Thermal methods of analysis

Thermal methods of analysis

A group of techniques in which the physical properties of a substance is measured as a function of temperature while the substance is subjected to controlled temperature program.

The most commonly used techniques are those which measure changes of mass or changes in energy of a sample of a substance

Thermal methods of analysis

1. Thermogravimetry Analysis (TGA)

2. Derivative Thermogravimetry (DTG)

3. Differential Thermal Analysis (DTA)

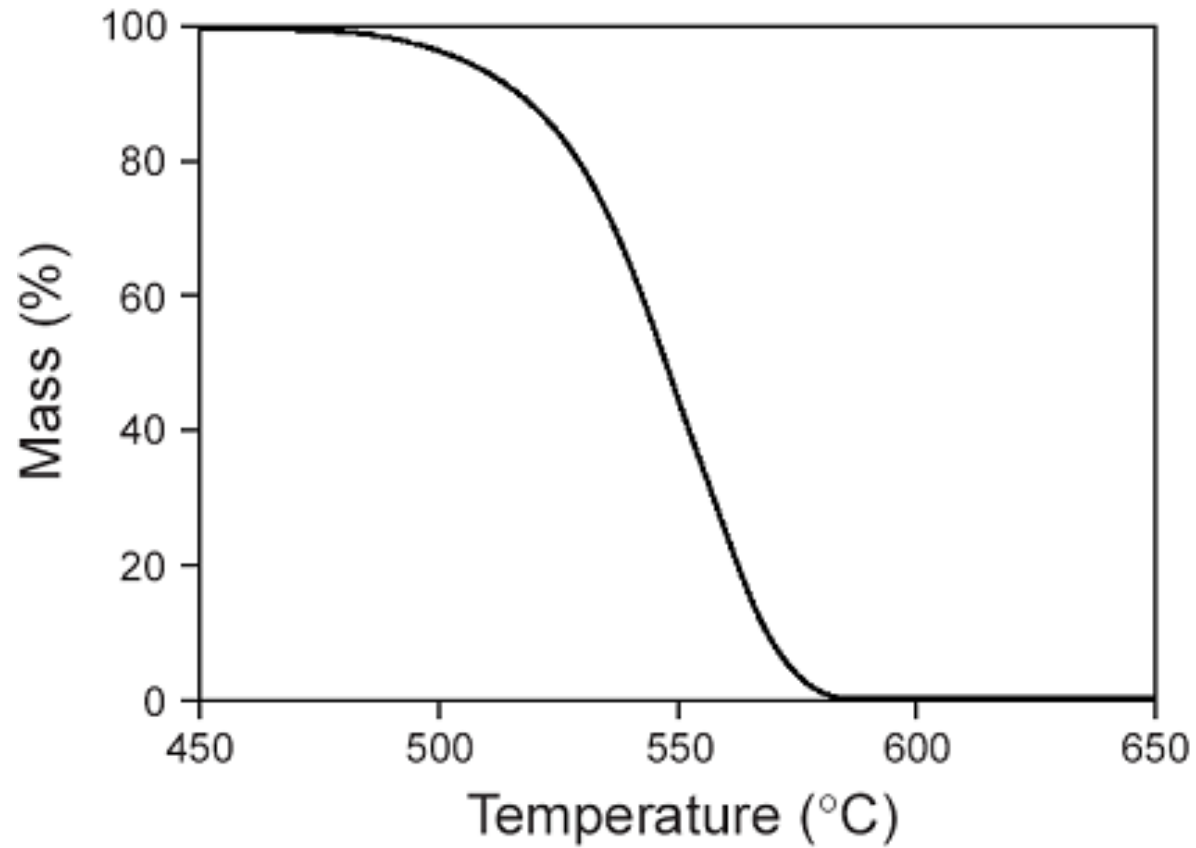4. Differential Scanning Calorimetry (DSC)

Thermal gravimetric analysis (TGA)

A technique in which the mass of a substance is monitored as a function of temperature or time

Samples are subjected to a controlled temperature program in a controlled atmosphere

What does a TGA thermal curve look like?

Data recorded in form of curve known as thermogram

❑Change in sample composition

❑Thermal stability

❑Decomposition reactions and temperatures

❑Absorbed moisture content

❑Kinetic parameters for chemical reactions in the sample

❑Purity

Different types of TGA

Isothermal or Static TGA: sample is maintained at a constant temperature for a period of time during which change in weight is recorded.

Quasi-static TGA: sample is heated to a constant weight at each of a series of increasing temperature.

Dynamic TGA: the sample is subjected to condition of a continuous increase in temperature at a constant heating rate, i.e., usually linear with time.

Instrumentation

The main components of the TGA apparatus are:

Analytical thermo balance:
For the measurement of mass with reproducibility with the order of ±10 micro gram

Furnace (made up of quartz): Programmed to increase the temperature "linearly a predetermined rate of 0.5 – 25 °C/min from r.t. – 1200 °C.

Environment control equipment: For providing inert atmosphere for the sample whenever desired.

The auto sampler: Helps to load the samples on to the microbalance.

A recorder: That gives a graph of *m* (or *dm/dt*) as a function of T.

