

2: Thermogravimetry

Learning Objectives

After completing this chapter, you should be able to:

- Describe the effect of heat on materials.
- Identify physical and chemical transitions.
- Describe the essential features of a thermobalance.
- Draw and interpret thermogravimetric and derivative thermogravimetric curve for a known system.
- Illustrate the range of applications of thermogravimetry.
- Calculate % weight loss at every stage of decomposition and predict stoichiometry.

Thermogravimetry is a technique used to detect any physical or chemical transitions which are accompanied by a weight loss or weight gain as the sample is heated in a controlled manner.

2.1 Effect of heat on matter

We need to first understand the effects of heat on matter. And For further explanation please see Introductory Chemistry in *Libretexts*



[https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Introduction_to_General_Chemistry_\(Malik\)/01%3AMatter_energy_and_their_measurements/1.09%3AHeat_and_changes_in_physical_states_of_matter](https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Introduction_to_General_Chemistry_(Malik)/01%3AMatter_energy_and_their_measurements/1.09%3AHeat_and_changes_in_physical_states_of_matter)

Now, we have understood the effects of heat on matter and also able to identify the processes involving change in weight on heating through Activity 1D. It is important to keep in mind that the change in weight could be due to physical or chemical transitions. To be able to distinguish between physical and chemical transition, let us go through the next sub-topic.

2.2 Changes in matter: Physical and Chemical Changes

For further explanation please see Introductory Chemistry in *Libretexts*



[https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Introductory_Chemistry/03%3AMatter_and_Energy/3.06%3AChanges_in_Matter - Physical and Chemical Changes#:~:text=3.6%3A%20Changes%20in%20Matter%20%20Physical%20and%20Chemical,4%20Summary%20...%20%20Contributions%20%26%20Attributions%20](https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Introductory_Chemistry/03%3AMatter_and_Energy/3.06%3AChanges_in_Matter_-_Physical_and_Chemical_Changes#:~:text=3.6%3A%20Changes%20in%20Matter%20%20Physical%20and%20Chemical,4%20Summary%20...%20%20Contributions%20%26%20Attributions%20)



Activity 2.1: Can you assign which of these transitions will be physical transitions /chemical transitions? **(please tick)**

Phenomenon	Physical	Chemical
Adsorption		
Dehydration		
Desorption		
Fusion (melting)		
Chemisorption		
Vaporization		
Decomposition		
Redox reactions		
Reduction in gaseous atmosphere		

(Dodd & Tonge, 2008)

2.3 Principle and Instrumentation of TGA

The instrument used to carry out thermogravimetric analysis is known as “thermobalance”.

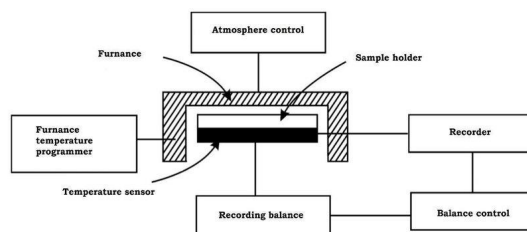


Figure 2.3 Schematic diagram of a thermobalance. (Source: <https://images.app.goo.gl/uyRxxbkVNkxLF3nT7>)

Working: Please go through the *Chemlibre* link to understand the principle and working of a thermobalance.



[https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Instrumental_Analysis_\(LibreTexts\)/31%3A_Thermal_Methods/31.01%3A_Thermogravimetric_Methods](https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Instrumental_Analysis_(LibreTexts)/31%3A_Thermal_Methods/31.01%3A_Thermogravimetric_Methods)

2.4 Interpretation of thermogravimetric curve

The graphical information obtained from thermogravimetric analysis is known as thermogram/pyrolysis curve. TG curve is a plot of weight (W) decreasing downwards on the y-axis (ordinate), and temperature (T) increasing to the right on the x-axis (abscissa). A typical thermogram for a single step decomposition is shown in Fig. 2.4.

The plateau ‘AB’ indicates no change in weight or the temperature range over which the sample is thermally stable. At point ‘B’ the sample starts decomposing which is indicated by an inflexion.

Please read the following text explaining the interpretation of thermogram and then attempt Activity 2B.



[https://chem.libretexts.org/Courses/Franklin_and_Marshall_College/Introduction_to_Materials_Characterization_CHM_412_Collaborative_Text/Thermal_Analysis/Thermogravimetric_analysis_\(TGA\)](https://chem.libretexts.org/Courses/Franklin_and_Marshall_College/Introduction_to_Materials_Characterization_CHM_412_Collaborative_Text/Thermal_Analysis/Thermogravimetric_analysis_(TGA))



Activity 2.2: A typical thermogram is shown below, observe and fill in the blanks by choosing the most appropriate answer. (Hint: Initial mass at ‘A’ is considered as 100%)

