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QUANTITATIVE THERMOGRAVIMETRIC ANALYSIS OF BINARY MIXTURES
Magnesium hydroxide and magnesium acetate

E. M. van der Merwe[1*] *and C. A. Strydom*[2]

[1]Department of Chemistry, P.O. Box 392, UNISA, 0003, South Africa
[2]Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa

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Abstract

Thermogravimetric analysis is used to determine the amounts of $Mg(OH)_2$ and $Mg(CH_3COO)_2$ in a mixture thereof. The application and suitability of different analysis methods are discussed. In the first method the mass losses in the temperature ranges as indicated by the decomposition of the pure compounds were used. Results obtained using these temperature ranges were unusable. The percentage mass losses due to the decomposition of $Mg(OH)_2$ and $Mg(CH_3COO)_2$ were then determined in a second method using the minimum in the derivative mass *vs.* temperature curves. The results obtained by this method compared well with the actual values for mixtures containing more than 15% magnesium acetate. The third method employed the total experimental mass loss of both decomposition reactions. The results obtained using this method compared well to the actual values, giving a R^2 value of more than 0.99. This method of using the total mass losses can however only be used for binary mixtures that consist only of magnesium hydroxide and magnesium acetate.

Keywords: magnesium acetate, magnesium hydroxide, quantitative determination, TG

Introduction

The preparation of hydromagnesite from both magnesium hydroxide and magnesium oxide have been studied previously [1]. It was found that the reaction has not gone to completion when MgO is used as starting material, and that the preparation from $Mg(OH)_2$ is preferred. The influence of experimental conditions during the preparation of hydromagnesite from $Mg(OH)_2$ is critical, and influences the characteristics of the product formed, especially the number of carbonate *vs.* hydroxide groups in the final product. The rehydration characteristics of a commercially available and two synthetically produced basic magnesium carbonates have been studied previously to obtain the chemical compositions of the products that were formed for vari-

* Author for correspondence: E-mail: vdmerem1@unisa.ac.za

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ous experimental conditions [2]. MgO is available as a by-product during the synthesis of magnesium carbonates in the local industry.

Thermogravimetric analysis can be applied to determine the degree of hydration of magnesium oxide to magnesium hydroxide by comparing the experimental mass loss to the theoretical mass loss of the decomposition of $Mg(OH)_2$. This decomposition reaction takes place between 300–400°C according to the following scheme:

$$\mathrm{Mg(OH)_2}(s) \qquad \mathrm{MgO}(s)\mathrm{+H_2O}(g)$$

Magnesium acetate can be used to enhance the degree of hydration of magnesium oxide [3]. The magnesium hydroxide product obtained from the hydration of magnesium oxide in magnesium acetate solutions usually contains some magnesium acetate. Magnesium acetate decomposes in the same temperature range as magnesium hydroxide, which complicates the quantitative analysis of hydrated samples.

According to [4], magnesium acetate decomposes following the next scheme:

$$\mathrm{Mg(C_2H_3O_2)_2}(s) \qquad \mathrm{MgO}(s)\mathrm{+CO_2}(g)\mathrm{+CH_3COCH_3}(g)$$

In this paper, suitable methods to determine the amounts of magnesium hydroxide and magnesium acetate in a mixture thereof are discussed.

Experimental

Pure $Mg(OH)_2$ and $Mg(CH_3COO)_2\ 4H_2O$ was obtained from Merck. To remove moisture and water of crystallization, the samples were dried at 200°C for 2 h. Different mass percentage ratios of the two compounds were mixed and ground together.

A Q500 TG (TA Instruments) was used to perform the thermogravimetric analysis of the pure compounds and mixtures. A heating rate of 10°C min^{-1} was used in an oxygen atmosphere. Platinum pans were used, and the sample masses were between 8–11 mg. Three thermogravimetric curves were obtained for each sample.

Results and discussion

The TG curves of some of the mixtures are shown in Fig. 1. Decomposition of the sample containing only $Mg(OH)_2$ revealed a mass loss of 26.8% between 200–450°C. The difference between this mass loss percentage and the theoretical value (30.9%) can be ascribed to the presence of MgO and some impurities.

