

Thermogravimetric Analysis (TGA)

Introduction:-

Definition:

“It is technique whereby the weight of substance, in an environment heated or cooled at a controlled rate is recorded as a function of time or temperature.”

“Thermogravimetry (TG) is the branch of thermal analysis which examines the mass change of a sample as a function of temperature (in the scanning mode) or as a function of time (in the isothermal mode).”

“Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss)”

Principle:

- Changes in the mass of a sample are studied while the sample is subjected to a program.
- Changes in temperature affect the sample. Not all thermal changes/events bring a change in mass of sample i.e. melting, crystallization but some thermal events i.e. desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition bring a drastic change in mass of sample.
- It is used in analysis of volatile products, gaseous products lost during the reaction in thermoplastics, thermosets, elastomers, composites, films, fibers, coatings, paints, etc.

Description:

It is a technique which is studied under thermal analysis and is employed for detection of such type of materials which undergo mass change (gain or loss) when subjected to thermal events viz. decomposition, oxidation, reduction, etc. Hence, it is used to analyze the decomposition, thermal stability and kinetics of materials under a variety of conditions taking place in the sample. For this reason, it is very significant to optimize those conditions/factors on which the change of mass of sample depend throughout the operation/experiment. Conditions/factors such as sample mass, volume, physical form, shape and nature of the sample holder, nature and pressure of the atmosphere in the sample chamber and the scanning rate greatly influence the recordings.

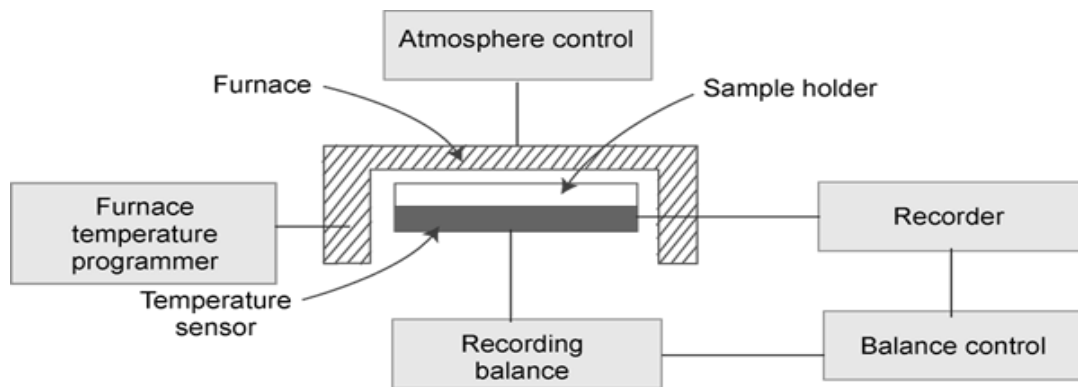
Types of TGA:

There are three types of thermogravimetry:

- 1. Dynamic TGA:** In this type of analysis, the sample is subjected to condition of continuous increase in temperature usually linear with time.
- 2. Isothermal or Static TGA:** In this type of analysis, sample is maintained at a constant temperature for a period of time during which change in weight is recorded.
- 3. Quasi-static TGA:** In this technique sample is heated to a constant weight at each of a series of increasing temperature.

Recording Of Result:

The instrument used for themogravimetry is a programmed precision balance for rise in temperature known as Thermobalance.



Results are displayed by a plot of mass change versus temperature or time and are known as Thermogravimetric curves or TG curves. TG curves are normally plotted with the mass change (Dm) in percentage on the y-axis and temperature (T) or time (t) on the x-axis. A typical TG curve has been shown (Figure 1). There are two temperatures in the reaction, T_i (procedural decomposition temp.) and T_f (final temp.) representing the lowest temperature at which the onset of a mass change is seen and the lowest temperature at which the process has been completed respectively. The reaction temperature and interval ($T_f - T_i$) depend on the experimental condition; therefore, they do not have any fixed value.

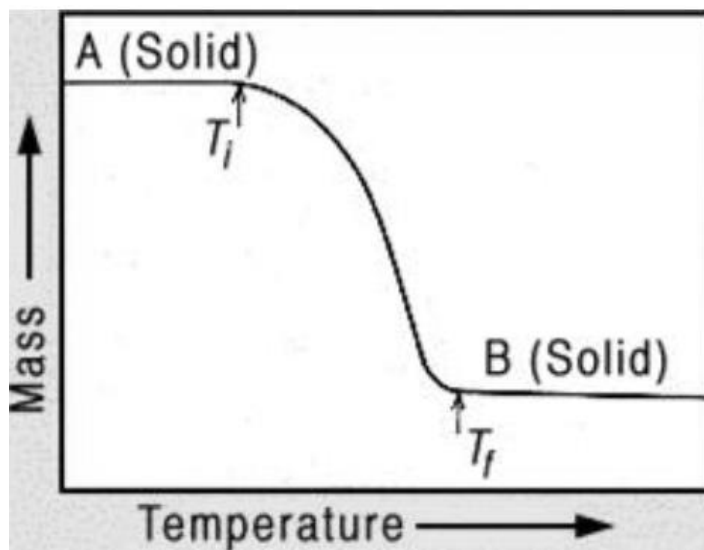


Fig.1.Characteristics of a single-stage mass-loss curve

Interpretation of TG Curves:

Types of TG Curves (Figure 2):

TG curves are classified according to their shapes into seven types.