Block diagram of TGA
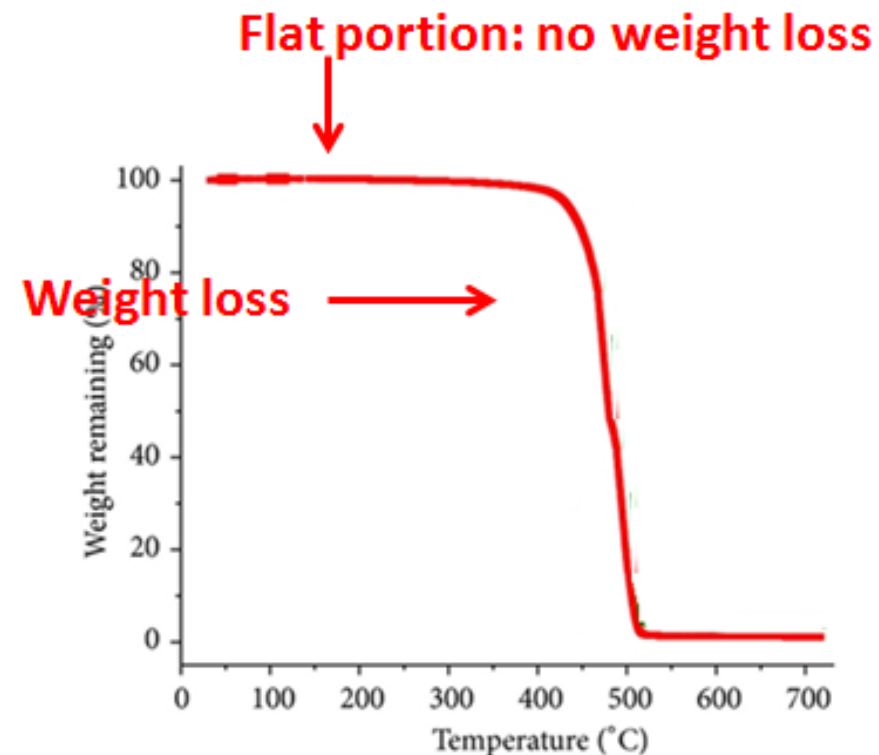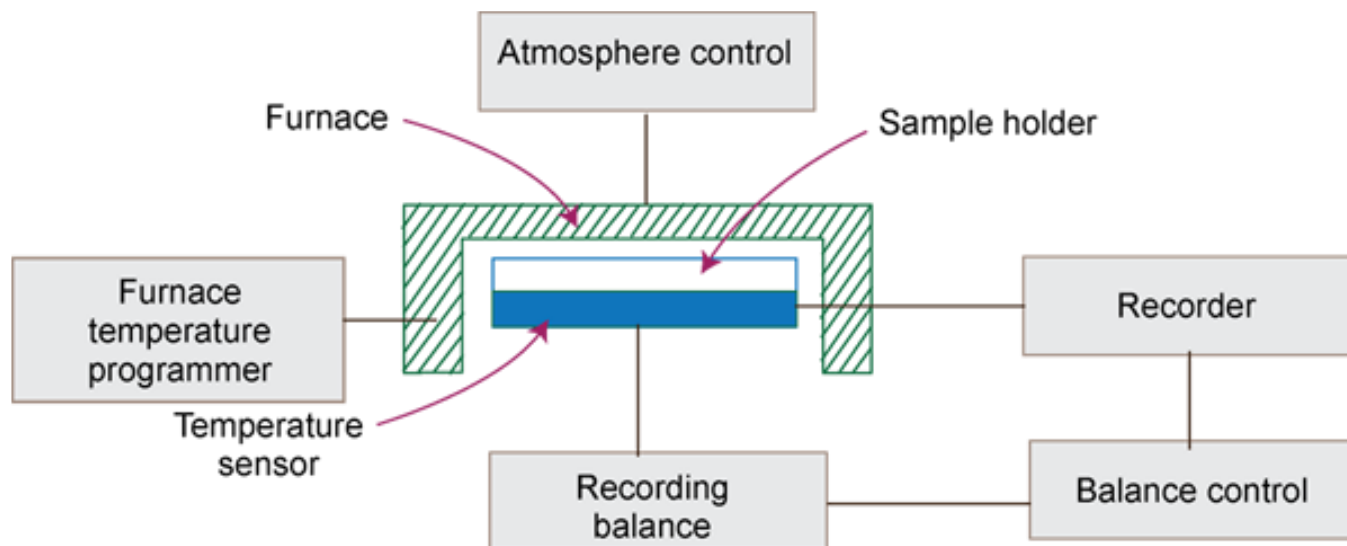
Horizontal portion indicate
there is no mass change, an indication of the thermal stability of the sample

The slanding portion indicate weight loss due any physical or chemical process like dehydration / formation of volatile products due to decomposition or dissociation etc.

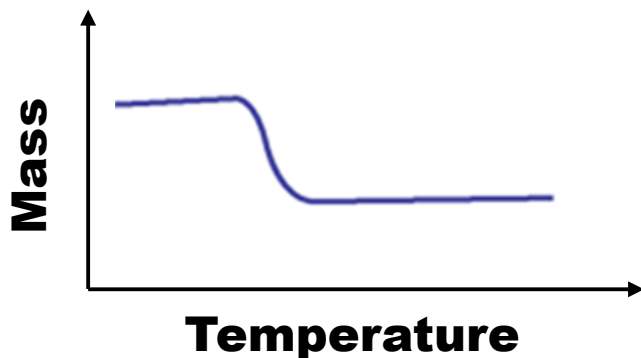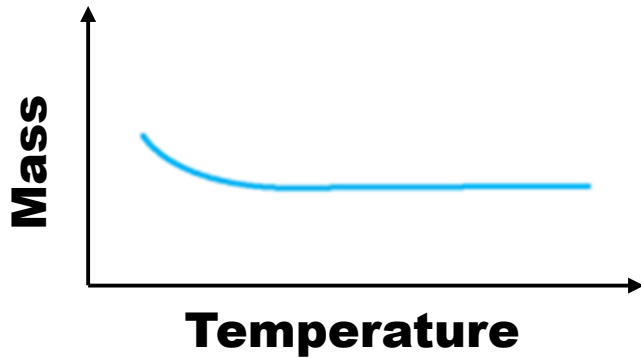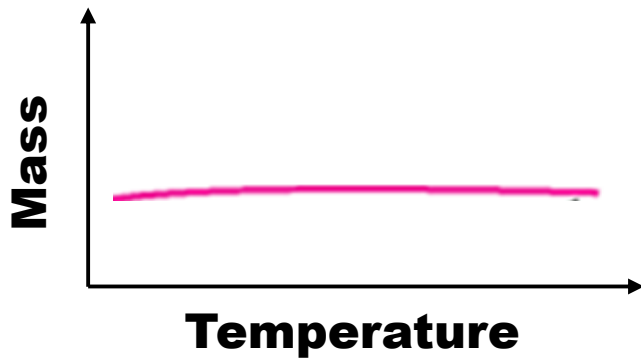# Types of TGA curves

Curve 1:

No change: depicts no mass change over the entire range of temperature, the decomposition temperature is greater than the temperature range of the instrument.
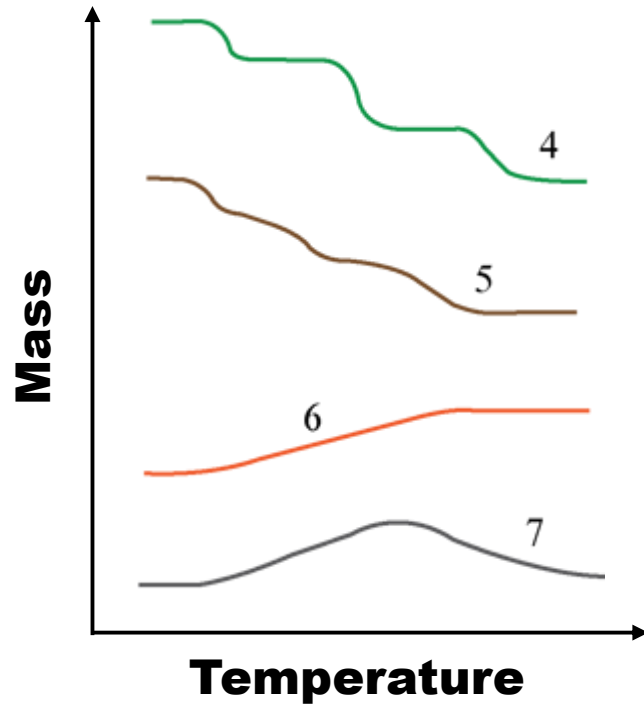
Curve 2:

Desorption/drying: This curve shows that the mass loss is large followed by mass plateau. This is formed when evaporation of volatile product(s) during desorption, drying or polymerization takes place

Curve 3:

Single stage decomposition: This curve is typical of single-stage decomposition temperatures having T_i and T_f.

Types of TGA curves

Curve 4: Multistage decomposition: This curve reveals the multi-stage decomposition processes as a result various reactions.

Curve 5: Similar to 4, but either due to fast heating rate or due to no intermediates.

Curve 6: Atmospheric reaction: This curve shows the increase in mass. This may be due to the reactions such as surface oxidation reactions in the presence of an interacting atmosphere.