All samples containing magnesium acetate have shown a small mass loss between 30 and 150°C. Although both the $Mg(OH)_2$ and $Mg(CH_3COO)_2\ 4H_2O$ was dried at 200°C before mixing, it was clear that by the time the thermal analysis runs were performed, the magnesium acetate in the samples have already started to rehydrate again.

The theoretical mass loss for the decomposition of $Mg(CH_3COO)_2$ to MgO is 71.7%. To determine the mass loss of the decomposition of the $Mg(CH_3COO)_2$ sample, the mass loss due to the uptake of water of crystallisation had to be subtracted first.

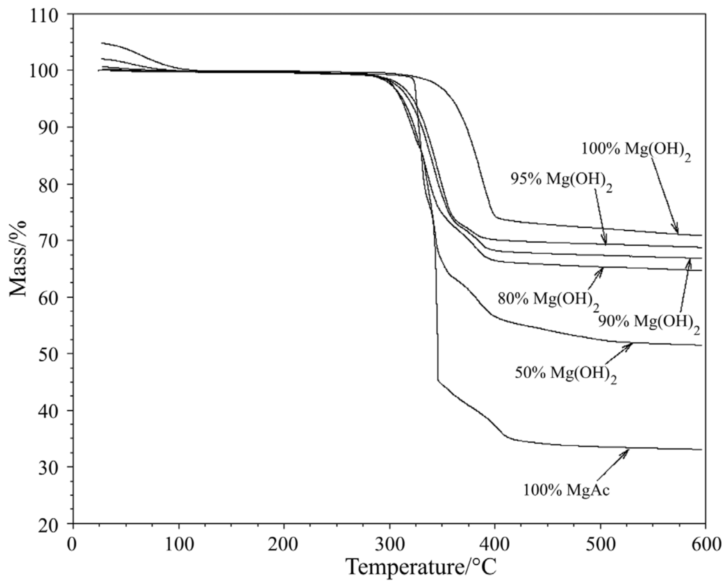

Fig. 1 TG runs of different mass percentage mixtures of $Mg(OH)_2$ and $Mg(CH_3COO)_2$ (MgAc)

This gives a new initial mass at 150°C, from which the mass percentages are recalculated. The average mass loss obtained for the decomposition of the samples containing only magnesium acetate was 69.6%, which compared well to the theoretical value.

In the first method, the amount of $Mg(OH)_2$ in the mixtures was determined by obtaining curves of mass (%) and derivative mass (% $°C^{-1}$) *vs.* temperature (°C). The percentage mass losses due to the decomposition of $Mg(OH)_2$ and $Mg(CH_3COO)_2$ was then determined by using the minimum in the derivative mass *vs.* temperature curve at about 370°C, as indicated in Fig. 2. The thermogravimetric curve of the mixture containing 90% $Mg(OH)_2$ and 10% $Mg(CH_3COO)_2$ is used as example. The first mass loss (27.7%, 200–370°C) is due to the decomposition of $Mg(OH)_2$, and the second (4.4%, 370–450°C) due to decomposition of $Mg(CH_3COO)_2$. The two decomposition reactions, however overlap between 350 and 370°C. After calculating the new initial mass at 150°C, the values obtained for these mass losses were 26.3 and 6.0%, respectively. Using the mass loss obtained for the sample containing $Mg(OH)_2$ only, the calculated mass percentage for the sample is 98.1%, and similarly, that for $Mg(CH_3COO)_3$ is 8.6%.

However, when the same analysis technique was applied to the sample containing 50% $Mg(OH)_2$ and 50% $Mg(CH_3COO)_2$ (Fig. 3), the mass loss percentages obtained were 41.3 and 7.9%. Using these results to calculate the mass percentage composition of the sample, 154.1% was obtained for $Mg(OH)_2$ and 11.4% for magnesium acetate, which was not possible.