Type A- this curves shows no mass change over the entire range of temperature. It can be concluded that the decomposition temperature for sample is greater than the temperature range of instrument.

Type B- this curves shows that there is large mass loss followed by mass plateau and is formed when evaporation of volatile product(s) during drying, desorption or polymerization takes place. If a non-interacting atmosphere is present in the chamber, type B curve will change into type A curve.

Type C- this curve shows the single-stage decomposition temperatures (T_i and T_f).

Type D- this curve shows the multi-stage decomposition processes where reaction is resolved.

Type E- this curve shows the multi-stage decomposition reaction where reaction is not resolved.

Type F- this curve shows the increase in mass in the presence of an interacting atmosphere e.g. surface oxidation reactions.

Type G- this curve shows multiple reactions one after the other e.g. surface oxidation reaction followed by decomposition of reaction product(s).

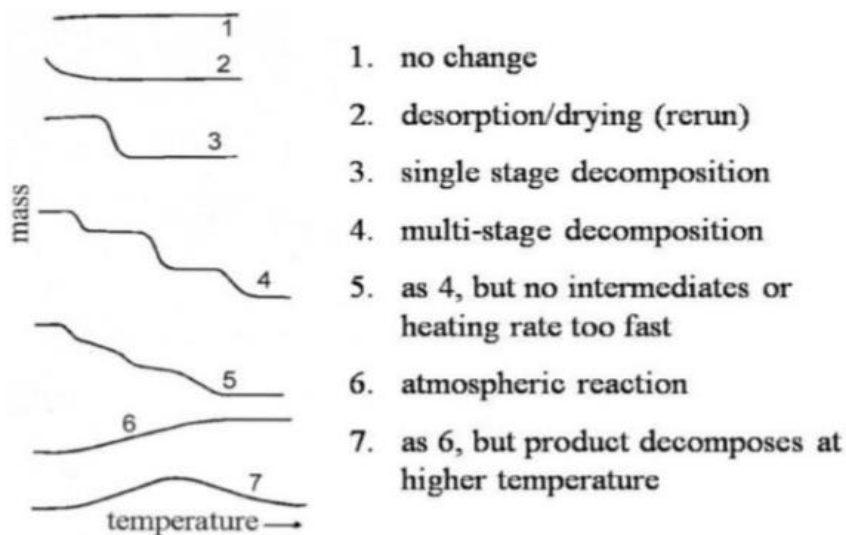


Fig.2. Classification of TG Curves

Plateau:

A plateau (AB, Fig.3.) is that part of the TG curve where the mass is essentially constant or there is no change in mass.

Procedural Decomposition Temperature:

The initial temperature, T_i , (B, Fig.3.) is that temperature (in Celsius or Kelvin) at which the cumulative-mass change reaches a magnitude that the thermobalance can detect.

Final Temperature:

The final temperature, T_f , (C, Fig.3.), is that temperature (in Celsius or Kelvin) at which the cumulative mass change reaches a maximum.

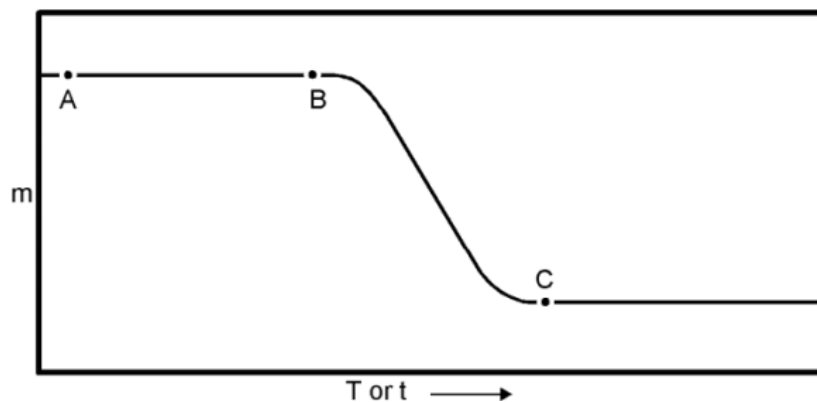


Fig.3. Formalized TG Curve

Reaction Interval:

The reaction interval is the temperature difference between T_f and T_i .

Isobaric Mass-change Determination:

A technique in which the equilibrium mass of a substance at constant partial pressure of the volatile product(s), is measured as a function of temperature while the substance is subjected to a controlled temperature program. The record is the isobaric mass-change curve; the mass is plotted on Y-axis and temperature on X-axis increasing from left to right.

Evolved Gas Detection (EGD):

A technique in which the evolution of gas from a substance is detected as a function of temperature while the substance is subjected to a controlled temperature program.

Evolved Gas Analysis (EGA):

A technique in which the nature and/or amount of volatile product(s) released by a substance are/is measured as a function of temperature while the substance is subjected to a controlled temperature program. The method of analysis should always be clearly stated.

Information from TG Curve:

The plot of weight/mass against temperature or time produced by a thermogravimeter is called Thermogram. The following features of TG curve should be noted from Figure 1 or 3.

Plateau: a region of no mass change indicates the thermal stability of the sample/substance.