Curve 7: Similar to curve 6, but product decomposes at high temperatures. For example, the reaction of surface oxidation followed by decomposition of reaction product(s).

TGA experiment: Processes that leads to weight gain and loss

Process	Weight gain	Weight loss
Adsorption or absorption	✓	
Desorption, drying		✓
Dehydration, desolvation		✓
Sublimation		✓
Vaporization		✓
Solid-state reactions (some cases)		✓
Solid-gas reactions	✓	✓
Magnetic transitions	✓	✓

Applications of TGA

In Qualitative analysis

Allows a **comparison of thermal stabilities** of the related materials.
Materials Characterization/Purity: fingerprinting of materials for identification / quality control.

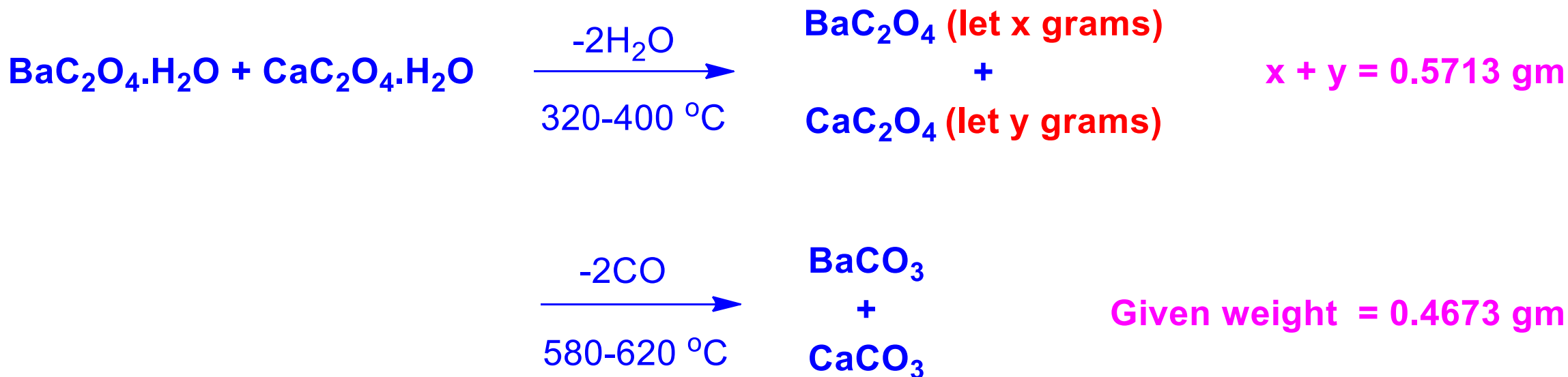## In Quantitative analysis

Compositional analysis: filler content in polymers; carbon black in oils; ash and carbon in coals, and the moisture content of many substances.

Corrosion studies: Study oxidation or some reactions with other reactive gases or vapors.
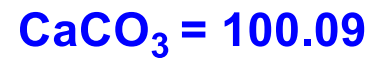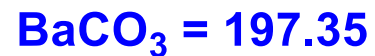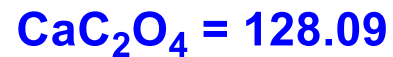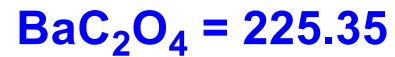
It aims how much of a substance is present in the sample: e.g. how much Ba^{2+} and Ca^{2+} is present in a mixture.

Q. Calcium and Barium ions were precipitated as monohydrated oxalates ($BaC_2O_4.H_2O$ and $CaC_2O_4.H_2O$). 0.6025 sample was taken and subjected to heating rate of 5 °C/min. They left a residue that weighed 0.5713 gm in 320-400 °C range and mass loss in this temperature range corresponds to the combined loss of water by monohydrated oxalate of Ca and Ba. A further loss in mass was observed in the temperature range of 580-620 °C and the left residue of $BaCO_3$ and $CaCO_3$ weighed 0.4673 gm.

Calculate the percentage of Ca^{+2} and Ba^{+2} ions in the sample?

$$BaC_2O_4.H_2O + CaC_2O_4.H_2O \xrightarrow[\text{320-400 °C}]{-2H_2O} \begin{array}{c} BaC_2O_4 \text{ (let x grams)} \\ + \\ CaC_2O_4 \text{ (let y grams)} \end{array} \qquad x + y = 0.5713 \text{ gm}$$

$$\xrightarrow[\text{580-620 °C}]{-2CO} \begin{array}{c} BaCO_3 \\ + \\ CaCO_3 \end{array} \qquad \text{Given weight} = 0.4673 \text{ gm}$$

We know that the molecular weight of

$BaC_2O_4 = 225.35$

$CaC_2O_4 = 128.09$

$BaCO_3 = 197.35$

$CaCO_3 = 100.09$

no. fo moles of BaC_2O_4 = no. of moles of $BaCO_3$
and no. fo moles of CaC_2O_4 = no. of moles of $CaCO_3$

Thus,

$$(x/225.35) \times 197.35 + (y/128.09) \times 100.09 = 0.4673 \quad \text{-------→ (1)}$$

