THERMO-ANALYTICAL METHODS!

Thermoanalytical methods ⟹ use of thermal energy to analyze sample.

- Thermal Analysis is widely used technique for analysis of solid samples like inorganic precipitates, glass materials and ceramics.

↗ heat = temperature.

- In thermal analysis, **some physical or chemical property of a sample is measured as a function of temperature.**

- When a sample is heated, it undergoes certain physical and chemical changes. These changes take place over a wide range of temperatures. This changes certain physical and chemical property.

  Physical Changes- Melting, Boiling

  Chemical Changes- Decomposition, Glass transition.

- The physical and chemical changes which a substance undergoes are characteristic of the substance under study. By measuring the temperatures at which these changes occur and the heat involved, **it is possible to characterize the compound present in the sample and thus identify the sample**.

Measure certain physical or chemical property as a function of temperature.

Different Methods of Thermal Analysis:

1. **ThermoGravimetric Analysis (TGA):**
   Mass of sample is measured as a function of temperature ie. Change in weight is measured as a function of temperature.

2. **Differential Thermal Analysis (DTA) :**
   Difference in temperature between the sample (T_S) and a suitable reference material (T_R) is measured as a function of temperature. The temperature difference, $\Delta T = T_S - T_R$ is measured at different temperature.

3. **Differential Scanning Calorimetry (DSC):**
   Energy required to establish zero temperature difference between sample and reference material is measured as a function of temperature.

4. **Thermometric Titrations (TT):**
   Changes in temperature are measured during the course of the titration.

Weight v/s Temperature = Thermogravimetric analysis.

A. ThermoGravimetric Analysis (TGA):

Physical Change → change in state, MP, BP.
Chemical Change → Decompost^n, evolution of gases.

change in weight is measured as a function of temperature.

A technique wherein the weight of the substance in an environment heated or cooled at a constant rate is recorded as a function of temperature.

In TGA, the weight of the substance is recorded over a period of time when its temperature is being changed at a constant rate.

change in weight.

Process which on heating show mass change can be studied by TGA. Like,

1. Reactant → Product + Gas (evolution of volatile products) → decrease in mass.
2. Reactant + Gas → Product (formation of heavier products) → increase in mass.

Type 1 :- Sample → product + Gases.

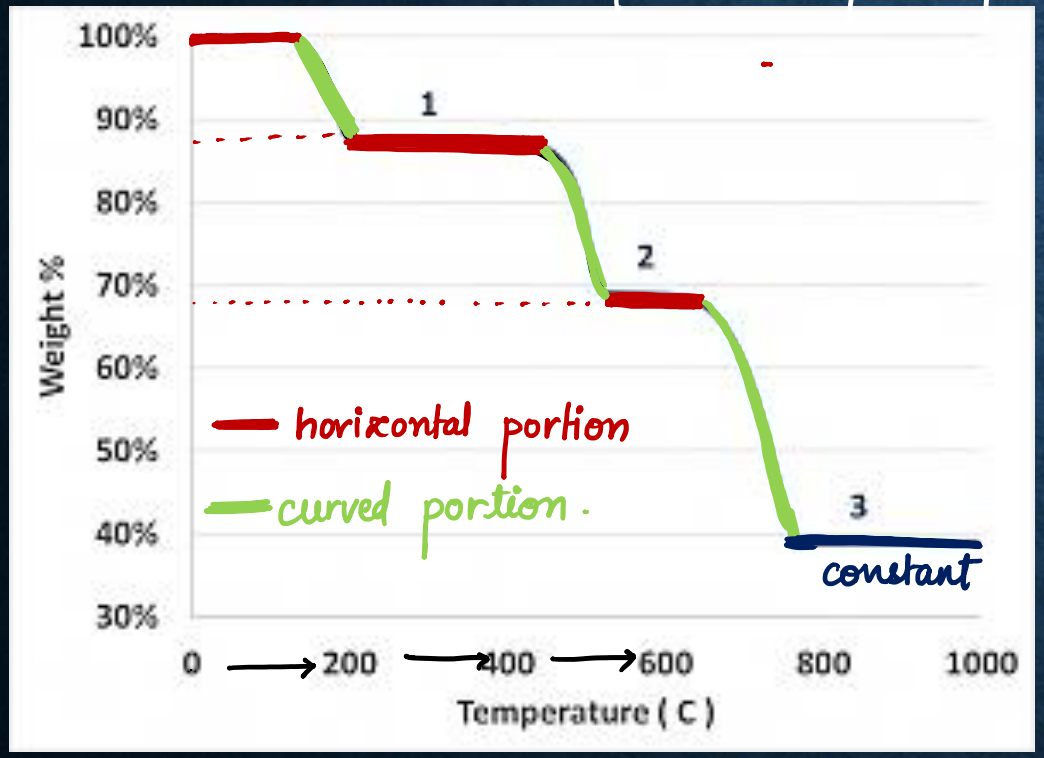
$CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$ (evolution of gas)