Thermal stability is the ability of a substance to maintain its properties as nearly unchanged as possible on heat. This information about thermal stability is significant for engineers as they then know the temperature ranges of in which substances like alloy, building materials, polymers, etc. can be used.

Weight/Mass Loss: heating a sample to given temperature causes it to lose weight/mass.

Mass/weight loss is informative to inorganic chemist who can then determine the composition of substance/sample and understand the reaction involved in decomposition.

Procedural Decomposition Temperature: by looking at thermogram, one can determine the procedural decomposition temperature (T_i) indicating the decomposition or evaporation of sample/substance.

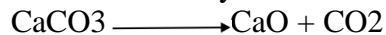
Composition: weight/mass lost by heating helps determine the composition of substance/sample, also allow analytical chemists to identify unknown compound or determine the amount/percentage/weight of a compound in mixture of different compounds.

Example of determination of weight:

Before analyzing the sample, we must preview the information related to sample. Let us take the example of CaCO_3 . The information we knew about our sample is:

i. It is hygroscopic (it absorbs or attracts moisture from the air).

ii. Upon heating calcium carbonate it undergoes a reaction in which CO_2 is released from the material and only calcium oxide remains after the experiment.



iii. Calculating the weight:

Done by substituting the atomic mass in the formula.



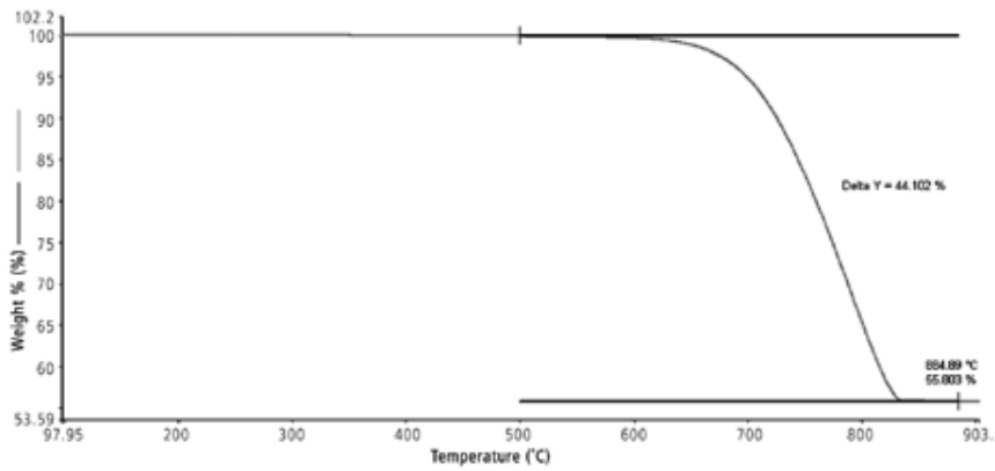


Fig.4. TG Curve Showing the Atomic Mass of CaCO₃

Where: Ca = 40.08 atomic mass units (amu)

C = 12.011 amu

O = 15.9994 amu

Ca + C + O₃

(40.1) + (12.0) + [(16) x (3)]

CaCO₃ → CaO + CO₂

100.1 [(40.1) + (16)] + [(12.0) + (16) x (2)]

100.1 (56.1) + (44)

(100.1) (100.1) amu

The measured values are almost equal to the calculated values. The Delta Y Software calculation was used to measure the “TG-run” (Table 1). Therefore, it is clearly mentioned that the sample we are using is very pure. **Table 1**

Component	Expected/Calculated Values	Measured Value
CaO	56.1 amu	55.803 amu
CO ₂	44 amu	44.102 amu

Extrapolated onset temperature that denotes the temperature at which the weight loss begins can also be calculated. We use the extrapolated onset Temperature (T_o) because it is a reproducible temperature calculation.

The extrapolated onset Temperature is 704.69 °C. The next calculation that is useful and finalizes the characterization of calcium carbonate is the peak calculation derived at first weight loss curve. The first derivative curve is displayed by Delta Y Software. The first derivative peak temperature (T_p) is 789.03 °C. The peak of the first derivative indicates the point of greatest rate of change on the weight loss curve. This is also known as the inflection point.

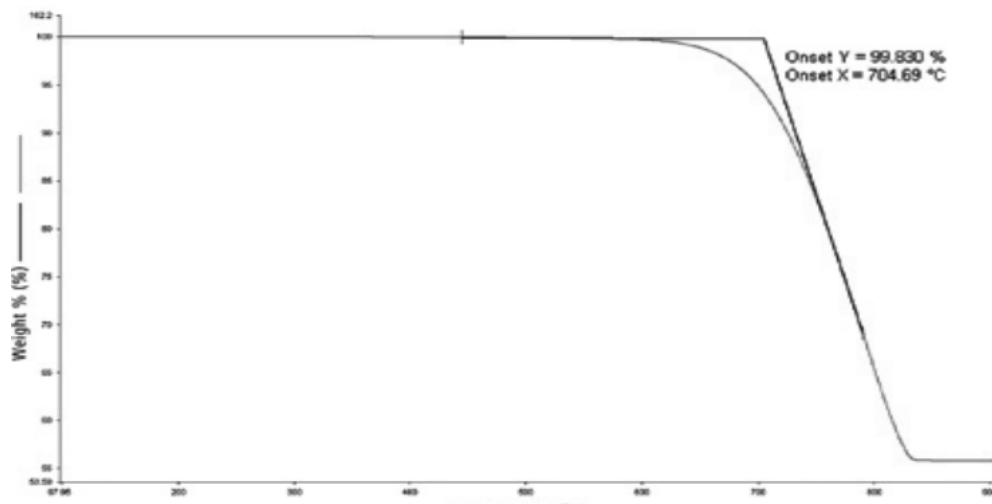


Fig.5. TG Curve showing Temperature Changes Associated with Thermal Events occurring to CaCO₃