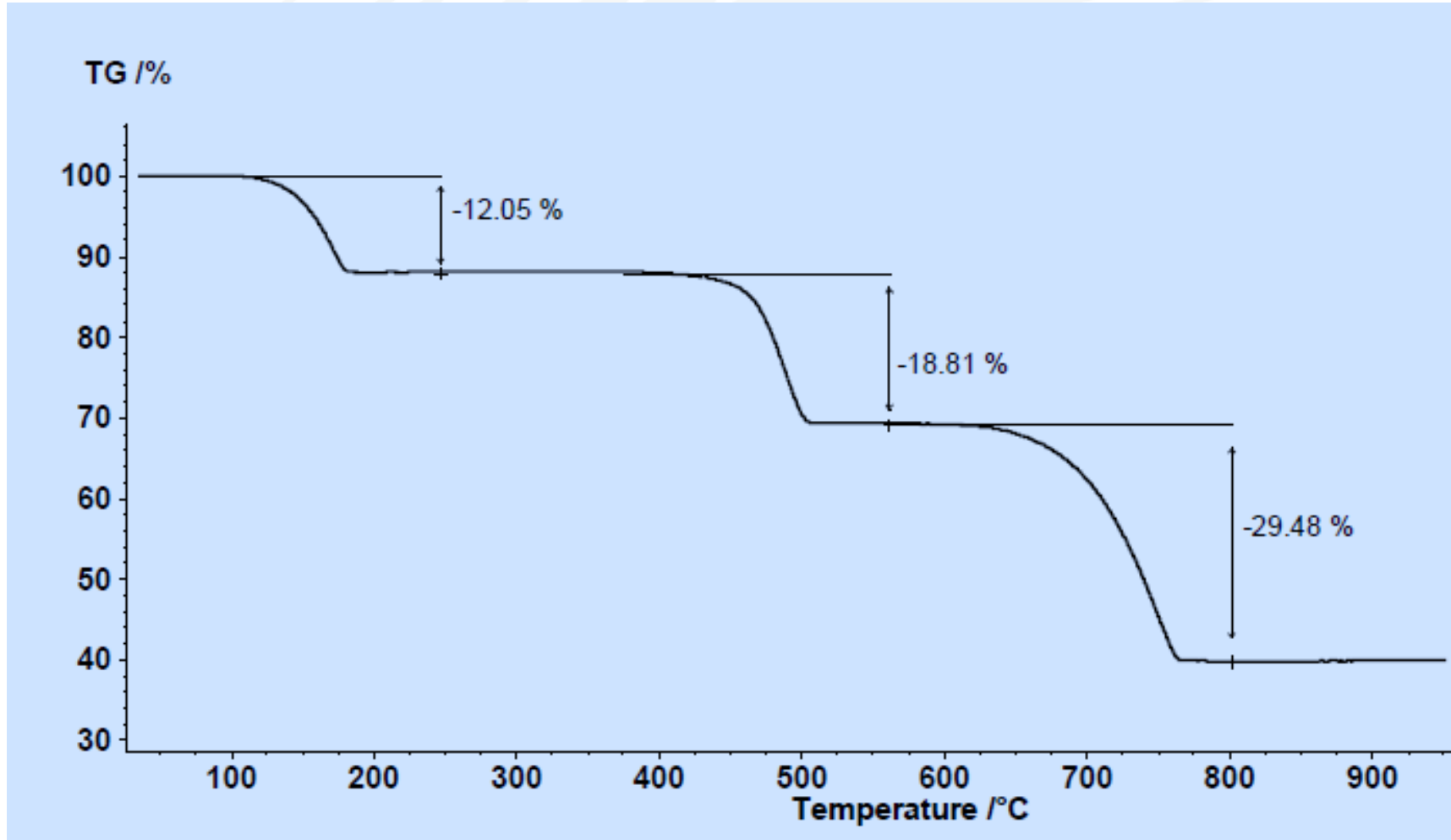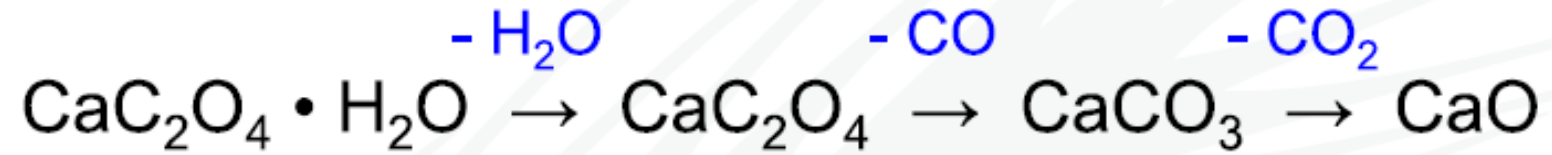$$x + y = 0.5713 \text{ gm} \quad \text{-------------→ (2)}$$

From **1 and 2**:

$x = 0.221389$ gm of BaC_2O_4

$y = 0.34993$ gm of CaC_2O_4

Now, grams of Ba = (137.35 (m.wt. of Ba)/m.wt. of BaC_2O_4) x 0.221389

= 0.13492 gm

Hence the percentage of Ba = (0.13492/0.6025) x 100 = 22.39%

Calcium oxalate monohydrate display three weight loss when heated

$$CaC_2O_4 \cdot H_2O \xrightarrow{-H_2O} CaC_2O_4 \xrightarrow{-CO} CaCO_3 \xrightarrow{-CO_2} CaO$$

Thermogram of calcium oxalate monohydrate

$$Ca(COO)_2 \, H_2O \rightarrow [180°C] \rightarrow Ca(COO)_2 + H_2O \, (g)$$

$$Ca(COO)_2 \rightarrow [480°C] \rightarrow CaCO_3 + CO \, (g)$$

$$CaCO_3 \rightarrow [750°C] \rightarrow CaO + CO_2 \, (g)$$
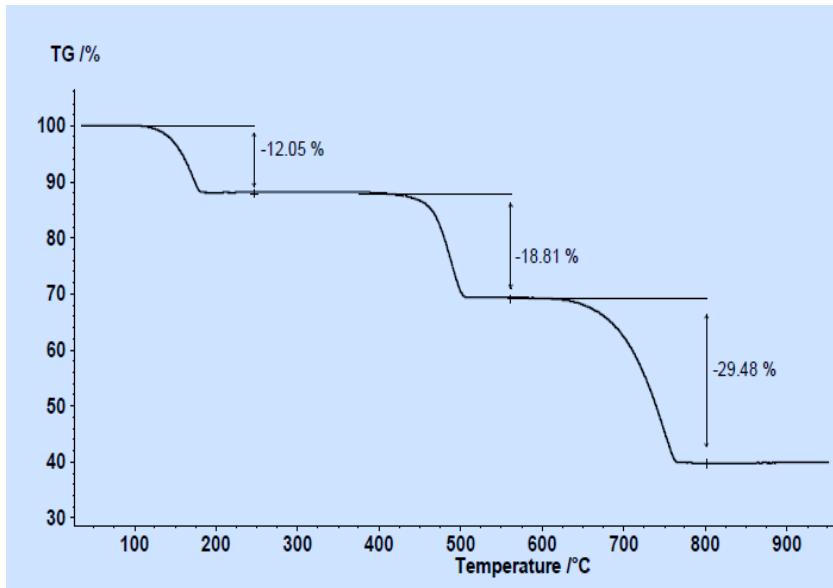
CaCO$_3$ in polyester can be determined by TGA curve as follows:

Decomposition of polyester and removal of volatiles

Liberation of CO$_2$ from CaCO$_3$
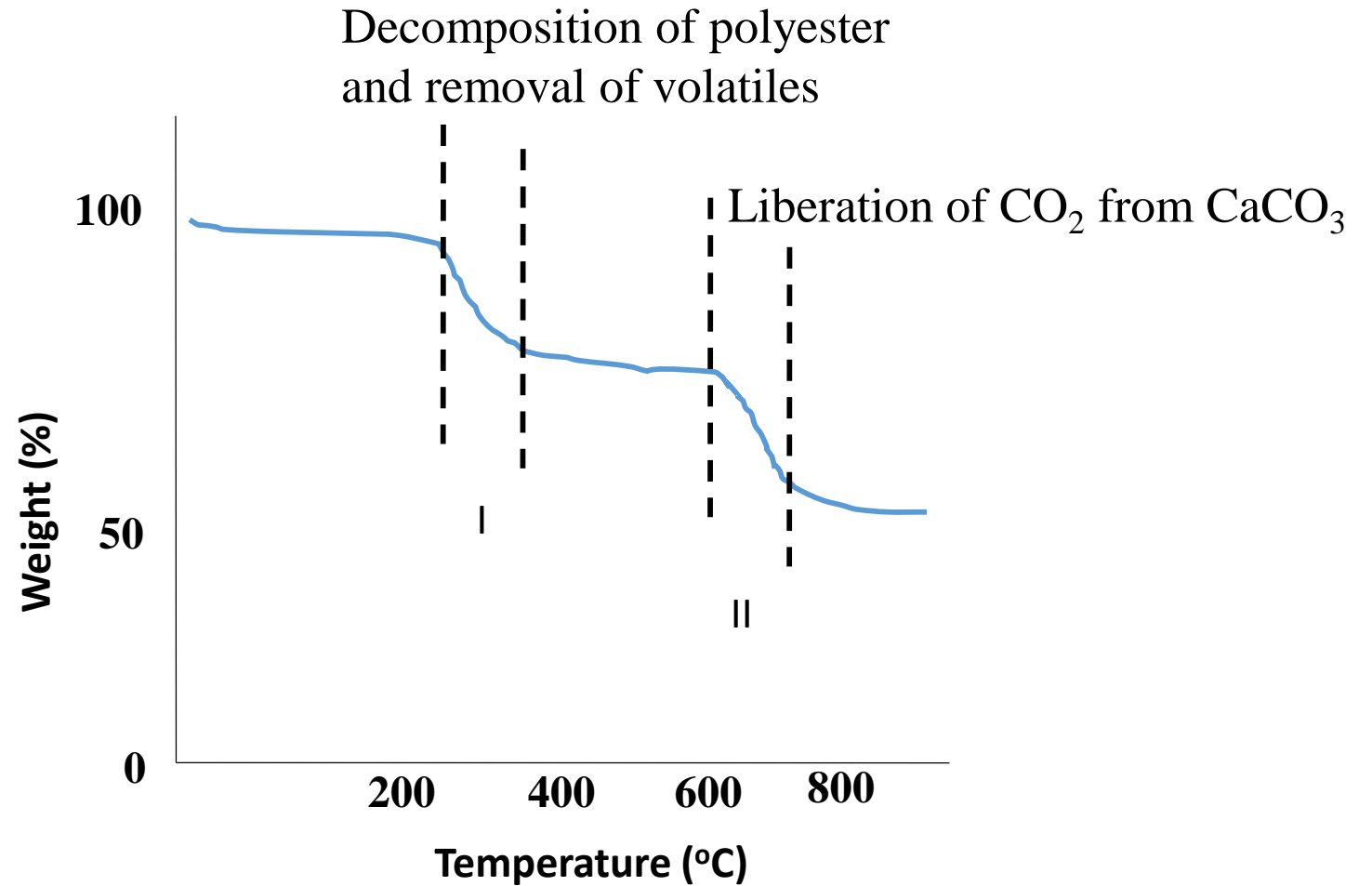
$$\% \text{ of } CaCO_3 = \% \text{ of } CO_2 \frac{\text{molecular weight of CaCO}_3}{\text{molecular weight of CO}_2}$$

Limitations of TGA

For TGA to be useful, only when temperature variation must bring about a change in the mass of analyte.

Thus TGA method is largely limited to decomposition and oxidation reactions and to such physical processes as vaporization, sublimation and desorption.

TGA method cannot be used for

- Pure fusion reactions
- Crystalline transitions

- Glass transition and crystalline temperature of polymer
- Solid state reactions with no volatile products

Rhombic Sulphur $\rightleftharpoons$ Monoclinic Sulphur

Where there is no weight change but absorption or evolution of heat

Derivative Thermogravimetry (DTG)

Plots change in mass with temperature, dm/dt, and resolves changes more clearly
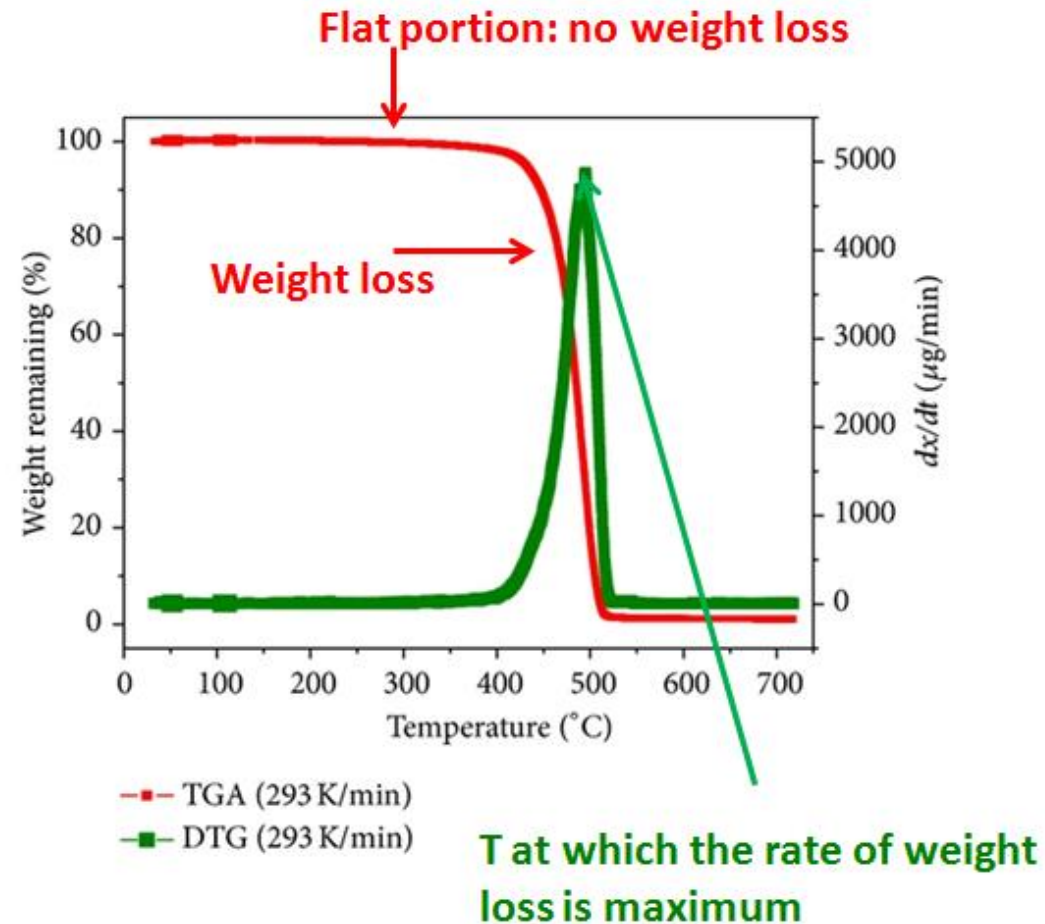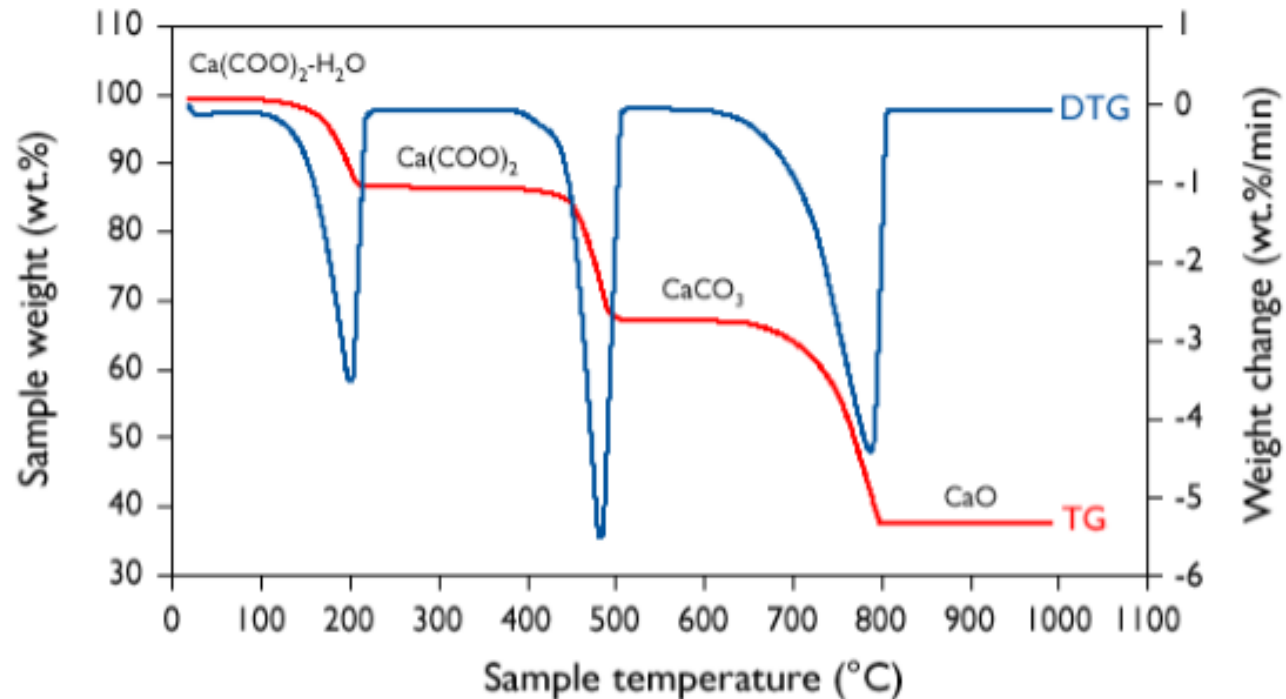
Factors that affect the results