Type 2 :- Sample + Gas → Product.

$CaO + CO_2 \longrightarrow CaCO_3$ (formation of heavier product)

The plot of mass of the sample against the temperature is known as **thermogram or pyrolysis curve.**

independent quantity = X-axis = temperature.
dependent quantity = Y-axis = mass



The Horizontal portion/ plateaus represent regions where there is no change in the mass on heating of the sample.

The curved portion indicates weight losses due to transformation of sample or occurrence of a chemical reaction.

It is thus possible to determine from the thermogram, the temperatures at which the physical and chemical changes occur.

Thermogram: plot of mass of sample v/s temperature.
↳ also called as 'pyrolysis curve'

Thermogravimetric curves are characteristics of a given compound because the physico chemical reaction occur at definite temperatures and reaction rates which are related to the molecular structure.

Change in mass are a result of the breaking and/or formation of heavier products as indicated before.

From thermogravimetric curves, we get valuable information about the energetics and kinetics of the chemical reaction, reaction mechanism and intermediate and final products.

The usual temperature range in TGA is **ambient to 1800K with inert and reactive atmospheres**.

✱ Ambient temperature to 1800 K ⟶ temp. used in TGA.
can go beyond 1800.

INSTRUMENTATION:

1. A sample holder.
2. A sensitive balance.
3. A furnace.
4. An unit for measurement and control of temperature.
5. A recorder that provides a plot of sample mass vs temperature.
6. Auxiliary/ equipment to control the atmosphere around the sample.