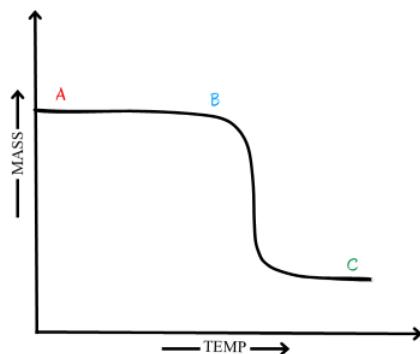


Figure 2.4 Typical TG curve

Activity 2.3: For the processes given in the table, predict the nature of thermogram (Type-X /Type-Y or None of these)

Phenomenon	Type
Melting	
Adsorption of gas	
Desorption of gas	
Vaporisation	
Dehydration	
Decomposition	
Sublimation	

Type X

Type Y

2.5 Need for Derivative Thermogravimetry (DTG)

In the above example (Fig. 2.4), we have considered the thermogravimetric curve which represents a single stage decomposition. Figures '1.2.5a' and '1.2.5b' show two-stage and three-stage decompositions respectively. In both these figures (2.5a and 2.5b) there is an overlay of TGA and DTG thermograms, clearly depicting advantages of DTG over TGA thermogram in locating the exact decomposition temperature.

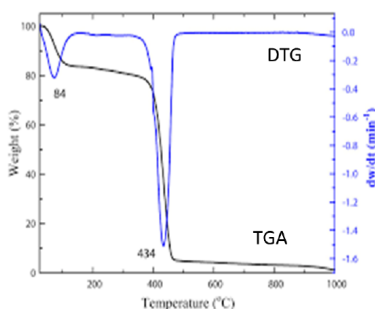


Figure 2.5a. Thermogravimetric (TG) and Derivative thermogravimetry (DTG) curves for PVP at a heating rate of 10°C/min. (Source: Al-Hada et al., 2014) <https://images.app.goo.gl/fWChwNji9uxfHZAj7>

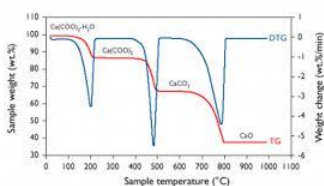



Figure 2.5b. TGA test result of calcium oxalate monohydrate (Source: Chegg.com) <https://images.app.goo.gl/1Hbp2vSV2rBjeFc4A>

Figure '2.5b' is for the decomposition of calcium oxalate monohydrate, the weight loss commences just above 100°C and continues up to 200°C. Between about 400 °C and 500°C further decomposition occurs, to give a product which is stable up to

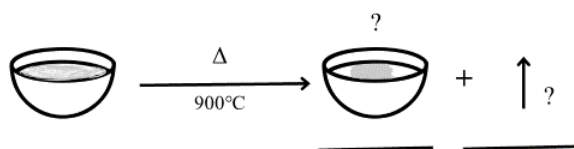
700°C before decomposing to give another stable compound at 800°C. Every process of decomposition continues over a range of temperature hence the DTG curve is useful in providing information regarding precise decomposition temperature at every stage.


 **Activity 2.4:** (James & Tonge, 2008)

 **Activity 2.5:** Complete the following reaction for the decomposition of calcium carbonate.

- Identify the volatile and stable compound/s remaining in the crucible post decomposition and indicate these on a thermogram.

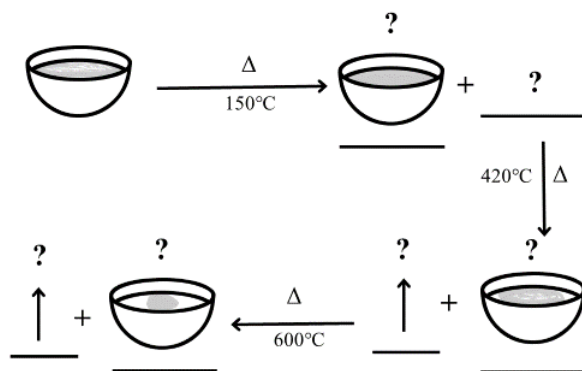
CALCIUM CARBONATE




 **Activity 2.6:** Observe the image given below for the decomposition of magnesium oxalate monohydrate ($\text{MgC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and complete the activity.

- Identify the volatile product and the residue remaining in the crucible at each stage of decomposition.
- Write the decomposition reaction taking place at each stage.
- Draw a thermogram for the decomposition of magnesium oxalate monohydrate.

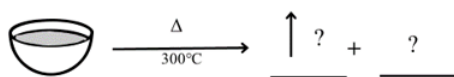
MAGNESIUM OXALATE MONOHYDRATE



 **Activity 2.7:** Observe the image given below for the decomposition of ammonium nitrate (NH_4NO_3) and complete the activity.

- Identify the volatile product/s and the residue remaining (if any) in the crucible after decomposition.
- Write the decomposition reaction.
- Draw a thermogram for the decomposition of ammonium nitrate.

AMMONIUM NITRATE



2.6 Applications of Thermogravimetric analysis

I. Thermogravimetric analysis of a binary mixture of calcium and magnesium oxalates:

Following thermogram shows decomposition curve for a mixture of oxalates.

