass Spectrometer (MS) system. While confirming the progress of the reaction from TG and MS data, experimental results also showed that such a reaction was diffusion controlled.

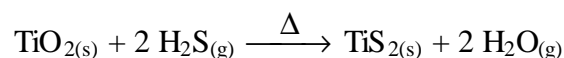
#### Introduction

For materials scientists, it is necessary to study the endurance of materials under different environments.<sup>i,ii,iii,iv</sup> These include temperature, temperature cycling, pH, pressure, corrosive gases, etc. A common approach involves studying the raw materials under “accelerated” experimental conditions. The “accelerated” condition means that the material is put in an environment that will cause it to corrode, break, or degrade at a faster rate than if run under actual use conditions. By obtaining the information about the material’s reaction mechanism, the endurance of the material can be projected more cost effectively.

For metallurgists, many interesting reactions involve corrosive gases. However, corrosion and decomposition mechanisms are very difficult to study when reaction gases like H<sub>2</sub>S, SO<sub>2</sub>, HCl, HF, H<sub>2</sub>SO<sub>4</sub>, or halogen gases, are utilized. Therefore, it is important to have instruments that are resistant to the effects of these types of reactive gases.

Thermogravimetry (TG) has been extensively used for the study of the gas-solid reactions, by monitoring the weight change of the sample as a function of temperature and time.<sup>v,vi,vii,viii,ix</sup> It will provide information about the reaction mechanism, reaction rate, and kinetic parameters. By attaching an Evolved Gas Analyzer (EGA) to the vent port of the TG instrument, the evolved gases can be identified. One of the most commonly used TG/EGA techniques is a TG coupled with a Mass Spectrometer (MS). A unique coupling system is used to reduce the effect of the reaction gas on the sensitive MS system. With the information provided by the MS data, the reaction mechanism and kinetic parameters can be further supported and explained. It’s especially useful when a mixture of gases is evolved from the reactions.<sup>x,xi,xii</sup>

In order to demonstrate the capability of a TG/MS system under a corrosive environment, this paper will illustrate the use of pure hydrogen sulfide as the reaction gas to sulfuret a sample. The process is similar to the reaction of oxygen with a metal to form a metal oxide. The sulfurization process requires heat to initiate the reaction and is characterized by a small increase in the sample’s weight and the evolution of water or other gases. For this paper, the reaction is:



Such a reaction was monitored by the TG/MS system, along with other typical reactions that are normally used for demonstrating the capabilities of a TG/MS system.

## Experimental Set-up

### *Apparatus*

Experimental apparatus was a Thermo Cahn TG/MS synergy system. The system consists of a Thermo Cahn TG-131 system, a Thermo Finnigan Mass Spectroscopy (MS) Automass II system, and TG/MS interface. The Thermo Cahn TGA has a sample capacity of 100 grams, with a sensitivity of 1  $\mu\text{g}$ . The TG is designed in such a way that the balance is protected by an inert purge gas, while the sample is exposed to the desirable reaction gas(es). Since it's also vacuum tight, the system is capable of handling a corrosive gas without losing the sensitivity and accuracy of the weighing mechanism.

The MS has a mass range of 4 to 1000 amu. The dual turbo-pumps in the system provided a very high intake flow rate and the shortest residence time. With the vacuum tight design, which is minimum requirement for any MS system, it is also capable of handling a wide variety of corrosive gases.

The synergy style TG/MS interface is designed in such a way that the effluents from the sample located in the reactor tube of the TG are immediately analyzed by the MS. The TG/MS interface is kept at 150  $^{\circ}\text{C}$  during the experiments to prevent any condensation and MS spectra were collected simultaneously during the TG experiment.

### *Materials and Experimental Parameters*

Four different reactions were monitored by the TG/MS system. The decomposition of calcium oxalate monohydrate (from Aldrich-Sigma, Part #28984-1) under nitrogen, the burning of a bituminous coal (from VWR Scientific Products, Part #WL7073Z-07) sample under air, the decomposition of a polyimide resin (from Aldrich-Sigma, Part #18464-0) under nitrogen, and the sulfurization of titanium dioxide (from Aldrich-Sigma, 99.999% purity) under hydrogen sulfide.