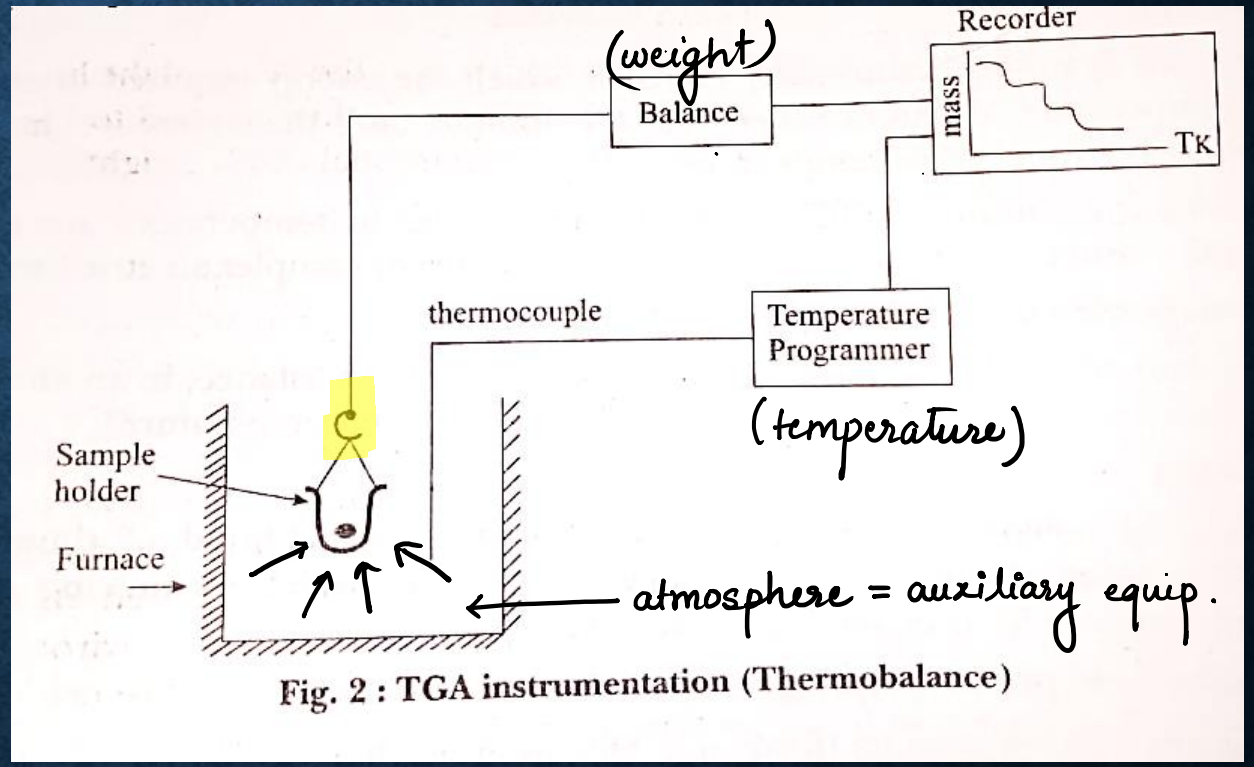


Fig. 2 : TGA instrumentation (Thermobalance)

1. Sample Holder:

The size, geometry and the material of the sample holder have an important effect on the shape of the TGA curve.

In TGA, **cylindrical or V shaped** cups are usually used.

flat - diffusion of gases is easy.

Generally, a crucible with **flat bottom** is used to ease the diffusion of evolved gases.

The sample required is in the range of **2-25 mg**.

The sample holder is suspended to the furnace using a **helical spring**.

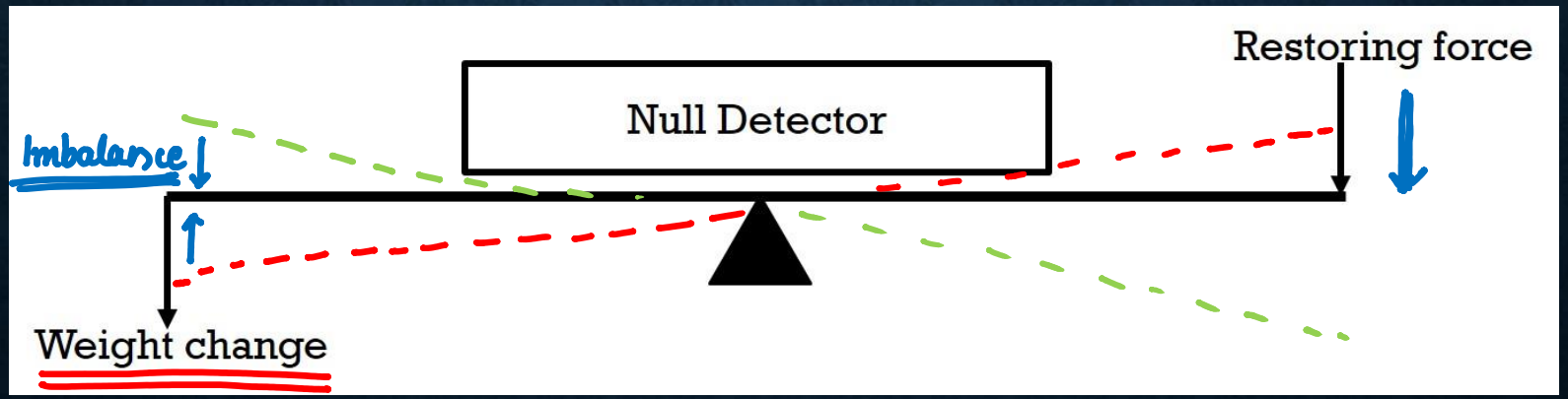
2. Balance: A Null point balance (Cahn Electrobalance) is generally used in TGA.

In TGA, sample mass is recorded over a wide range of temperature (ambient to 1800 K). Hence a good balance should satisfy the following requirement:

a. A rapid response to weight changes over the entire temperature range.
b. The change in mass of sample should be converted into the electrical signal which must be suitable for recording.
c. The balance should be sensitive to small sized samples.

In Cahn Electrobalance, a sensor detects the deviation of the beam of the balance from its null position. A restoring force is applied to the beam to restore it to its null position. This restoring force is directly proportional to the weight change and is measured as an electric current in the balance.

Cahn Electrobalance.



∝ weight change.

3. Furnace:

The furnace of a TGA set up should provide the temperatures ranging from ambient to 1800 K.