The average values obtained from the results of three TG curves for each mixture, using this first method, are summarized in Table 1. It is clear that by increasing the

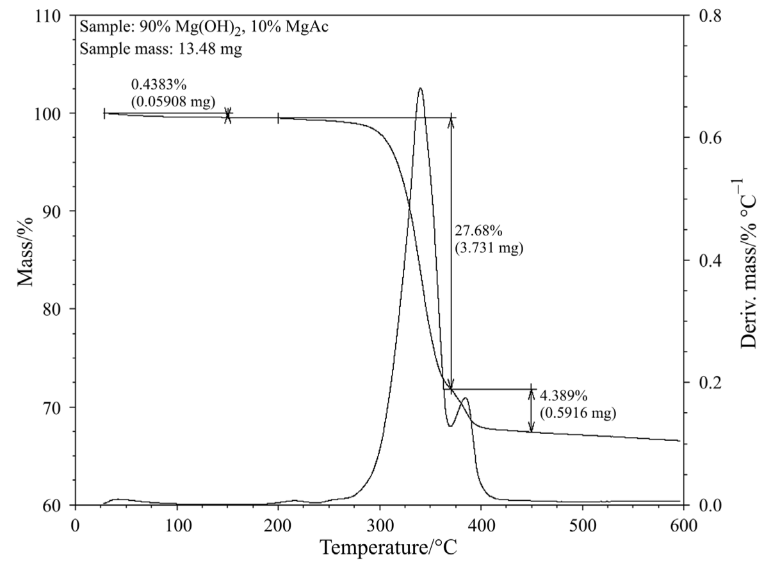

Fig. 2 TG curve for the determination of the amount of $Mg(OH)_2$ in a sample containing 90% $Mg(OH)_2$ and 10% $Mg(CH_3COO)_2$ (First method)

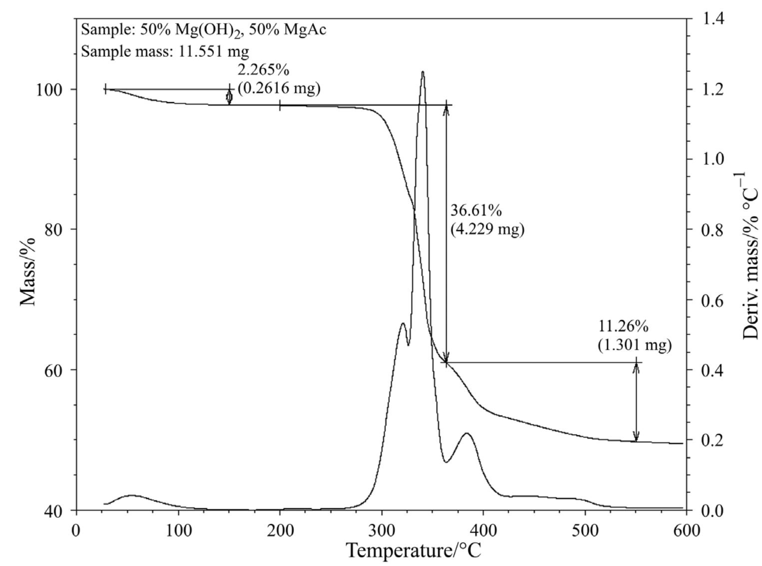

Fig. 3 TG curve for the determination of the amount of $Mg(OH)_2$ in a sample containing 50% $Mg(OH)_2$ and 50% $Mg(CH_3COO)_2$ – Analysis 1 (First method)

amount of magnesium acetate in the mixtures, the inaccuracy of the obtained results were increased. Therefore, it was found that this first method was not suitable for a quantitative analysis of these mixtures, and a more suitable method had to be evaluated.