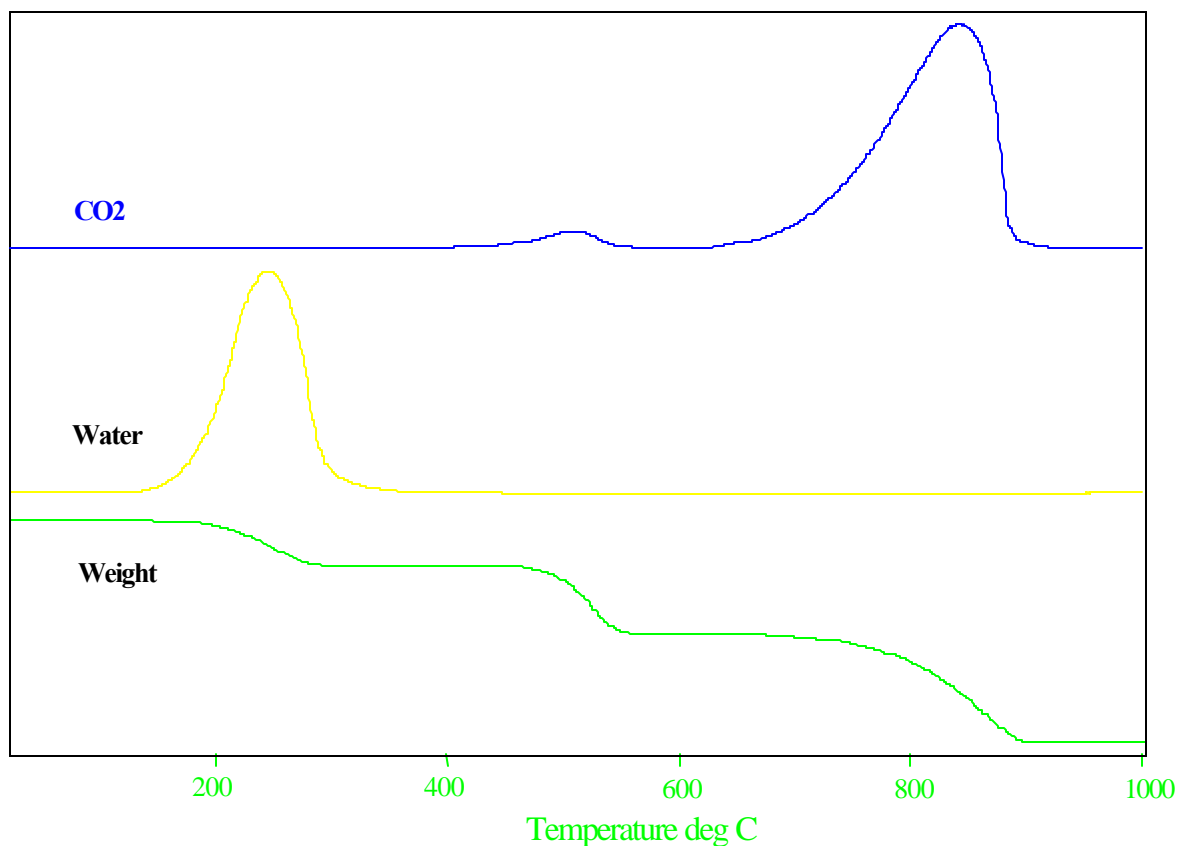
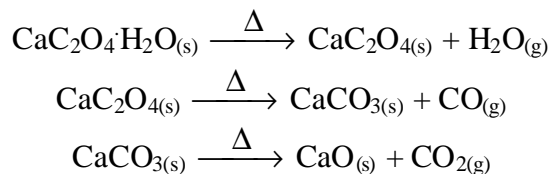
Sample 1, Calcium oxalate monohydrate, was heated from room temperature to 1000  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}/\text{min}$  with a nitrogen reaction gas flow rate of 50 cc/min. Sample 2, bituminous coal was heated from ambient temperature to 1000  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ , under a 50 cc/min flow of air. The sample was held at 1000  $^{\circ}\text{C}$  for 15 minutes to ensure the completion of the reaction. A polyimide resin sample was heated from room temperature to 950  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}/\text{min}$  in nitrogen at a flow rate of 50 cc/min. The titanium dioxide sample was heated from ambient temperature to 800  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ , and held at 800  $^{\circ}\text{C}$  for 20 minutes. In this sample, hydrogen sulfide was used as the reaction gas at a flow rate of 50 cc/min. The experimental parameters for each sample are summarized in Table 1.

