<< THERMAL METHODS OF ANALYSIS >>

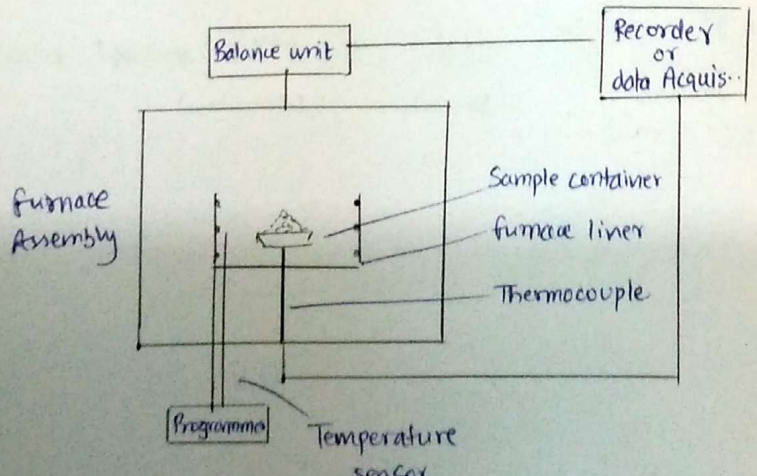
It can be defined as the technique in which change in physical or chemical property of a substance is measured as a function of temperature.

i> Thermogravimetry or Thermogravimetric Analysis (TG/TGA)
ii> Differential thermal Analysis (DTA)
iii> Differential Scanning calorimetry (DSC).

* THEROGRAVIMETRY (TG) OR THERMOGRAVIMETRIC ANALYSIS (TGA)

It is a technique in which change in weight of a substance is measured as a function of temperature. or time.

The basic requirements of a thermogravimetry is a precision balance and furnace Assembly for linear rise of temp. with time. Modern thermobalances are computer-controlled and can attain almost any temperature profile. Samples are placed in shallow platinum crucible (sample container) which is connected to a automatic reading microbalance. The most usual type of balance-system is null-point balance system. As there is any change in weight of sample, the needle deflects from its usual position. This deflection is detected by a sensor and a force acts which pulls the needle back to its usual position. The restoring force is proportional to change in weight.



main components of thermobalance

The TG curve for $CuSO_4 \cdot 5H_2O$ is shown in fig.

i> Horizontal portion signifies regions of no weight loss.

ii> Curve portion signifies regions of weight loss.

The four decomposition rxn are :

$CuSO_4 \cdot 5H_2O$	$\longrightarrow$	$CuSO_4 \cdot H_2O + 4H_2O$.	90 - 150°C
$CuSO_4 \cdot H_2O$	$\longrightarrow$	$CuSO_4$	200 - 275°C
$CuSO_4$	$\longrightarrow$	$CuO + SO_2 + \frac{1}{2}O_2$	700 - 900°C
$2CuO$	$\longrightarrow$	$Cu_2O + \frac{1}{2}O_2$	1000 - 1100°C

The weight is due to decomposition of sample at higher temperature.
↳ loss.

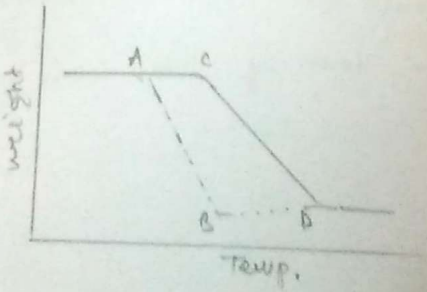
The DTG curve is shown in fig 4.

* The region of no - weight loss signifies $dw/dT = 0$.
* The peak in DTG curve represents maximum slope point on TG curve.
* In regions B and C, there is change in slope of weight loss - curve, these are called inflexion points.
* Inflexion at B arises due to formation of $CuSO_4 \cdot 3H_2O$
* Inflexion at C arises due to formation of $2CuO \cdot SO_3$.

* FACTORS INFLUENCING THERMOGRAVIMETRY RESULTS.

i> Heating rate: When a substance is heated at a faster rate, the temperature of decomposition will be higher than that obtained at a slower rate of heating. For a single-step rxn, decomposition curve is shown.

AB = slower rate curve
CD = faster rate curve



$T_A < T_C$

$T_B < T_D$

$(T_A - T_B) < T_D - T_C$.

where T_A & T_C are Temperatures at starting of decomposition

* Heating rate has less effect for fast reversible rxn.
* The detection of intermediate compounds by TG is very dependent upon heating rate employed.

ii> furnace Temperature : The nature of atmosphere arround the sample [Furnace Atmosphere] have a huge impact on decomposition temperature.

eg: The decomposition of $CaCO_3$ occurs at much higher rate if carbon is used as atmosphere rather than nitrogen.

The function of atmosphere is to remove the gas products obtained so that the atmosphere throughout the experiment remains as constant as possible. Mostly, vacuum is used.

* Three types of mostly used atmospheres :

i> Static air : Air from sorrounding flows through furnace.

ii> Dynamic air : Compressed air from cylinders is passed through furnace.

iii> Nitrogen gas : Oxygen free- nitrogen gas provides inert atmosphere.