Process	Weight gain	Weight loss
Ad- or absorption	√	
Desorption, drying		√
Dehydration, desalvation		√
Sublimation		√
Vaporization		√
Decomposition		√
Solid state reaction		√
Solid gas reaction	√	√
Megnatic transition	√	√

2.10. Processes that Leads to Weight Gain And Loss In TGA Experiment: Second example of determination of constituents and mass of Chewing Gum:

Analysis of Chewing Gum with Auto Stepwise TGA:

Chewing gum is a complex mixture of a number of components, including natural elastomers, glycerin, softening agents, and carbonates, flavoring agents, sweeteners and colorants because of which stickiness, softness and chew ability is present. Sample is heated at a constant rate until a weight loss takes place. Heating is automatically resumed, at a constant rate, until the next significant weight loss event. By this process, we are able to determine decomposition events and provide quantitative analysis of a sample (Figure 6 & 7).

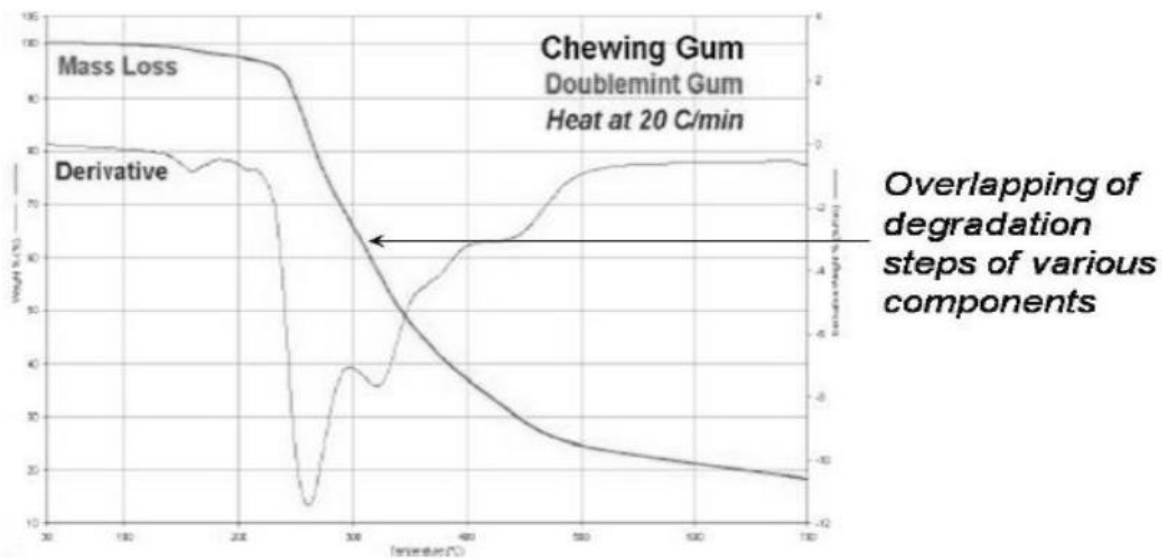


Fig.6. Standard TGA Result Doublemint Chewing Gum Sample

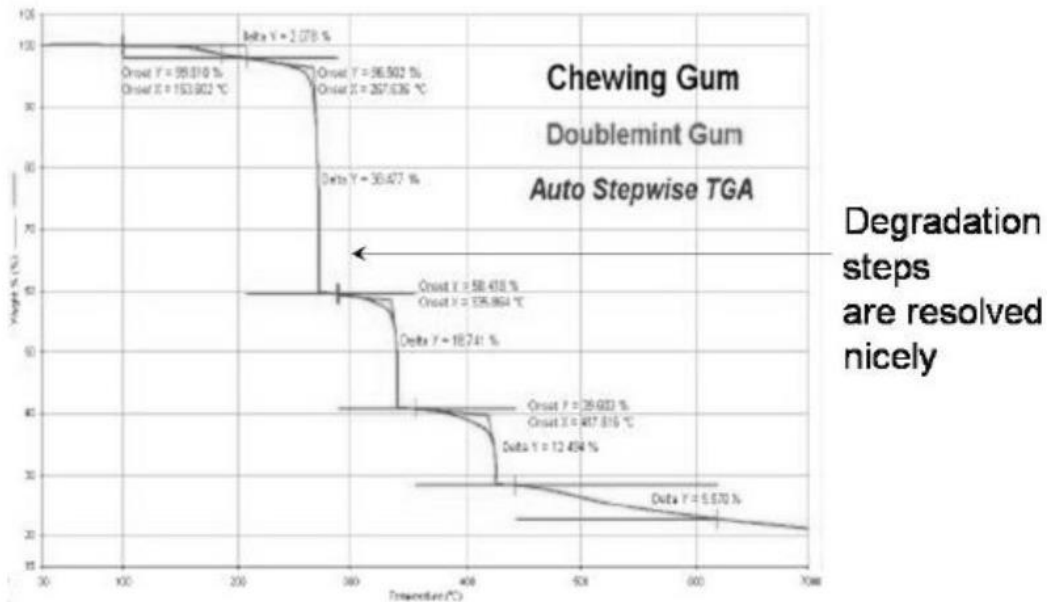


Fig.7. TGA Auto step wise Result for Doublemint Chewing Gum Sample.