It should provide a linear variation of temperature with time ie. linear and reproducible heating rate. The heating rate vary from 0.5 to 25 K per minute.

The design of the furnace should ensure that the heat of the furnace is localized over the sample. All parts of the sample must receive the same amount of the heat so that the temperature remains uniform over the entire sample.

* Heating can be done using resistance heaters of Nichrome (Ni-Cr), Kanthal (Cr Al Fe) wires, infrared or microwave radiation or by heat transfer from hot liquids or gases.

Heat flow into the environment or the balance must be avoided and minimized by cooling the exterior of the oven (furnace) and by locating the furnace as far as possible from the balance.

The furnace is provided with a temperature programmer to ensure constant heating rate.

4. Unit for Temperature Measurement and Control:

Temperature measuring devices used in TGA are usually **thermocouples** placed as near the sample as possible.

The **thermocouple generates an emf** when the sample is heated and the temperature of the sample is measured from the emf generated.

2 EMFs are generated :-
① thermocouple = Temperature = X-axis
② balance = mass = Y-axis

5. Recorder:

The change in mass of the sample is measured in terms of the electric signal obtained from the balance.

The **emf generated by the thermocouple is applied to the X-axis** of the recording system and the **electric signal obtained from the balance is applied to the Y-axis**.

Thus the mass of the sample is plotted against temperature to give the thermogram of the sample.

6. Control of the Atmosphere:

The composition of the atmosphere surrounding the sample is very important and it is necessary to monitor its properties.

Most thermogravimetric instruments provide a means of altering the atmosphere and a static or a flowing atmosphere of any desired composition can be provided.

Thermogravimetric analysis can also be done in vacuum or at elevated pressures.

❖ FACTORS AFFECTING THERMOGRAVIMETRIC RESULTS:

With commercially available thermobalances, a wide range of factors affect the results obtained. In addition, several sources of error can lead to both inaccurate temperatures and weight change losses. Therefore it is necessary to construct a correction curve.

When an empty crucible is heated from ambient to 1800K or more, there is appreciable gain in the weight. This weight gain is dependent on the heating rate employed, crucible weight and volume. A correction curve must be constructed giving the apparent change in order to calculate the actual change occurring in the sample.

I. Instrumental Factors: (Inaccuracy from the instrument or the instrument components)

a. Heating rate:

When the sample is heated at fast heating rate, the temperature of decomposition will be higher than that obtained at slower rate of heating. Hence if an intermediate compound is to be detected it is necessary to avoid a fast heating rate.

high heating rate - high decompost^{n} temp.
slow heating rate - low decomposition temp.

b. Furnace Atmosphere:

The nature of surrounding atmosphere has a profound effect upon the temperature of decomposition stage.

Eg. Decomposition of $CaCO_3$ occurs at a much higher temperature if CO_2 rather than N2. → $CaO + CO_2$

Normally the function of atmosphere is to remove the gaseous products evolved during thermogravimetry, so that the nature of the surrounding remains constant. The commonly used atmospheres in TGA are,

a. Static air- air from surrounding flow through the furnace.
b. Dynamic air- compressed air from cylinder is passed through the furnace at a measured flow rate.
c. Nitrogen gas- Oxygen free- Provides a Inert atmosphere. / Absence of Oxygen.

c. Crucible geometry-

A flat plate shape crucible is preferable because of easy diffusion of evolved gases.

II. Sample Characteristics:

The weight, particle size and the mode of preparation of sample affects the TGA results.

-A large sample can create deviation from linearity in the temperature rise.

-A large volume of a sample in a crucible can obstruct the evolved gases.