A) INSTRUMENTAL

• Heating rate
• Furnace atmosphere and flow-rate
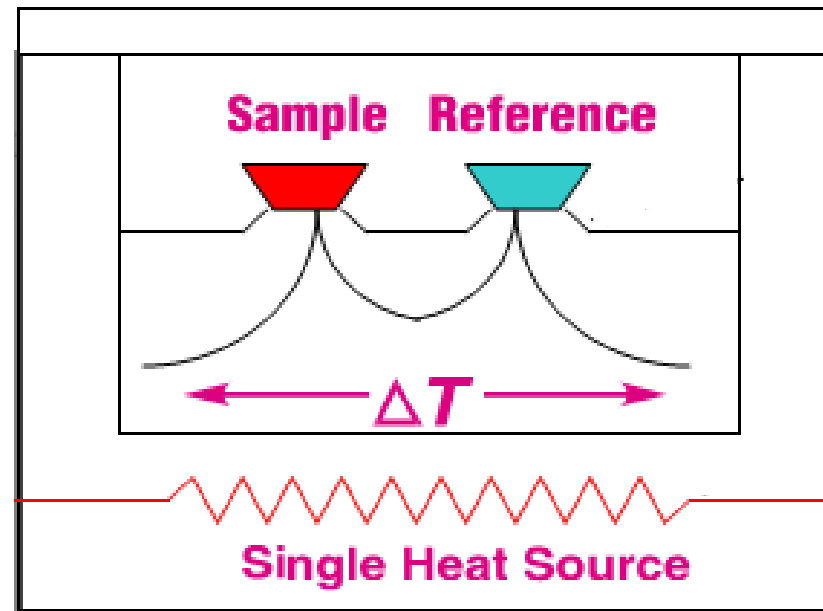• Geometry of pan and material

B) SAMPLE-RELATED

• Mass
• Particle size
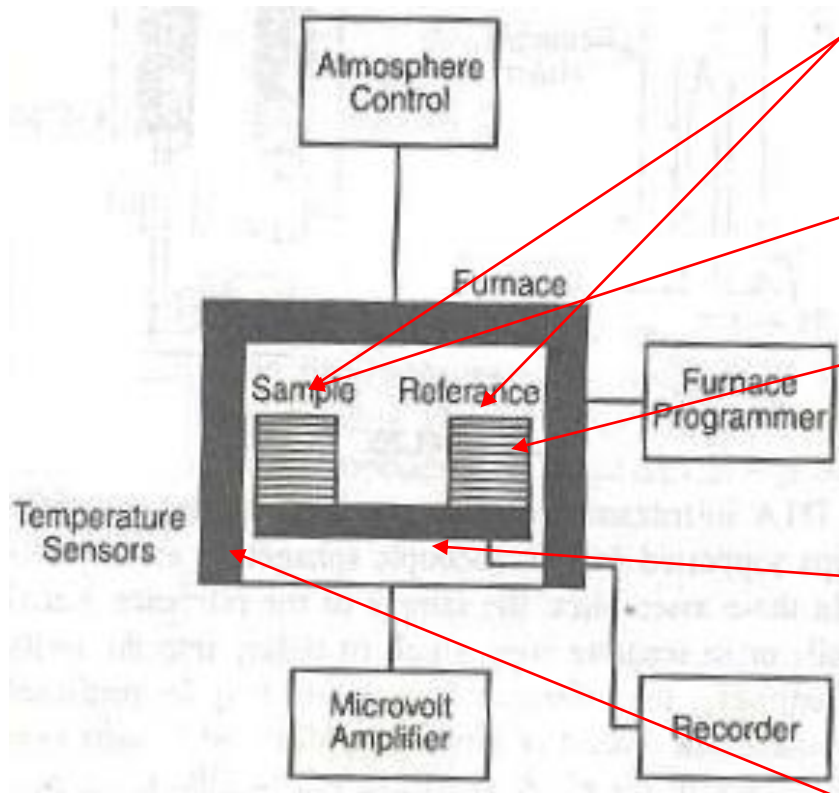• Sample history

TGA & DTG

Differential Thermal Analysis (DTA)

Measures the temperature difference between a sample and an inert reference as a function of temperature while the sample and reference is heated at a constant rate.

Glass transitions, phase changes, and melting points can be measured.

Schematic diagram of a typical DTA system

DTA contain two chambers which are ideal and symmetrical

Sample is placed in one chamber

Thermally inert reference in other (α-alumina)

Two chambers are controlled and connected to the same temperature sensor (usually thermocouple)

The temperature of the furnace and the two chambers are increased linearly at a rate of 5 -12 degree per min.