No	Sample ID	Reaction Gas	Flow Rate	Heating Profile
1	$\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}$	$\text{N}_2$	50 cc/min	RT to 1000 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ .
2	bituminous coal	air	50 cc/min	RT to 1000 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ , and 15 minutes isotherm at 1000 $^{\circ}\text{C}$ .
3	polyimide resin	$\text{N}_2$	50 cc/min	RT to 950 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ .
4	titanium dioxide	$\text{H}_2\text{S}$	50 cc/min	RT to 800 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ , and 20 minutes isotherm at 800 $^{\circ}\text{C}$ .

*Table 1. Experimental Parameters*

## Results and Discussion

Calcium oxalate monohydrate has been used commonly for the testing of TG/MS systems, because it will show three distinguishable weight loss steps and give off a different component at each step. The decomposition steps of calcium oxalate hydrate are expressed as follows:



*Figure 1. Sample 1, Calcium Oxalate Monohydrate under Nitrogen*

Figure 1 shows the TG/MS results for heating of calcium oxalate monohydrate under nitrogen. The TG curve shows that there are three weight loss steps, the 1<sup>st</sup> one at around 200 °C, the 2<sup>nd</sup> one at around 500 °C, and the 3<sup>rd</sup> one at around 850 °C. They correspond to the above three decomposition steps. The MS data confirmed the above steps by monitoring the evolved gases. Since nitrogen was used as the reaction gas, which has the same mass as that of carbon monoxide, 28, the evolution of carbon monoxide was blanked by this reaction gas. The small amount of carbon dioxide detected on the 2<sup>nd</sup> weight loss step was caused by the small amount of oxygen presented in the reaction gas, which caused the oxidation of carbon monoxide into carbon dioxide.