Instrumentation of Thermogravimetry:

TG curves are recorded using a Thermobalance. It consists of an electronic microbalance, a furnace, a temperature programmer and a recorder (instrument connected to thermobalance to record the output/curves (Figure 8 & 9).

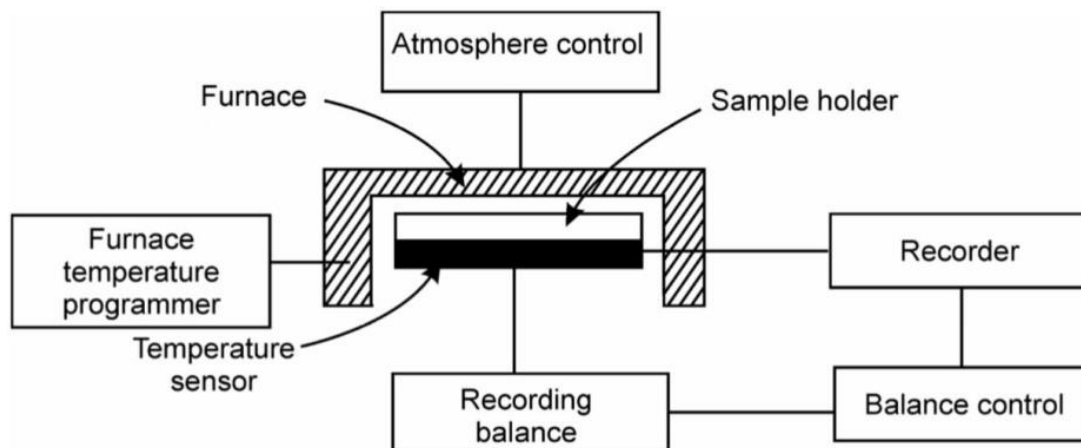


Fig.8. Block Diagram of a Thermobalance



Fig.9. A TGA Instrument

Microbalance:

It is the most important component of thermobalance. A microbalance is used to record a change in mass of sample/substance. There are different types of microbalances viz. beam, spring, cantilever and torsion balances. An ideal microbalance must possess following features:

- a.** It should accurately and reproducibly record the change in mass of sample in wide ranges of atmospheric conditions and temperatures.
- b.** It should provide electronic signals to record the change in mass using a recorder.
- c.** The electronic signals should provide rapid response to change in mass.
- d.** It should have the capacity of auto-weight/mass adjustment.
- e.** It should be stable at high ranges, mechanically and electrically.
- f.** Modern microbalances have the ability to be not affected by vibrations.
- g.** Its operating should be user friendly.

The thermobalance has a clamp which is used to hold the microbalance arm. The balance must return to zero after releasing the clamp. The transportation of thermobalance is not preferred by holding it with clamps as it has effect on zero point. After the sample has been placed on

microbalance, it is left for 10-15 min to stabilize.

Recorder balances are of two types: Deflection-type instruments and Null-type instruments.

Deflection Balances: They are of following types (Figure 10):

i. Beam Type- in these balances, the conversion of deflected beams takes place into the weight change. The curves formed are identified by the help of photographic recorded trace, signals generated by displacement-measuring transducers or electromechanically.

ii. Helical Type- in these balances, elongation or contraction of spring occurs with change in weight which is recorded by the help of transducers.

iii. Cantilevered Beam- in these balances, one end of beam is fixed and on other end sample is placed. It undergoes deflection which can be recorded by the help of photographic recorded trace, signals generated by displacement-measuring transducers or electromechanically.

iv. Torsion Wire- in these balances, the beam is attached to hard torsion wire which acts as fulcrum. The wire is attached to one or both ends of balance to make the deflection of beam proportional to weight changes, which can be detected by the help of photographic recorded trace, signals generated by displacement-measuring transducers or electromechanically.

Null-Point Balances (Figure 11):

It consists of a sensor which detects the deviation from the null point and restores the balance to its null point by means of a restoring force.