Temperature difference ($DT = Ts - Tr$) between the sample and reference will be recorded and plotted as a function of Temperature (T/Tr)

# Differential Thermogram: A graph with DT vs. Temp.(T)
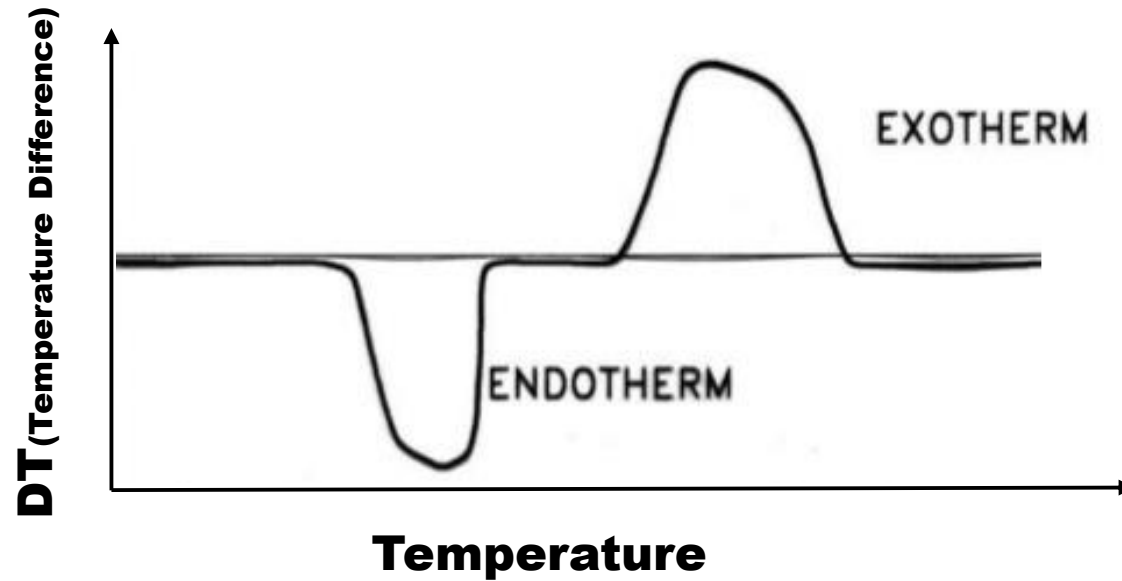
Endothermic changes ,the peaks are below zero; eg: absorption, desorption, sublimation, fusion, vaporization

A good information can be obtained about the nature of the test sample from the shape and sizes of these peaks

Sharp endothermic peaks: Fusion processes or changes in crystallinity

Broad endothermic peak: Dehydration reactions
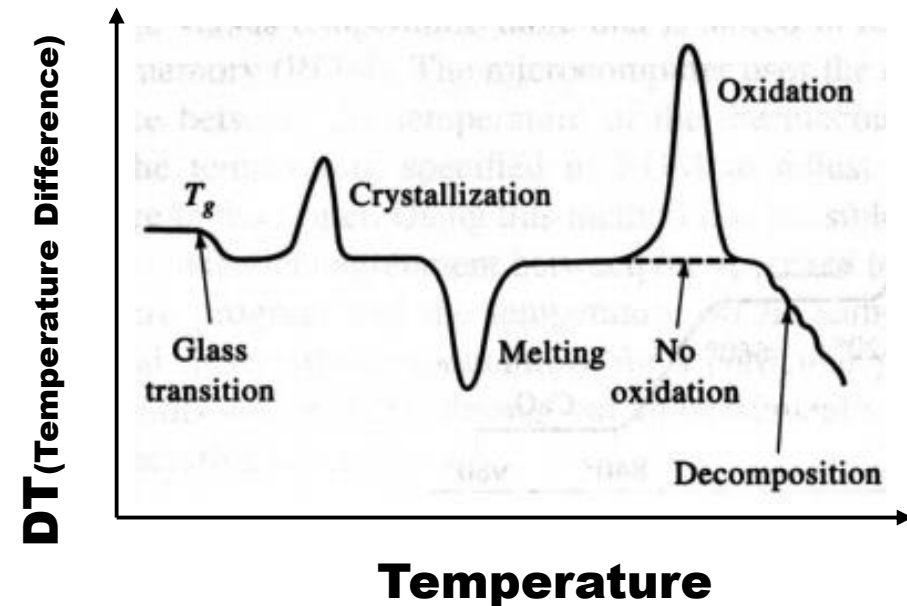
Applications

In Analytical chemistry

- Melting and boiling points and effect of pressure on it

- Identification of the substances (Identification of clays)

In Inorganic chemistry

Thermal stability of inorganic compounds and complexes

In Organic chemistry

Qualitative analysis of polymer
mixture by analyzing the characteristic melting point of each polymer

Differential Scanning Calorimetry (DSC)

DSC is a thermal analysis method where **differences in heat flow into a substance and a reference** are measured as a function of sample **temperature**, while both are subjected to a controlled temperature program.
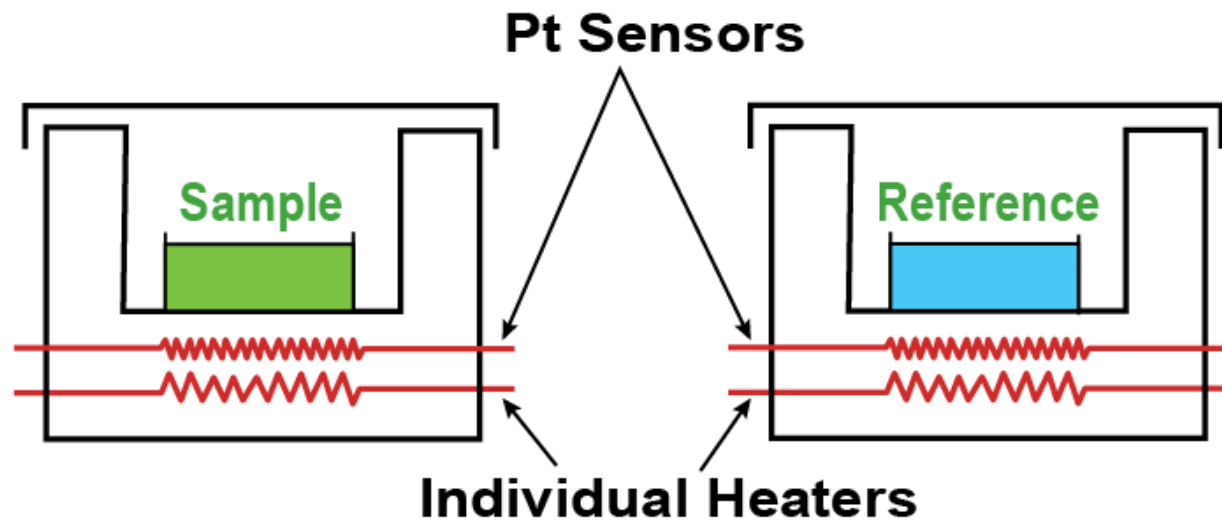
DSC measures the energy (heat) absorbed or released by a sample as a function of temperature or time

$Q = C \Delta T$ where c is the specific heat of the sample

The differences in the amount of heat (Q) required to increase the temperature (ΔT) of a sample and reference are measured as a function of temperature.

The reference sample should have a well defined heat capacity over the range of temperatures to be scanned and analyzed.

The underlying principle of DSC

Both the sample and reference are maintained at nearly the same temperature throughout the experiment.

"When the sample undergoes a physical transformation (phase transitions, etc), more or less heat will be needed to flow to it as compared to the reference to maintain both of them at the same temperature"

Depends on whether the process is exothermic or endothermic

Generally the heat energy supplied to the sample is given a +ve sign.