NOTE : Sample container should be made up of inert material. eg Platinum, Al.

iii> Crucible Geometry : The shape of crucible can vary the slope of TG curve 'flat - plate shaped' are preferred as diffusion of gases evolved is easier.

iv> Sample Characteristics : The weight, particle size of mode of preparation all alters the TG results. A large volume of sample can impede (hinder / obstruct) the diffusion of gases evolved. It is better to have small volume of sample and a small particle size.

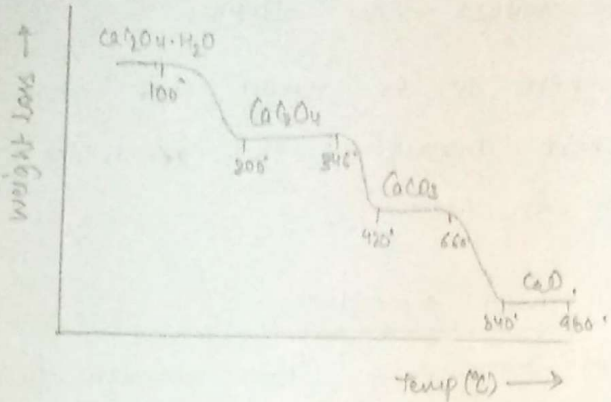
NOTE : Naturally occuring $Mg(OH)_2$ has diff. decomposition Temperature than precipitated $Mg(OH)_2$.

* APPLICATIONS OF & TGA :

i> determination of purity and chemical stability of primary and secondary standards.

ii> Investigating daying temperatures: many primary standards absorbs water, when exposed in moist air and hence using TGA technique, we can find extent of absorption from which most suitable drying Temperature can be determined.

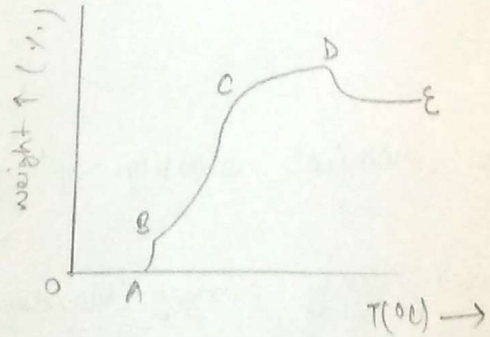
iii> in qualitative analysis: Any thermogram is a characteristic for a given. Fig. shows TG curve of $CaC_2O_4 \cdot H_2O$ heated at a rate of 5°C/min.



It is thermally stable upto 1000°C and loses water beyond 100°C. So, CaC_2O_4 is formed which is stable in range 200°C → 346°C. At slightly above 346°C, it starts losing CO and $CaCO_3$ is formed which is stable in range 420°C → 660°. Beyond 650°, CO_2 is released and $CaCO_3O$ formed is stable with in range 840° & 980°C only.

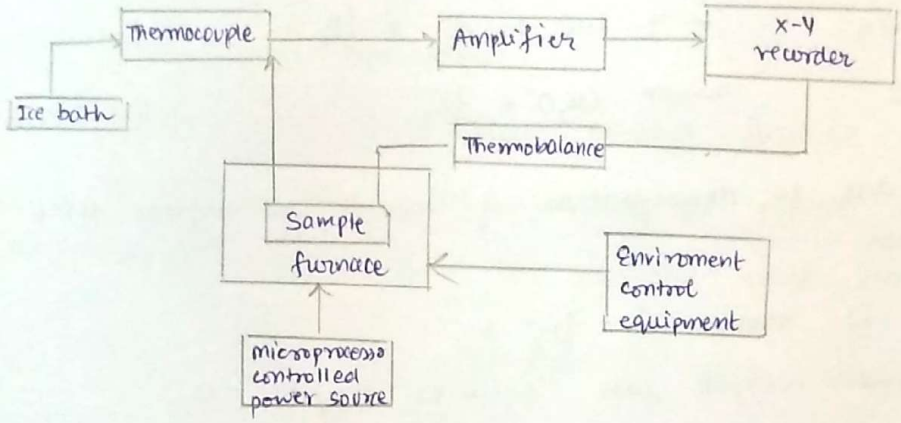
iv> in study of polymers: It has great application as it gives valuable information about decomposition mechanism of polymers. As polymers have unique pattern, so, it is also used for identification purpose. It is used in examining thermal stability of polymers. Using DTG curve, max. weight change temp. can be determined which is used to distinguish between them.

v> in study of oxidation of alloys:



oxidation of Co_5Sm by TG in air atmosphere is carried & following curve ~~was~~ is obtained. AB represents oxidation of Sm → Sm_2O_3 & BC represents ox^n of Co → Co_3O_4 and mix compound formation $CoSmO_3$. DE represents conversion of Co_3O_4 → CoO.

The sample container is placed in quartz or pyrex glass within furnace. A thermocouple (A thermoelectric device used to measure temperature & it consists of two metal wires) is located below sample container. The resulting signal is connected directly to x-axis of recorder.



• Block diagram of TGA.

* Characteristics of Good Thermobalance designs.

i> It should be capable of continuously registering weight change of sample.

ii> It should reach maximum desirable Temp. (−150 → 2400°C can be obtained with modern thermobalances).

iii> The rate of heating is linear and reproducible.

iv> The sample holder should be in hot zone of furnace and this hot zone should have uniform temperature.

v> The temperature of sample must be measured accurately.

* Methods of expressing TG Results:

The results can be expressed in form of TG curve or DTG curve.