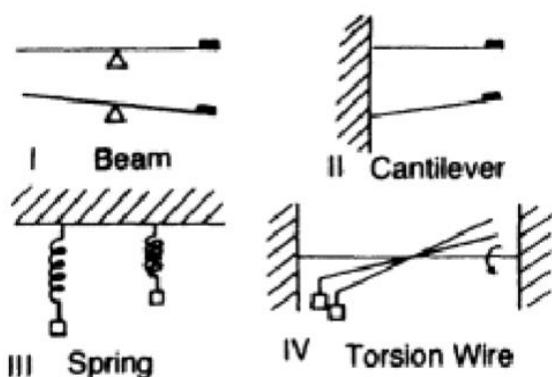


Fig.10. Different Types of Deflection Balances

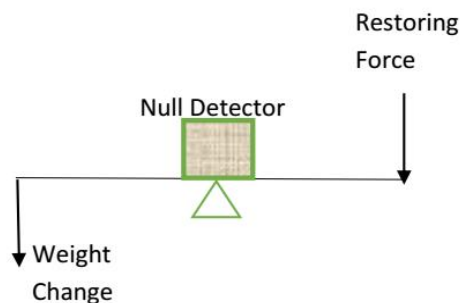


Fig.11. Null Type balance

Sample Holder or Crucible:

The sample to be studied is placed in sample holder or crucible. It is attached to the weighing arm of microbalance. There are different varieties of crucibles used. Some differ in shape and size while some differ in materials used (Figure 12). They are made from platinum, aluminum, quartz or alumina and some other materials like graphite, stainless steel, glass, etc. Crucibles should have temperature at least 100 K greater than temperature range of experiment and must transfer heat uniformly to sample. Therefore, the shape, thermal conductivity and thermal mass of crucibles are important which depends on the weight and nature of sample and temperature ranges. There are different types of crucibles. They are;

Shallow Pans:

These are used for such samples in which diffusion is the rate controlling step. Volatile substances produced during reaction must escape out which is determined as weight loss. In some sample i.e. polymers, byproducts may form, therefore, the sample is placed after forming a thin layer of it so that as soon as volatile substance is formed, it will escape.

Deep Crucibles:

These are used in such cases where side reactions are required such as in study of

industrial scale calcinations, surface area measurements, etc.

Loosely covered Crucibles:

These are used in self-generated atmospheric studies. Rate of temperature or weight loss is not important because the studies are done isothermally.

Retort Cups:

These are used in boiling point studies. It provides single plat of reflux for a boiling point determination.

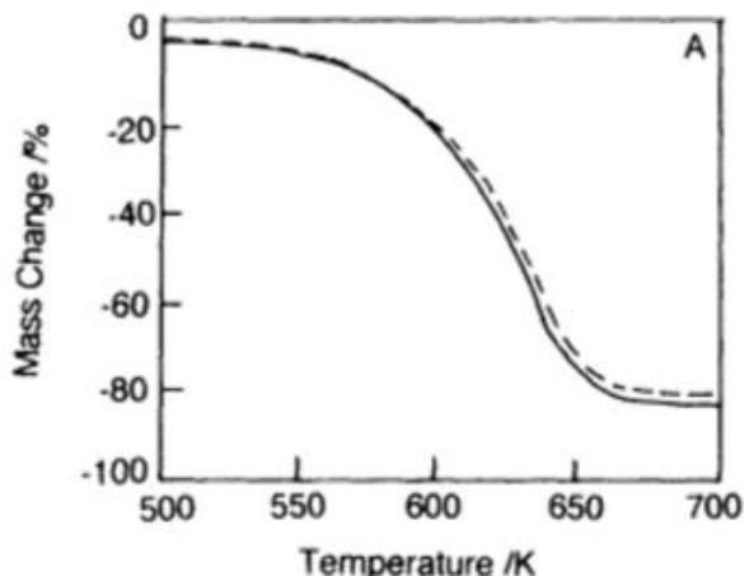


Fig.12. Effect of crucible thermal mass on the TG curves of powdered PMMA. Solid line, aluminium crucible

Different types of crucibles are used for different materials i.e. Flat crucibles with small lip are used for powdered sample whereas walled crucibles are used for liquid samples. Therefore, the form of crucibles used will determine the temperature gradients in sample. An example for change temperature change has been presented (Figure 13). TG curves recorded poly methyl methacrylate (PMMA) in a normal aluminium crucible and in aluminium crucible with an aluminium disc fitted at bottom to increase the thermal mass. The shapes and residue rates of curves are different. The temperature at which the rate of mass loss, is maximum increased by 5 K in crucible of greater thermal mass. A regular cleaning of crucible is required which can be done with methanol and pre-heating the crucible to its maximum temperature.

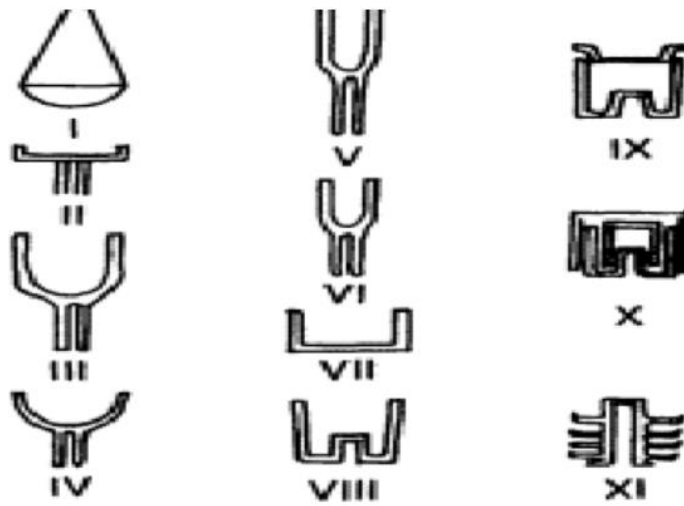


Fig.13. Different Types of Crucibles Used In TGA

Furnace (Heater/Boiler/Oven):