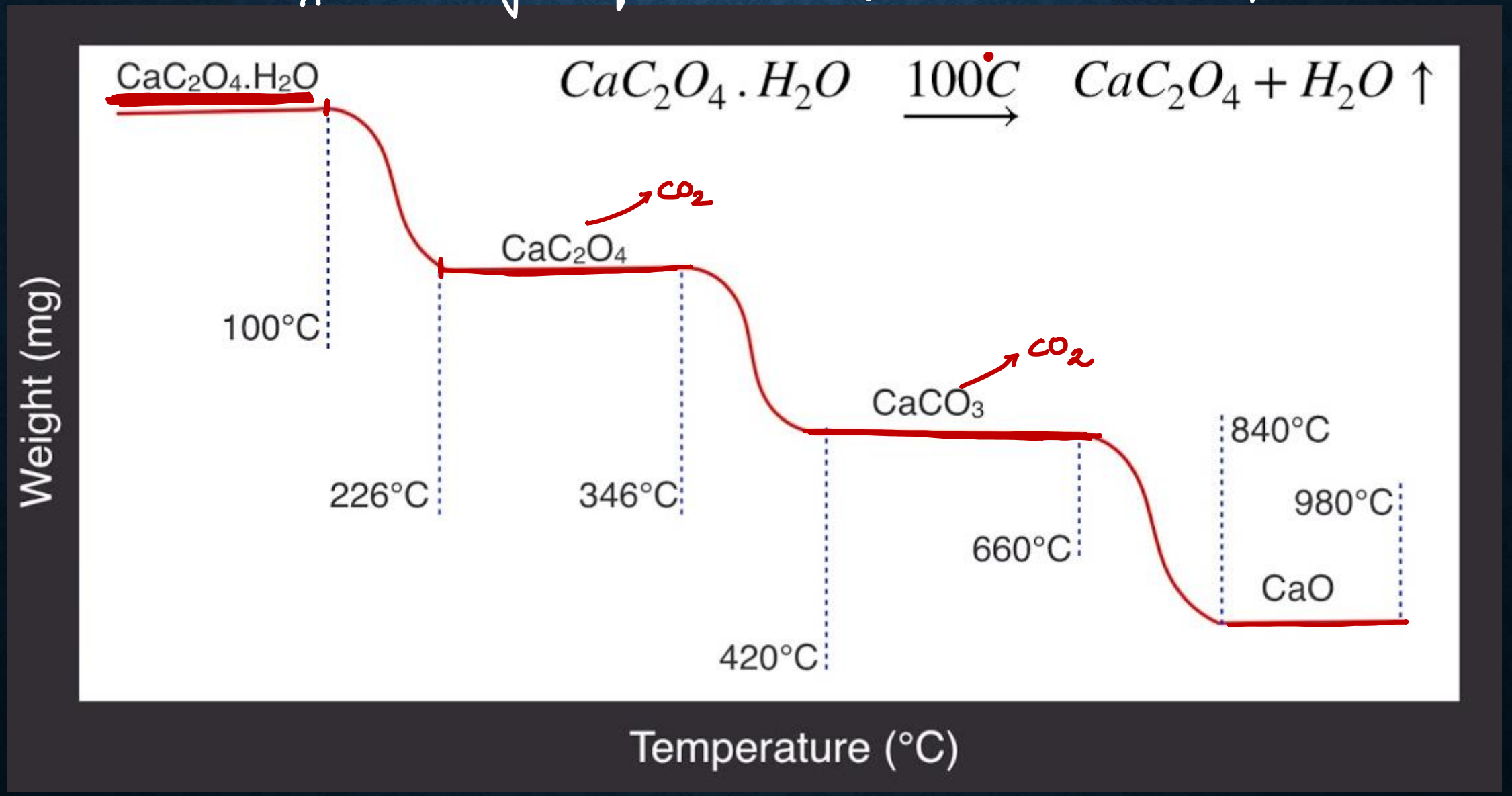
-A small sized sample with a particle uniform particle size is used.

-The source and method of preparation of sample can also affect the results obtained.

❖ APPLICATION OF THERMOGRAVIMETRY:

1. Study of Polymers. Thermograms give information about decomposition mechanisms of polymeric materials which are characteristics of each type of polymer and hence can be used for the identification of polymers.
2. Dehydration pattern of solids can be studied and accurate drying and ignition temperature for inorganic precipitates can be determined.
3. Thermal decomposition characteristics of glass, building materials, organic compounds can be studied.
4. Clay, soil samples can be analyzed for their water, carbonate and organic matter content.
5. Identification of compounds present in the mixture of materials. When a mixture is heated using a thermobalance, each component produces its own thermogram. These thermogram are super imposed on each other to provide single composite thermogram of the sample. The components are thus identified and also quantitatively estimated. (Determination of MgO and $MgC_2O_4.2H_2O$ content in the mixture)
6. Determination of correct drying temperature for precipitates, identification of gases given out when sample is heated, chemical process of heated materials and permits identification of the formulae of the residues.

⊛ Typical thermogram of $CaC_2O_4 \cdot H_2O$ (calcium oxalate monohydrate).




Thank You