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Experiment Number:	2
Experiment:	Dehydration of Ferrous Sulfate Heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) by Thermogravimetric Analysis (TGA)
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1. Introduction

The purpose of this experiment is to learn the basic concepts of thermogravimetric analysis and to analyze and interpret thermogravimetric data. This study can be important in the field of materials science and engineering because the results could be used quantitatively to tabulate mass changes associated with specific transitions or degradation processes in materials. The data and associated curves could also be used qualitatively to predict an unknown material, say a polymer, as each polymer would have characteristic transitions that occur at certain temperature ranges that are specific to that polymer only. We could thus use pre-made plots to distinguish between polymers and to characterize newly manufactured ones.

In this laboratory, we perform a thermogravimetric analysis of three different samples of Ferrous Sulfate Heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). Each sample has a different initial mass and is tested at different heating rates. The sample is heated following a fixed procedure, and the mass and temperature of the sample recorded at various times. The percentage of mass remaining in the sample at any time is given by the following equation:

$$\text{Weight \%} = \frac{W}{W_0} \times 100\% \quad (1.1)$$

where W_0 is the initial mass of the sample.

A plot of weight percent vs. temperature is constructed, and each individual drop in mass is associated with a molecule by comparing mass percents. At the end of the laboratory, we will be able to understand how the material of choice decomposes under high temperatures and how this decomposition is related to the initial mass of the sample and the heating rate at which it was subjected to. These results could be pivotal in the study of special engineering problems such as thermal shock [3] where materials are subjected to high temperatures at varying speeds. For example, the material of choice for a space shuttle's body [4] can be subjected to temperature changes in the laboratory—similar to that of the shuttle's re-entry into the atmosphere—to analyze the mechanism and temperature range of decomposition. This could provide us with crucial data about the suitability of a material for the given engineering application.

2. Materials and Equipment

1. Thermogravimetric Analyzer with Mass Flow Control
2. Ferrous Sulfate Heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) [60 mg]
3. Computer and data acquisition system
4. Analytical Balance
5. Data processing software

3. Procedure

This experiment required samples of Ferrous Sulfate Heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) to be tested at different heating rates with different initial masses. In order to draw conclusions on the experiment, the procedure was divided into three sections. All three experiments were performed using the Q50 Thermogravimetric Analyzer. Nitrogen (N_2) was used as the purge gas. The mass flow control was kept at a constant 40 mL/min and the sample purge was kept at a constant 60 mL/min throughout the experiment.

Initially, a small platinum sample pan was cleaned by burning off any residue over a Bunsen burner flame. It was then weighed (tared) by careful placement into the TGA Analyzer. The 'Tare' button was then pressed to begin the taring process.

The appropriate mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was measured using an electronic balance and transferred to the sample pan. Parameters to be controlled such as maximum temperature and heating rate were adjusted using the computer software. The sample was then loaded into the balance and the experiment started by touching the 'Start' key.

The following procedures were experimented upon:

- Initial mass of 20.0 mg, heating rate of 20 °C/min up to a maximum temperature of 700 °C.
- Initial mass of 20.0 mg, heating rate of 10 °C/min up to a maximum temperature of 400 °C.
- Initial mass of 5.0 mg, heating rate of 20 °C/min up to a maximum temperature of 400 °C.

Lastly, observations were made from the final sample. Results from the TGA Analyzer were tabulated and graphed for analyses.

4. Results

We imported the raw data from the computer-aided data acquisition system into Microsoft Excel for processing. The raw data provided us with the weight of the sample at various times during the experiment and the corresponding temperatures at those times. Our first task was to convert the mass of the sample to a percentage describing the mass remaining. We used equation (1.1) for this purpose.

For example, to calculate the percent mass remaining at a time $t = 10.596$ s for Sample 1, we apply equation (1.1):

$$\text{Weight \%} = \frac{W}{W_0} = \frac{13.163 \text{ mg}}{20.864 \text{ mg}} \times 100\% = 63.09\%$$

The results for all three samples were plotted and the following graph (Figure 1) was obtained.

It is clear from the graph that there is a very discernible change when a) the initial mass is varied, b) the heating rate is varied and c) both the initial mass and heating rate are varied.