The furnace should be designed in such a way that it produces a linear heating range. It should have a hot zone which can hold sample and crucible and its temperature corresponds to the temperature of furnace. The temperature ranges can affect the internal atmosphere of furnace chamber; therefore, it is necessary to choose specific type of furnace according to temperature ranges. There are different combinations of microbalance and furnace available. The furnace heating coil should be wound in such a way that there is no magnetic interaction between coil and sample or there can cause apparent mass change. Coils used are made of different materials with variant temperature changes viz. Nichrome wire or ribbon for $T < 1300$ K, Platinum for $T > 1300$ K, Platinum-10% rhodium Alloy for $T < 1800$ K and Silicon Carbide for $T < 1800$ K (Figure 14). The size of furnace is important. A high mass furnace may have a high range of temperature and obtain uniform hot zone but requires more time to achieve the desired temperature. Comparatively, a low mass furnace may heat quickly but it's very difficult to control rise in temperature and maintain hot zone. The position of furnace is also important. Quartz spring balance has the weighing system below the furnace but the beam balance has weighing system at several positions (Figure 15).

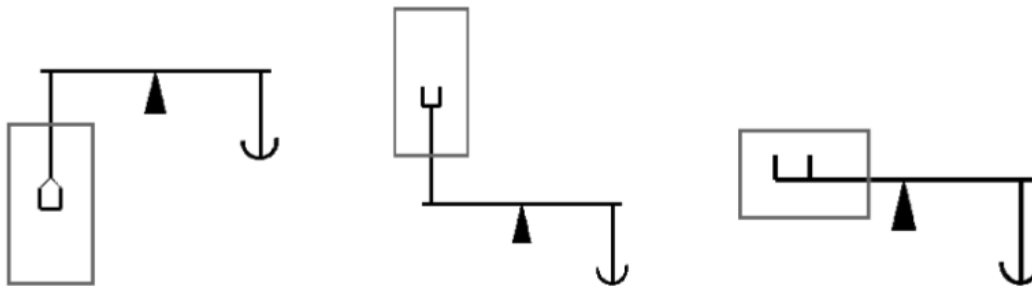


Fig.14. Position of Furnace with Respect to Balance

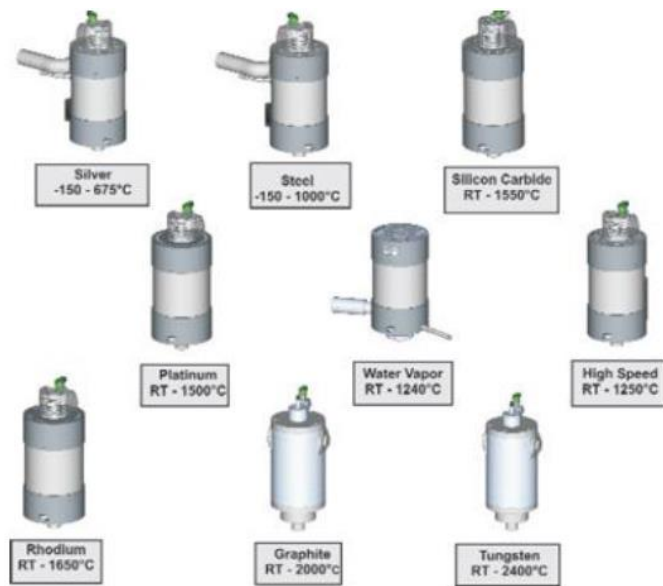


Fig.15. Different Types of Materials Used In Furnace

Temperature Measurement:

It is done with the help of thermocouple. Different materials are used for measuring different ranges of temperatures i.e. chromal or alumel (alloys of Platinum) thermocouples are used for $T=11000C$, tungsten or rhenium thermocouples are used for higher temperature.

The position of thermocouple is important. It can be adjusted in following ways (Figure 16):

- i. Thermocouple is placed near the sample container and has no contact with sample container. This arrangement is not preferred in low-pressures.
- ii. The sample is kept inside the sample holder but not in contact with it. It responds to small temperature changes only.
- iii. Thermocouple is placed either in contact with sample or with sample container. This method is best and commonly employed.

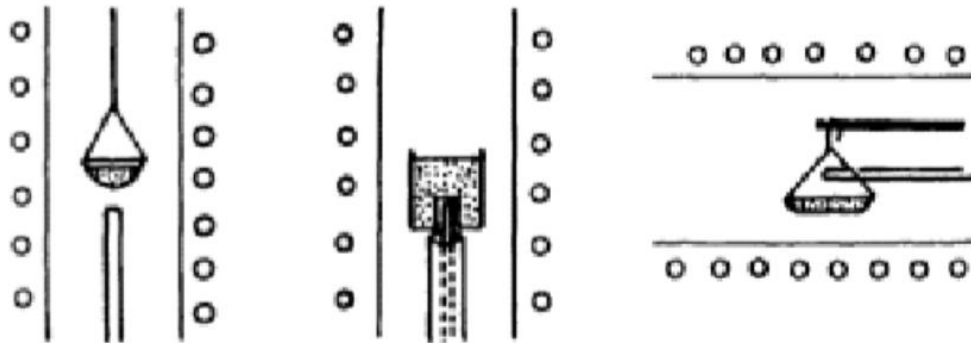


Fig.16. Positions of Thermocouple in a Thermobalance

Heating Rate:

The heating rate is the rate of temperature increase, which is customarily quoted in degrees per minute (on the Celsius or Kelvin scales). The heating or cooling rate is said to be constant when the temperature/time curve is linear.