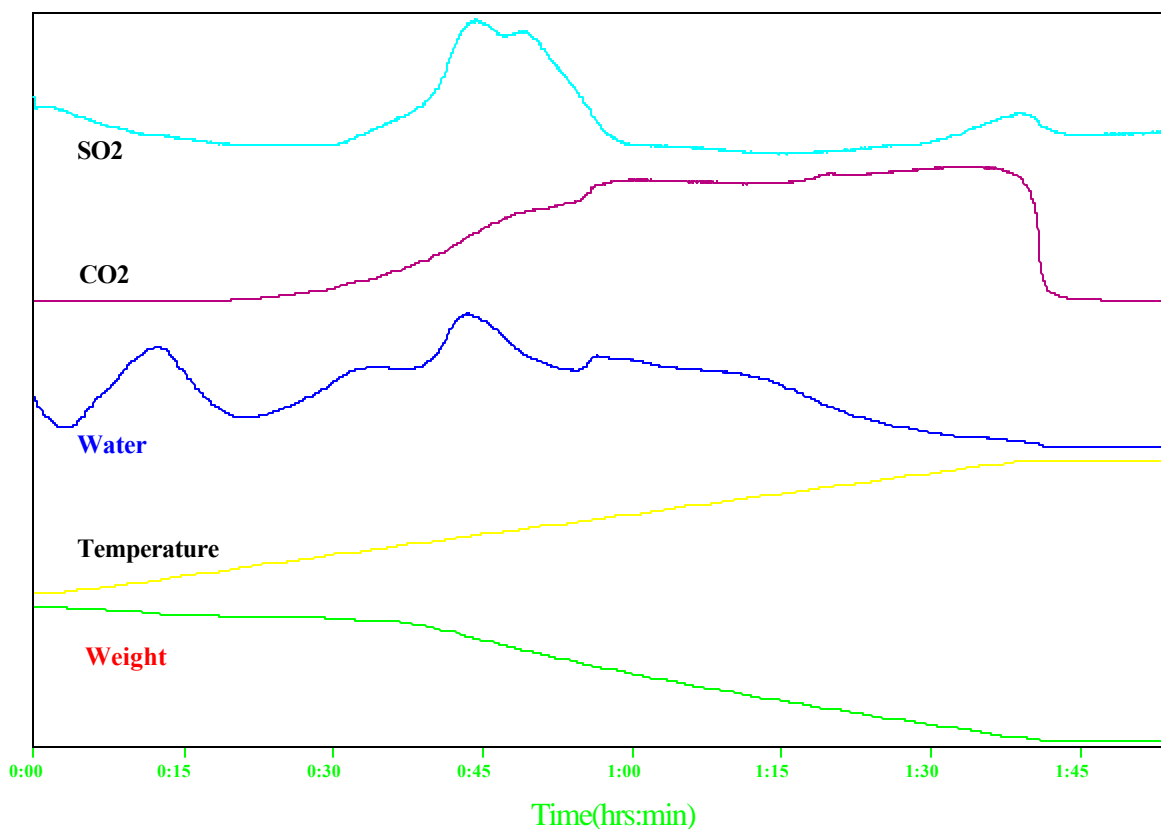
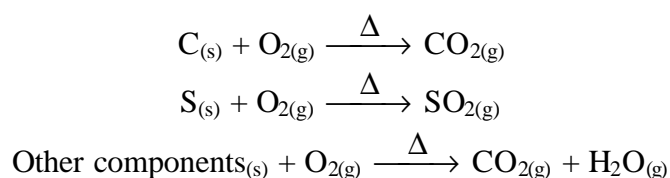
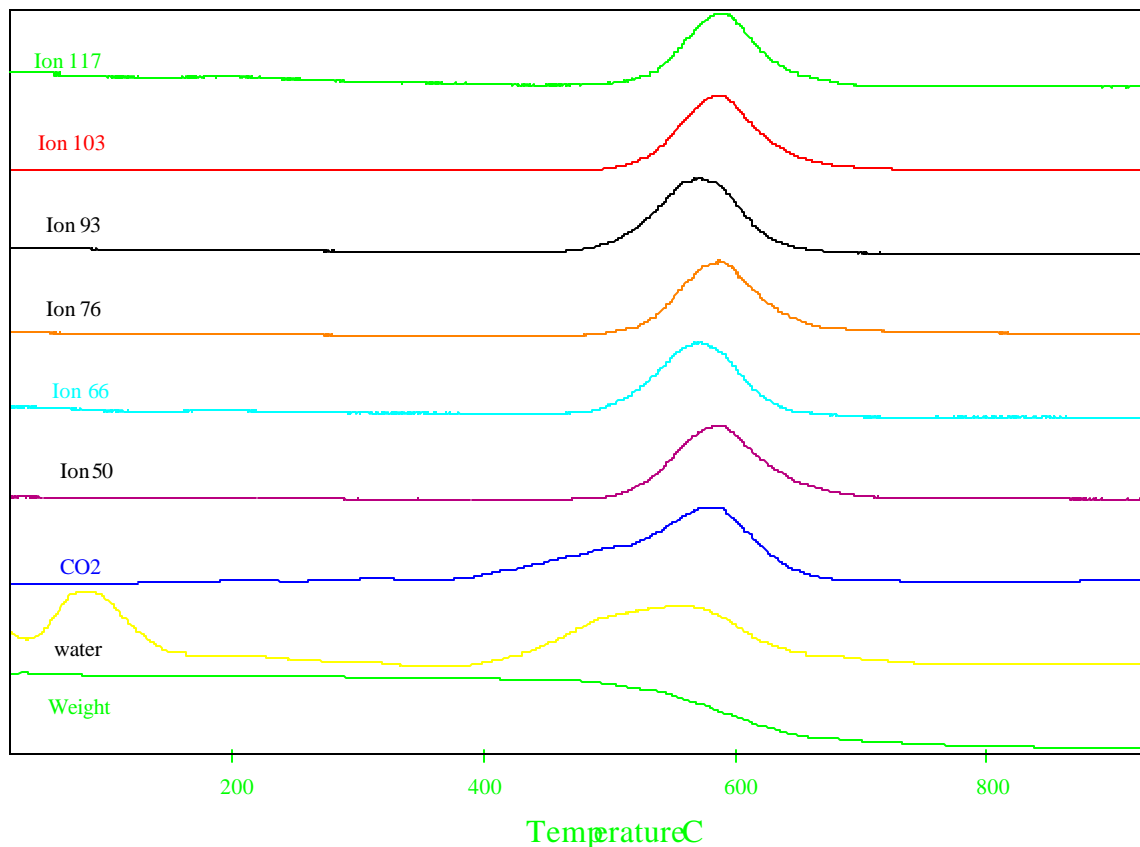