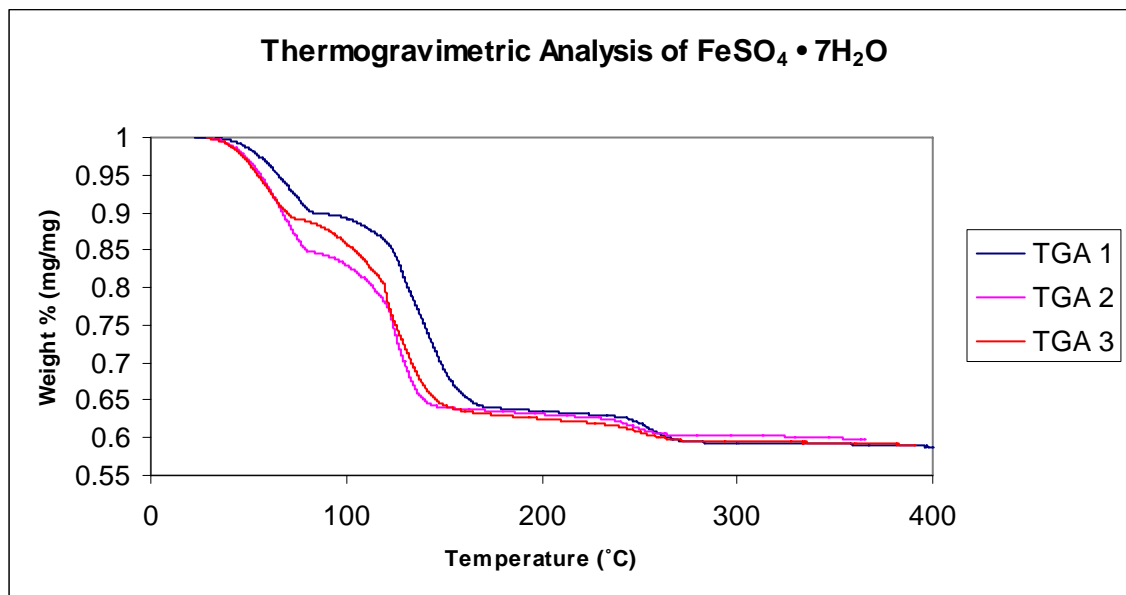


Figure 1 Comparison of TGA Values (chopped at 400 °C)

The heating procedure for each TGA profile is summarized below.

Sample #	Prescribed Initial Mass (mg)	Actual Mass (mg)	Heating Rate (°C/min)	T _{min} (°C)	T _{max} (°C)
TGA 1	20	20.2	20	22.4	700
TGA 2	20	25.5	10	30.8	400
TGA 3	5	5.3	20	28.4	400

Table 1 Sample Heating Procedure

5. Discussion

1. What were the key assumptions made in this lab?

Two major assumptions need to be stated before any analysis. First, it was assumed that all samples were identical and had the same structure. This means that it was

assumed that all of the samples were pure ferrous sulfate *heptahydrate* (and that no other hydrates were present). Also, it was assumed that the initial temperature and the maximum temperature did not have an effect on the results. In addition, it was assumed that the sample masses used for the trials were approximately the same as what was required to be used as specified by the manual [2]. Lastly, it was assumed that the humidity around the samples was the same for each.

2. *What were the predictions made for each sample before subjecting the samples to the TGA Analyzer?*

Sample 1

- As the temperature is increased, there should be certain sharp peaks where large proportions of constituents are decomposed.
- The final product might have a pale brown colour, assuming there is only iron oxide remaining.

Sample 2

- Slower rate might imply a more uniform (step like) removal of the hydrate.
- Sulfur trioxide will not be removed as the maximum temperature is 400 °C.
- Derivatives from the TGA data values should have a similar shape as the first one.

Sample 3

- Instrument error is predicted to have a larger effect on smaller mass samples, but since the instrument was designed to work well for small masses, this error may not be significantly visible in the results.
- A lighter sample may have a more uniform distribution over the pan, allowing for a more even thermal distribution.
- There should be less clumping of the crystals leading to the same conclusion as above.
- Because the maximum temperature and heating rate are held constant with respect to the first trial, the results from this sample should be similar to the results from Sample 1.