Data Recording Unit:

The output from the microbalance and furnace are recorded using either chart recorder or a microcomputer (work station). The advantage of microcomputer over chart recorder is that the microcomputer comes with such software which allows data to be saved and plotted while

performing mathematical problems. Besides that, multiple TG curves can be plotted simultaneously. In such microcomputers, we get plot of weight change versus temperature or time. Some other recording systems are also available viz. X-Y recorders and Time-Base Potentiometric Strip Chart Recorder. In X-Y Recorder, plot of weight directly against temperature is presented.

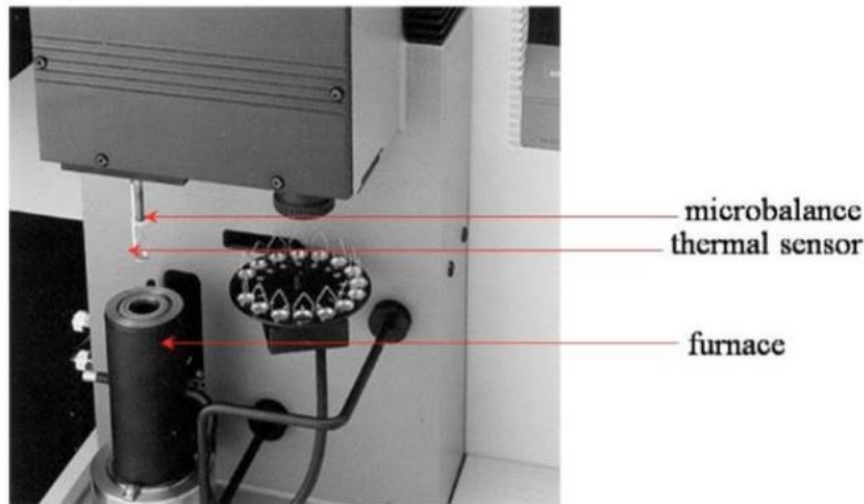


Fig.15. Multi Sample TG Analyzer

Applications:

Thermal stability

TGA can be used to evaluate the thermal stability of a material. In a desired temperature range, if a species is thermally stable, there will be no observed mass change. Negligible mass loss corresponds to little or no slope in the TGA trace. TGA also gives the upper use temperature of a material. Beyond this temperature the material will begin to degrade.

TGA is used in the analysis of ceramics and thermally stable polymers. Ceramics usually melt before they decompose as they are thermally stable over a large temperature range, thus TGA is mainly used to investigate the thermal stability of polymers. Most polymers melt or degrade before 200°C. However, there is a class of thermally stable polymers that are able to withstand temperatures of at least 300°C in air and 500°C in inert gases without structural changes or strength loss, which can be analyzed by TGA.

Oxidation and/or Combustion

The simplest materials characterization is the residue remaining after a reaction. For example, a combustion reaction could be tested by loading a sample into a thermogravimetric analyzer at normal conditions. The thermogravimetric analyzer would ion combustion the sample by heating it beyond the ignition temperature of a sample. The resultant TGA curve plotted with the y axis as percentage of initial mass would show the residue at the final point of the curve.

Oxidative mass losses are the most common observable losses in TGA.

Studying the resistance to oxidation in copper alloys is very important. For example, NASA (National Aeronautics and Space Administration) is conducting research on advanced copper alloys for their possible use in combustion engines. However, oxidative degradation can occur in these alloys as copper oxides form in atmospheres that are rich in oxygen. Resistance to oxidation is very important because NASA wants to be able to reuse shuttle materials. TGA can be used to study the static oxidation of materials such as these for practical use.

Combustion during TG analysis is identifiable by distinct traces made in the TGA thermograms produced. One interesting example occurs with samples of as-produced unpurified carbon nanotubes that have a large amount of metal catalyst present. Due to combustion, a TGA trace can deviate from the normal form of a well-behaved function. This phenomenon arises from a rapid temperature change. When the weight and temperature are plotted versus time, a dramatic slope change in the first derivative plot is concurrent with the mass loss of the sample and the sudden increase in temperature seen by the thermocouple. The mass loss could be the result of particles of smoke released from burning caused by inconsistencies in the material itself, beyond the oxidation of carbon due to poorly controlled weight loss.

Thermogravimetric Kinetics

Thermogravimetric kinetics may be explored for insight into the reaction mechanisms of thermal (catalytic or non-catalytic) decomposition involved in the Pyrolysis and Combustion processes of different materials. Activation energies of the decomposition process can be calculated using Kissinger method. Though a constant heating rate is more common, a constant mass loss rate can illuminate specific reaction kinetics. For example, the kinetic parameters of the carbonization of polyvinyl butyral were found using a constant mass loss rate of 0.2 wt %/min. Operation in Combinations with Instruments. The TGA instrument continuously weighs a sample as it is heated to temperatures of up to 2000 °C for coupling with FTIR and Mass spectrometry gas analysis.