Figure 2. Sample 2, Bituminous Coal Under Air

The TG/MS results for the burning of the bituminous coal sample are shown in Figure 2. It can be seen from the TG curve that there were two weight loss steps. One occurred at a low temperature and another at a higher temperature. From the MS data, it's confirmed that the first weight loss step was caused by the loss of moisture in the sample. The 2<sup>nd</sup> weight loss step was the burning of the coal, due to the detection of carbon dioxide by the MS. However, since the sample is a mixture containing other compounds, it also gave off water and sulfur dioxide during oxidation. Therefore, the reactions that occurred during the burning of bituminous coal sample were most likely:





*Figure 3. Sample 3. Polyimide Resin under Nitrogen*

The above two reactions were easy to follow and are often used to verify the operation of a TG/MS system. However, when a complex sample is analyzed, such as polyimide resin, the TG/MS data will require more sophisticated interpretation. Figure 3 shows the TG/MS data for a polyimide resin sample under a nitrogen environment. It can be seen from the TG scan that there were two weight losses. The first one occurred at around 100 °C and another around 550 °C. Based upon the MS results, water was released during the first weight loss step. The second weight loss was due to the decomposition of the polyimide resin sample. During this decomposition step, water and carbon dioxide were released, along with other compounds. In order to properly interpret the data, it is necessary to obtain more structural information about the sample. Additional experiments using TG/FTIR and TG/GC/FTIR/MS will be made and reported in a subsequent paper.

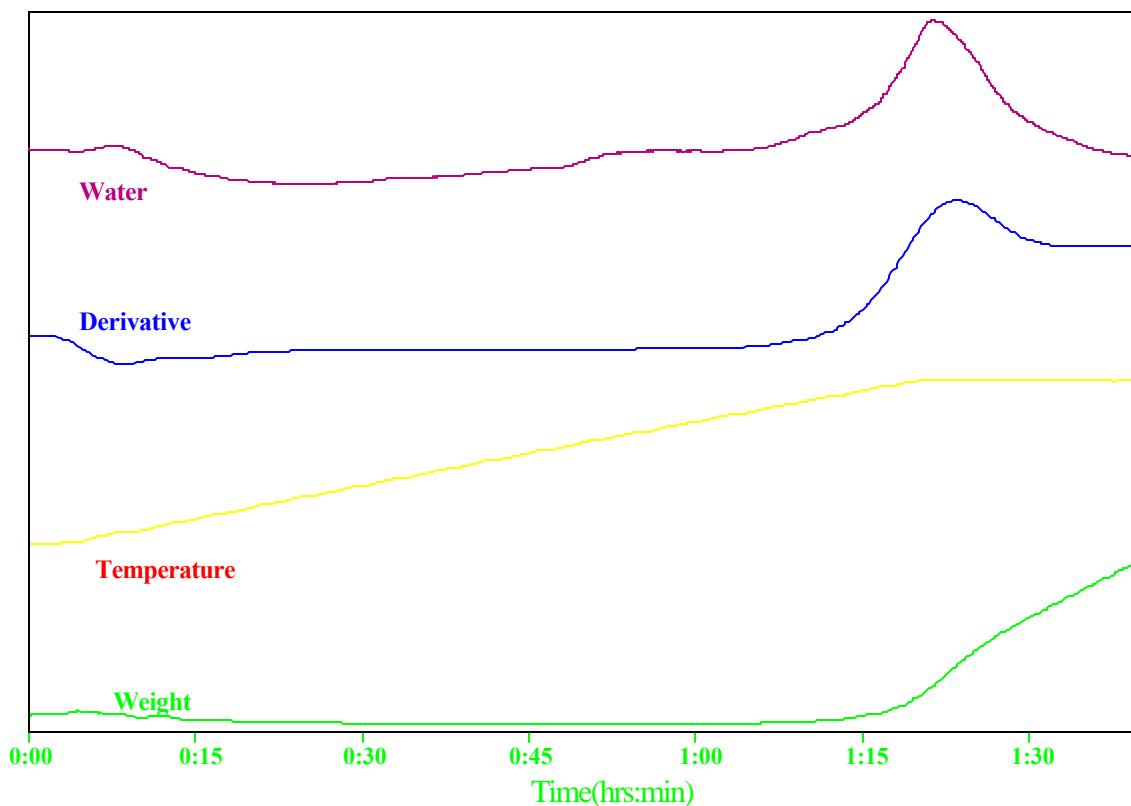
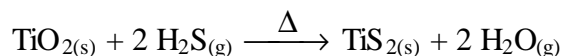