Table 1 Results of calculation of mass percentage composition of different mixtures of magnesium hydroxide and magnesium acetate by making use of the first method

Actual composition		Experimentally determined composition	
$Mg(OH)_2$/%	$Mg(CH_3COO)_2$/%	$Mg(OH)_2$/%	$Mg(CH_3COO)_2$/%
95	5	98.7	6.5
90	10	97.2	9.0
85	15	103.0	9.7
80	20	108.7	10.5
70	30	124.7	10.6
60	40	139.8	10.5
50	50	154.9	10.9

Comparing the TG curves in Fig. 1, it seems that by mixing these compounds, the decomposition temperature of $Mg(OH)_2$ is lowered with increasing amounts of magnesium acetate, while that of $Mg(CH_3COO)_2$ is elevated. The analyses of the TG curves of the sample containing 50% $Mg(OH)_2$ and 50% $Mg(CH_3COO)_2$ were repeated in Fig. 4 by using a second method. In this method, the mass loss due to decomposition of $Mg(OH)_2$ was taken as the minimum in the derivative mass *vs.* temperature curve of the first mass loss above 200°C, at temperatures between 200 and 327°C, and that for magnesium acetate for all steps thereafter (between 327 and 543°C). The temperature ranges these decomposition steps changed with a change in the sample composition. Calculation of the mass percentage composition of the sample containing 50% $Mg(OH)_2$

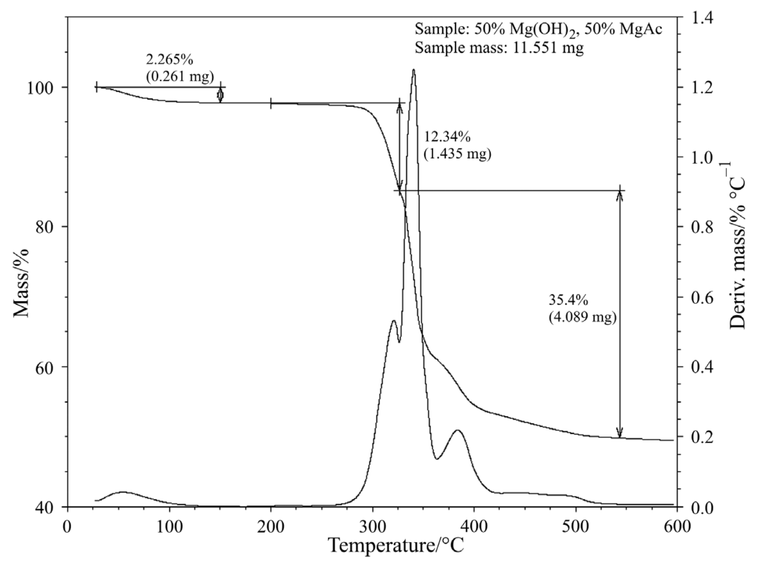

Fig. 4 TG curve for the determination of the amount of $Mg(OH)_2$ in a sample containing 50% $Mg(OH)_2$ and 50% $Mg(CH_3COO)_2$ – Analysis 2 (Second method)

and 50% $Mg(CH_3COO)_2$ resulted in 52.9% $Mg(OH)_2$ and 50.3% $Mg(CH_3COO)_2$, which compared well with the actual values. The method was repeated for all other mixtures, and gave good results for samples containing higher percentages of magnesium acetate, where there is a clear separation of the different decomposition steps.

The results obtained after calculation of the percentage composition of all mixtures using this second method are reported in Table 2. As expected, the method produced better results for samples containing more magnesium acetate, especially in calculating the amount of $Mg(OH)_2$, except where the percentage magnesium acetate is lower than 15%.

Table 2 Results of calculation of mass percentage composition of different mixtures of magnesium hydroxide and magnesium acetate by making use of the second method

Actual composition		Experimentally determined composition	
$Mg(OH)_2$/%	$Mg(CH_3COO)_2$/%	$Mg(OH)_2$/%	$Mg(CH_3COO)_2$/%
95	5	98.7	6.5
90	10	97.3	9.0
85	15	92.4	13.6
80	20	82.0	20.8
70	30	72.3	30.8
60	40	63.2	40.0
50	50	52.4	50.4

In the third method, the total mass loss for both decomposition reactions was obtained between 200–450°C. A plot of the total mass loss percentages *vs.* actual mass percentages $Mg(CH_3COO)_2$ was obtained and is given in Fig. 5. The values reported