The heat lost due to endothermic reaction is compensated by this supply

The heat energy supplied to the reference is given –ve sign

The heat gain as a consequence of exothermic reaction in the sample

When a solid sample melts into a liquid

It requires more heat flowing in to the sample to increase its temperature at the same rate as the reference

This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid

Similarly, when the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature

During a phase transition, a temperature difference (heat flux difference) between the sample and reference can be measured by means of a thermocouple
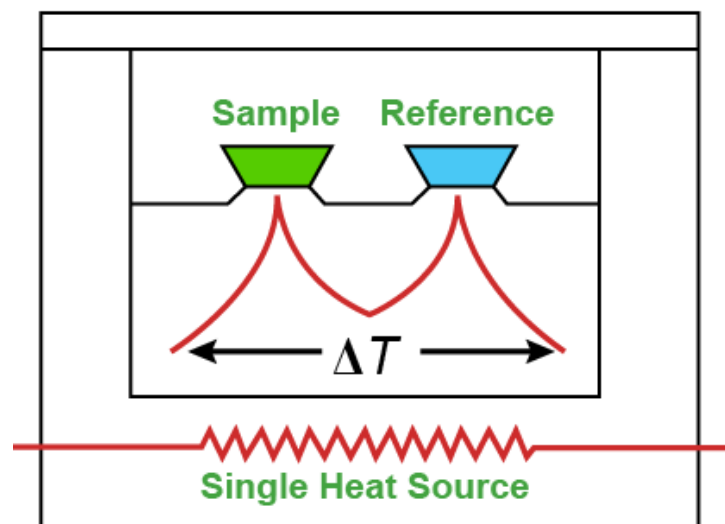
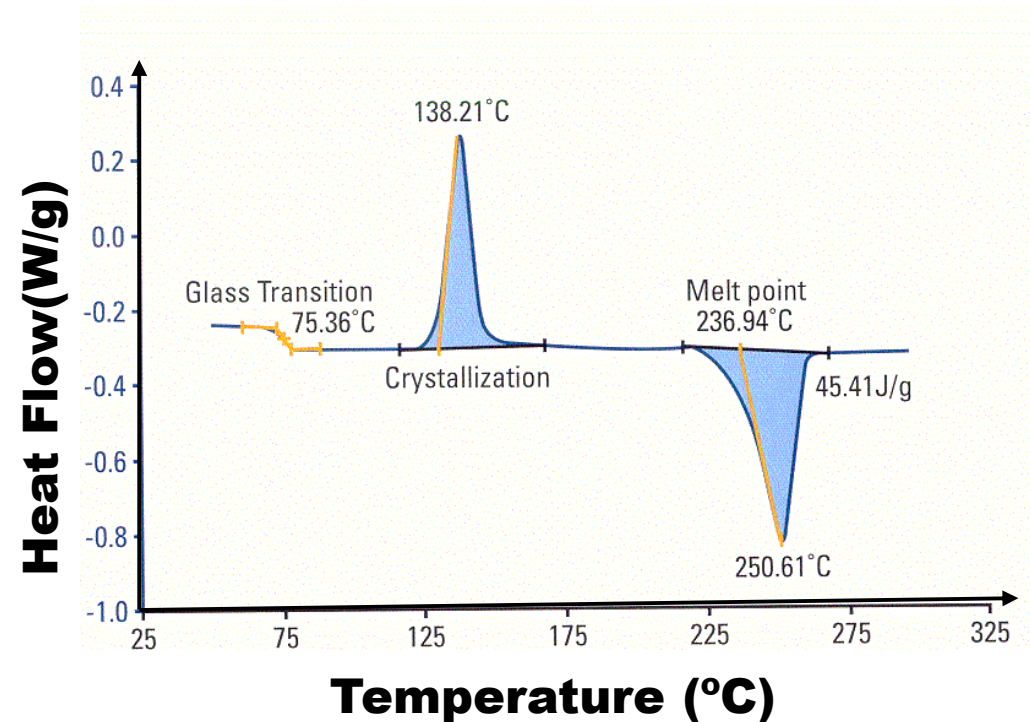**DTA**
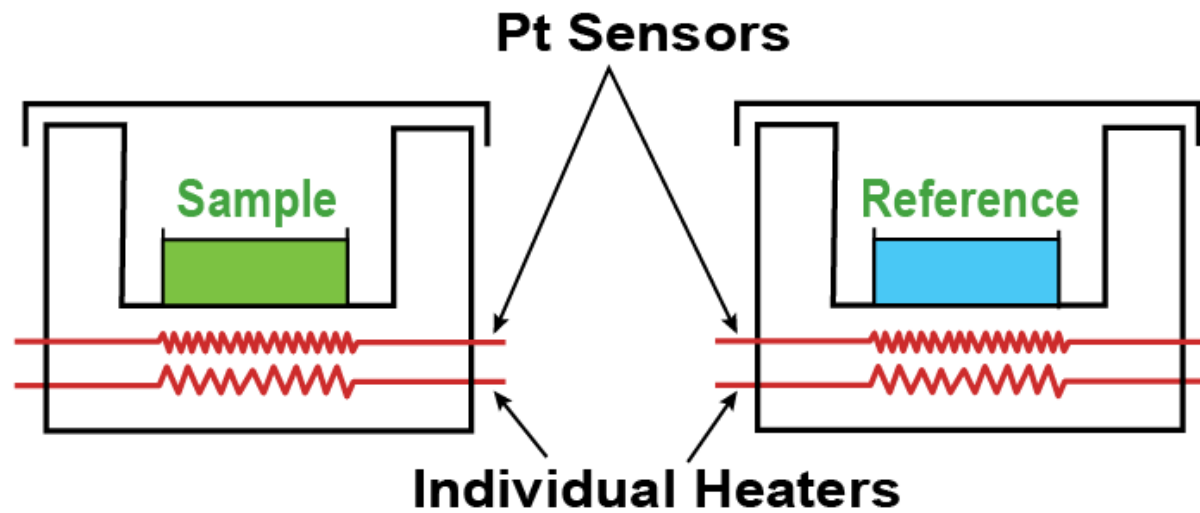
DSC

DSC thermogram

DSC thermogram is similar to DTA

The differences is only with the y axis *i.e, dQ/dt* is plotted Vs temperature

➢ The enthalpy change can be calculated by **integrating the area under the curve**.

Applications of DSC

1. Glass transitions

2. Crystallisation time and temperature

3. Percent crystallinity

4. Heats of fusion and reactions

5. Specific heat capacity

6. Oxidative/thermal stability

7. Rate and degree of cure

8. Reaction kinetics

DTA	DSC
1. Graph : ΔT and T 2. Sample size= 5-20 mg 3. Specific heat measurements are not accurate 4. Calorimetric accuracy in the temperature range of 190-1000 deg c. 5. Secondary power source is not required 6. The area of DTA peak is complex function of sample geometry, heat capacity and heat loses 7. Sensitivity of measurement of heat of transition is 0.5kJ/mole	1. Graph: dH/dt vs T 2. Sample size= 2-10 mg 3. Specific heat measurements are accurate 4. Calorimetric accuracy in the temperature range of 170-750 deg c. 5. Secondary power source is required 6. The area of DSC peak is directly related to the enthalpy change occurring. 7. Sensitivity of measurement of heat of transition is few J/mole

Basic Principle

Technique	Instrument	Parameter Measured	Drawing of the curve
Thermogravimetric Analysis (TGA)	Thermobalance	Mass	Mass vs temperature
Derivative Thermogravimetriy (DTG)	Thermobalance	dm/dT	dm/dT vs temperature
Differential Thermal Analysis (DTA)	DTA Apparatus	ΔT	ΔT vs temperature
Differential Scanning Calorimetry (DSC)	Calorimeter	dH/dt	dH/dt vs temperature