Figure 4. Sample 4. Titanium Dioxide under Pure Hydrogen Sulfide

The above reactions show the capability of the TG/MS when using non-corrosive reaction gases. The next phase of this study is to monitor a corrosive gas reaction. Figure 4 shows the TG/MS results for the sulfidization of titanium dioxide under a pure hydrogen sulfide environment.



It can be seen, from Figure 4, that there was an initial weight loss during the first 25 minutes. It was believed to be related to the loss of the absorbed moisture. After about 1 hour and 10 minutes into the run, at 660 °C, the sulfidization reaction occurred. From the derivative TG (DTG) curve, it can be seen that the reaction reached its maximum rate at around 1 hour and 23 minutes. After that, the reaction slowed down. It appeared from the shape of the DTG curve that the reaction occurred aggressively during the initial stage. It was suspected due to the conversion of  $\text{TiO}_2$  to  $\text{TiS}_2$  on the surface of the sample, the continued reaction was inhibited and may have followed a diffusion mechanism. This was confirmed by examining the residue after the run, which had a layer of yellow  $\text{TiS}_2$  on the surface of the sample. Upon crushing the sample, an internal white  $\text{TiO}_2$  layer was exposed.

The MS analysis result for the evolution of water in Figure 4 also showed a very similar shape as that of the DTG curve. This is in excellent agreement with the TG analysis results, and further confirmed that  $\text{TiO}_2$  was sulfidized to  $\text{TiS}_2$  under a diffusion reaction mechanism.

## Conclusions

Experimental results proved that Cahn TG/MS system can not only monitor the reaction under regular inert and oxidizing environments, but also study reactions under corrosive reaction gas environments. While the TG data provide the information about the reaction rate, reaction mechanism, and kinetics parameters, MS data can further support the TG analysis results by monitoring the evolved gases as an aid in determining the reaction mechanisms.

## References

- i. Pasquevich, D.M., and Carneiro, A., *Thermochimica Acta*, **1989**, 156, pp 275-283.
- ii. Soleiman, M. K., and Rao, Y. K., *Metall. Trans. B*, **1987**, 18, 459.
- iii. Grob, B., and Richarz, W., *Metall. Trans. B*, **1984**, 15, 529.
- iv. McNallan, M. J., and Liang, W. W., *J. Am. Ceram. Soc.*, **1981**, 64, 302.
- v. Turi, E. A., *Thermal Characterization of Polymeric Materials*, 2<sup>nd</sup> ed., Academic Press, **1997**, vols 1 and 2.
- vi. Dollimore, D., *Analytical Chemistry*, **1998**, 70, 27R-36R.
- vii. Dollimore, D., in *Analytical Instrumentation Handbook*, 2<sup>nd</sup> ed., Ewing, G. W., Ed., Marcel Dekker, New York, **1997**, Chapter 17, p 947.
- viii. Brown, M. E., *J. Therm. Analysis*, **1997**, 49, 17.
- ix. Flynn, J. H., *Thermochimica Acta*, **1997**, 300, 83.
- x. Bi, M., Li, H., Pan, W. P., Lloyd, W. G., and Davis, B. H., *Thermochimica Acta*, **1996**, 284, 153.
- xi. Wilkie, C., Mittleman, M. L., *Adv. Chem. Ser.*, **1993**, 236, 677.
- xii. Marini, A., Berbenni, V., Capsoni, D., Riccardi, R., Zerlia, T., *Appl. Spectrosc.*, **1994**, 48, 1468.

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