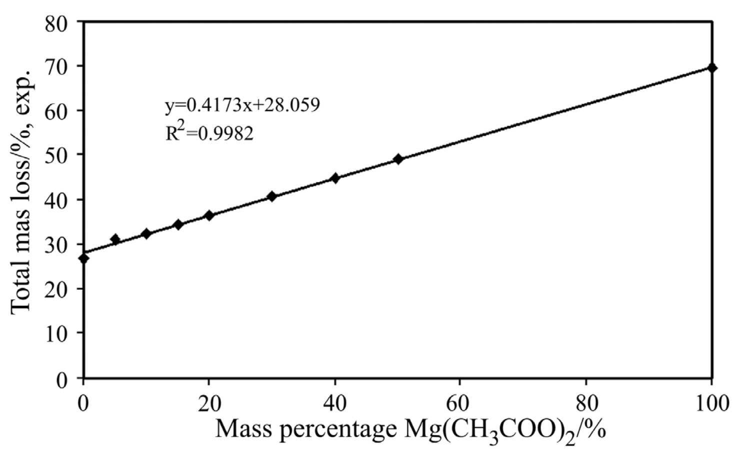

Fig. 5 Total mass loss (experimental) *vs.* mass percentage magnesium acetate (actual)

in the plot was the average of the three TG data sets, and regression analysis resulted in the following linear fit:

$$y=0.4173x+28.059;\ R^2=0.9982$$

where y=experimental mass loss between 200–450°C (%), x=actual mass percentage magnesium acetate.

Using this equation, the mass percentage magnesium acetate in a mixture of magnesium acetate and magnesium hydroxide can be determined. Subtracting the mass loss due to decomposition of magnesium acetate from the total mass loss, the mass percentage magnesium hydroxide can be calculated.

Table 3 Results of calculation of mass percentage composition of different mixtures of magnesium hydroxide and magnesium acetate by making use of the third method

Actual composition		Experimentally determined composition	
$Mg(OH)_2$/%	$Mg(CH_3COO)_2$/%	$Mg(OH)_2$/%	$Mg(CH_3COO)_2$/%
95	5	97.4	7.0
90	10	94.1	10.2
85	15	89.0	15.1
80	20	83.8	20.2
70	30	73.0	30.6
60	40	63.1	40.1
50	50	52.4	50.4

The results obtained for the calculation of the composition of the different mixtures by the third method are given in Table 3. These results were very similar to the results obtained for the second method (Table 2), especially for the mixtures containing higher percentages of magnesium acetate. However, it seemed as if this method yielded improved results for the mixtures containing between 5 and 15% magnesium acetate.

Conclusions

Three methods for the quantitative determination of the amounts of magnesium hydroxide and magnesium acetate by thermogravimetry were discussed. The first method involved the determination of the amounts of $Mg(OH)_2$ and $Mg(CH_3COO)_2$ by using the minimum in the derivative mass *vs.* temperature curve to determine the decomposition mass losses for the mixtures over the same temperature range as for the pure compounds. Because the decomposition temperatures of both $Mg(OH)_2$ and $Mg(CH_3COO)_2$ changed as the composition of the mixture changed, this method yielded very inaccurate results.

The second method also entailed the use of the derivative mass *vs.* temperature curve for each TG curve. The minimum values in these curves were used to determine the mass losses in the TG curves for the two decomposition reactions. The first mass loss above 200°C was taken as due to the decomposition of $Mg(OH)_2$, while all other steps was considered due to the decomposition of $Mg(CH_3COO)_2$. The results obtained by this method compared well with the actual values, but needed some improvement for mixtures containing percentages $Mg(CH_3COO)_2$ lower than 15%.

The third method was found to be the most reliable, due to the fact that this method employed the total experimental mass loss of both decomposition reactions. The results obtained using this method compared well to the actual values, giving a R^2 value of more than 0.99. This method of using the total mass losses can however only be used where the mixtures consist only of magnesium hydroxide and magnesium acetate.

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