3. *Discuss possible reaction steps and mass losses*

The following calculations were performed during the laboratory:

$$\begin{aligned} \text{Molecular Weight of FeSO}_4 \cdot 7\text{H}_2\text{O} &= 55.845 + 32.065 + 4(16.00) + 7(18.02) \\ &= 278.05 \text{ g/mol} \end{aligned}$$

$$\text{Weight \% of H}_2\text{O} = \frac{2.02 + 16.00}{278.05} = 6.48\%$$

$$\begin{aligned} \text{Weight \% of SO} &= \frac{32.065 + 16.00}{278.05} = 17.3\% \\ \text{Weight \% of SO}_2 &= \frac{32.065 + 32.00}{278.05} = 23.04\% \\ \text{Weight \% of SO}_3 &= \frac{32.065 + 48.00}{278.05} = 28.8\% \\ \text{Weight \% of SO}_4 &= \frac{32.065 + 64.00}{278.05} = 34.5\% \\ \text{Weight \% of FeO} &= \frac{55.845 + 16.00}{278.05} = 25.8\% \end{aligned}$$

In sample 1's plot of the data, we see that at 86.94 °C, there is a 10.16% drop in mass, which is close to a 2*(molar mass % of water) = 12.96%. This is classified as the dehydration of 2 of the 7 H₂O molecules. The next drop finishes at 201.35 °C and is a 26.33% mass drop, which could be classified as the removal of the sulfur dioxide (molar mass % of 23.04), or the removal of sulfur monoxide and 1 or 2 water molecules, or just 4 water molecules. For this step, even though the mass % drop is remarkably similar to the mass % of FeO, it is not likely, for there was a rusty brown coloured substance left in the sample pan at the end of the experiment (evidence that FeO does not contribute to any mass loss). We are more likely to attribute this drop to the 4 water molecules as this is the only step we can account for it if we are to get a total of 7 water molecules for the entire process.

For the third mass loss at about 401.2 °C, 4.706% of the initial mass was lost. This could only be another water molecule (~6.48 mass%). In the fourth and final step, at about 685.80 °C, 28.94% of the initial sample mass was lost, leading us to believe that this is where the sulfur trioxide (mass % of 28.80) was removed.

In the plot for sample 2, there is a mass loss at about the same temperature as sample 1; yet this time, we see a 15.29% mass loss at that temperature. This leads us to believe that 3 water molecules were released at this stage, as opposed to the 2 in sample 1. As we know, the humidity of the laboratory cannot be kept constant, and this could have led to there being more water molecules inside the interstitial sites of the ferrous sulfate than in sample 1. (i.e. It is possible that sample 1 was not actually a heptahydrate, and that it was actually octahydrate, or a mix of both or any combination of different hydrates.) The next step, this time at around 184.87 °C, was a loss of 21.30%, giving us more grounds to classify this step as the removal of sulfur dioxide, yet it is more convincing that 3 or 4 water molecules were lost in this step instead. The third and final mass step logged for sample 2 was the 3.234% drop located at 327.32 °C. This mass loss could be nothing other than another water molecule. As well, as predicted, we could not see the removal of the sulfur trioxide molecules, as the maximum temperature was only 400°C. The derivatives of the curves were similar, as predicted.

In Sample 3, the first mass loss is at 72.28 °C, where 10.51% was lost, which once again, is indubitably characteristic of the dehydration of two water molecules. The next step was a loss of 26.57%, characteristic of the aforementioned removal of 4 more water molecules or possibly the removal of sulfur dioxide. Finally, the third mass step of the heating was a drop in mass of 3.396%, which could only be another water molecule. As in sample 2, the removal of the sulfur trioxide molecule was not observed.

6. Conclusion

From the above results and following discussion, we have seen that subjecting a sample of ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) to thermogravimetric analysis leads to a thermal decomposition profile as follows:

- Two water molecules at 87 °C.
- Four water molecules at 201 °C.
- One water molecule at 401 °C.
- One SO_3 molecule at 686 °C.

The end product obtained is initially brown, but turns reddish brown upon exposure to air. This leads us to conclude that the end product is either ferrous or ferric oxide.