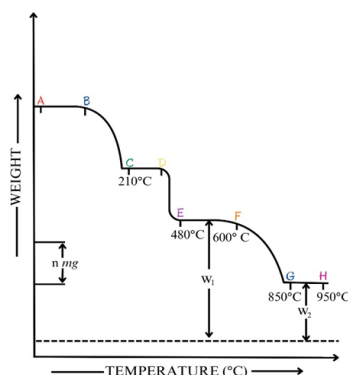


Figure 2.6a. Decomposition curve for a mixture of calcium and magnesium oxalate dihydrate

- There is a significant loss which occurs before 210°C- due to loss of water from the sample.
- The mixture of anhydrous carbonate then shows some weight loss by about 480 °C owing to the reaction



- No further weight loss occurs before 600 °C. (EF)
- CaCO_3 decomposes between about 600 °C and 900 °C. (FG)



- Thus, EF represents a mixture of MgO and CaCO_3
- The plateau GH represents the residue of MgO and CaO



Activity 2.8: Construct separate decomposition curves for calcium oxalate dihydrate and magnesium oxalate dihydrate based on the above information.

II. Thermogravimetric analysis of plaster for safety screening:

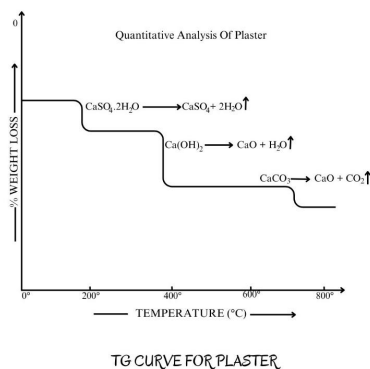


Figure 2.6b. TG curve for plaster

Plaster contains following ingredients,

Gypsum--- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Lime--- $\text{Ca}(\text{OH})_2$

Chalk--- CaCO_3

From the weight loss at each step on the curve, the quantity of each ingredient can be determined in the original sample. In the manufacture of Portland cement, 5% gypsum is added to reduce the rate of setting. The gypsum is added to the fused clinker during processing, and the two components are subsequently milled to obtain uniform mixing and the required particle size. During milling, the thermal energy generated may cause partial dehydration of gypsum to hemihydrate $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ which adversely affects (increases) the rate of setting of the cement. Hence it is important to monitor the presence of each hydrate in the final cement. In order to provide quantitation at the required levels, this problem can be solved by TGA and DTA or DSC.

The dehydration of gypsum occurs as a two-stage endothermic process.



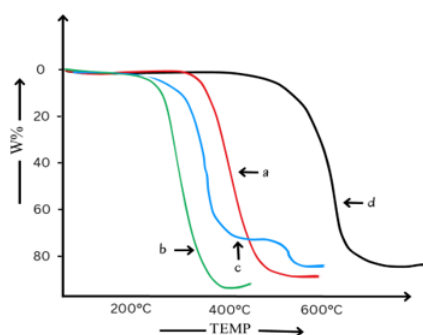
So, if there is conversion of gypsum to hemihydrate, the TG curve in Fig. 2.6b will show two step decomposition for gypsum instead of one.

Activity 2.9: (James & Tonge, 2008)

A manufacturer wishes to incorporate a plastic coating on the inside of a utensil. One factor to be evaluated is the stability of the following polymer.

- Polyethylene
- Polypropylene
- PVC
- Polytetrafluoroethylene

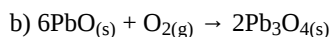
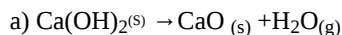
Figure below gives TG curves for the above polymers.



So far, we have discussed qualitative applications of TGA. Let us see some quantitative applications of thermogravimetric measurement.

Activity 2.10: Solve the following numerical problems.

1) Calculate the percent weight changes W% for each of the following reactions which occur on heating the parent material.

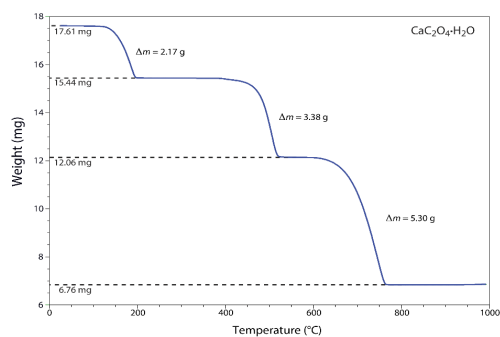


[Ca=40.1, H=1.0, O=16.0, Pb=207.2]

2) A mixture of calcium oxide and calcium carbonate is analysed by thermogravimetry. The resultant curve indicates one decomposition only between 600-900° C during which the weight of sample decreases from 250.6 mg to 190.8 mg. What is the percentage of calcium carbonate in mixture by weight?

[Atomic mass: H=1.0, Pb=207.2, C=12.0, O=16.0, Ca= 40.1]

3) The thermogram given below shows the mass of a sample of calcium oxalate monohydrate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, as a function of temperature. The original sample of 17.61 mg was heated from room temperature to 1000°C at a rate of 20°C per minute. Calculate the % weight loss at each step.



Activity 2.11: Solve the puzzle



<https://thewordsearch.com/puzzle/6923734/thermal-analysis/>

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