More results were apparent upon further examination. Conducting the analysis at a slower rate leads to a steeper curve and a higher percent loss. This characteristic was attributed to a more uniform thermal distribution within the molecules which led to a greater number of molecules possessing the required kinetic energy to break away from the internal bonds. Also, a slower heating rate provided more time for heat to be transferred from the outer surface molecules to the inner insulated ones.

Further analysis revealed that the initial mass of the sample also played a critical role in the shape of the thermal decomposition profile for ferrous sulfate. We concluded that a larger mass meant more clumping and therefore more uneven heating throughout the sample. This would result in more plateau-like dips in the curve with percent losses smaller than they would have been for samples with smaller initial masses.

Overall, the experiment was a success. We understood the basic working of a thermogravimetric analyzer and discovered new relationships between heating rates and mechanisms of decomposition. This helped reinforce our knowledge on high temperature material decomposition and also provided insight into how scientific experimentation and testing was to be carried out.

7. Questions

1. *What is the effect of the heating rate on the TGA curves? Provide reasons for this behaviour.*

To comment on the effect of the heating rate on the TGA curves, we need to analyze experiments one and two, because these were the only two samples where the heating rate was changed while keeping other variables (notably initial mass) constant. (See Table 1)

Since the second trial was tested up to a maximum temperature of 400 °C, trial one and trial two are compared up to that temperature. As seen in Table 1, the first trial had twice as fast of a heating rate as the second. This difference was visible upon the weight percent of the decomposing constituents. Near 70 °C, it can be noticed that the second trial had a more significant weight loss.

By slowing down the heating rate, more time is given for the heat to penetrate into the middle of the sample through the thermal distribution. The even thermal distribution leads to a steeper rate of decomposition since more of the inner molecules were being decomposed as the surface molecules. The inner molecules must have gained a more equal amount of thermal energy as opposed to when there is a quicker heating rate to explain the steep curve in Figure 1 in the vicinity of 75 °C. The molecular mass percent of water was calculated to be 6.48%, and so a removal of two water molecules should result in 12.96% mass percent change. However, from the second sample, about 15% mass percent change was observed. This can be explained by certain uncontrolled random variables which induced some errors in the data. An example would be the presence of some external humidity undesirably absorbed from the surroundings.

There are more variables which can affect our results in this analysis; namely, humidity, initial temperature and initial mass. To ideally analyze the relationship between the heating rates and the TGA curves these variables need to be constant and/or controlled. It was noted that there were some differences in the sample mass from the prescribed sample mass. For example, the second mass sample weighed 25.5 mg as opposed to 20 mg. Also, the starting temperature was not room temperature for the second trial, but was a bit higher (30.8 °C, as opposed to 22.4 °C). Lastly, the room humidity was assumed to be constant; however, had this not been the case, the composition of the hydrate would have been different for each trial, thus affecting our subsequent percent weight calculations.

Had it not been for deviations in these parameters and variables, irregularities in the data would not have been observed and all the mass percent changes in different temperatures would have been integer multiples of the mass percentages from water and other decomposing constituents. Consequently, it would have been easier to find a constant of proportionality between the heating rate and the

mass percent change of the constituents. However, in general, it can be stated that a lower heating rate results in a better decomposition and a better heat distribution within the sample.

2. *Does the initial sample mass affect the experimental data? If so, why?*

In order to comment on the effect that the initial sample mass has on the data, we must consider experiments 1 and 3. As Table 1 indicates, these were the only two experiments where the initial sample mass was varied by keeping the heating rate constant.

Experiment 1 had an initial mass of 20.0 mg and experiment 3 had an initial mass of 5.0 mg. This is exactly one fourth of experiment 1's initial mass. With a different sample mass, there will be differences in surface area. For example, with a larger mass, there would not be a uniform distribution of each granule on the platinum sample pan. If there is not a uniform distribution, the heat energy may not have been transferred to the inner granules of say, a pile of the sample. Here, the outer granules would insulate the inner granules, preventing them from getting the heat. When the heat is not available to the granules, it will show up as a less steep line on the mass percent vs. temperature curve. The drop will be smaller as a fewer percentage of molecules have the required kinetic energy to dehydrate or break away from the sphere of hydration.

When we take a look at our curves for TGA 1 and 3, we see that TGA 3 has a steeper curve due to a more uniform distribution of the granules as previously explained.

8. References

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