Thermogravimetry (TGA)

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

It is of three types -

(a) Isothermal or Static Thermogravimetry. In this technique the sample weight is recorded as a function of time at constant temperature.

(b) Quasistatic Thermogravimetry. In this sample is heated at constant weight at each of a series of increasing temp

(c) Dynamic Thermogravimetry The sample is heated in an environment whose temperature is changing at a linear rate

most of the studies are carried by this technique, so it is usually called as Thermogravimetry.

Instrumentation for Thermogravimetry

Principle continuous weighing of the sample which is heated to elevated temperatures.

The Instruments is called thermo balance. A thermo balance consists of following components-

(a) Recording balance (b) sample holder (c) Furnace

(d) Furnace temperature controller (e) Recorder

[A] Recording Balance: A good balance must fulfil the following requirements (i) It should be accurate, sensitive, reproducible etc. (ii) Its capacity should be similar to those of groups that it should have an adequate range of automatic operation without. (iii) It should have a high degree of mechanical and electronic stability. (iv) It should have a response to weight changes. (v) It should be insensitive to vibrations (vi) Each Balance should be simple to operate and serviceable.

These Recording balances are mainly of two types i.e. Deflection balance. These are of four types —

(a) Beam Type: In this balance the beam deflection about the fulcrum converts in to weight change curve, which are recorded by either suitable displacement measuring transducers or are drawn electromechanically.

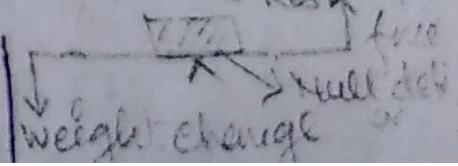
(b) Helical Type In this there is change in length of the spring of the balance with the weight change which is recorded by transducers. The quartz fibre is generally used as spring.

(c) The Cantilevered Beam The one end of the beam is fixed and the other on which sample is placed is free to undergo deflection which is recorded by transducers or electro-mechanically.

(d) Torsion wire. The beam is attached to a taut wire (or a metallic ribbon) which acts as fluerum. It is firmly fixed at one or both the ends so that the deflection is proportional to weight changes which are recorded by transducers or electromechanically.

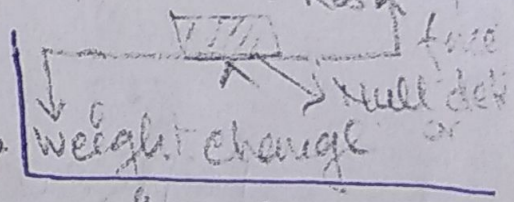
(4) Null-Point Balances. In these balances there is a sensor to detect the deviation of the balance beam from its null position.

- A restoring force, either in the form of electrical or mechanical weight loading is applied to the beam to restore its null position.
- This restoring force is proportional to the weight change which is recorded by transducers.



2. Sample Holders - These are generally of glass.

• This restoring force is proportional to the weight change which is recorded by transducers.



2. Sample Holders - These are generally of glass, quartz, alumina, stainless steel, platinum or graphite etc.
• The geometry, size and material of the sample holder effect the shape of TG-curve.
• Size & shape and material depends upon the nature & weight of the sample and maximum temp. range to be employed. These are of four types -

(i) Shallow pans These are used when -
• A volatile material is produced throughout the sample mass which should diffuse to the surface instantaneously to escape and weight loss is registered.
• Sample is arranged in a thin layer (like in polymers) so that as soon as the volatile fragment is formed it is free to escape.

(ii) Deep Crucibles These are used in the cases where -
- Slower reaction and/or partial equilibrium is required.
- In the study of Industrial scale calcinations.
- In surface area measurements.

(iii) Loosely Covered Crucibles These are mainly used when
- self-generated atmosphere is required and the studies are to be done isothermally, when only the weight loss not the temp change is important

(iv) Retort Cups. This is like Al chemist's retort and are useful in boiling point determinations.

3. The Furnace

- The furnace and control system must produce a linear heating rate over the whole working temperature range.

Heating Element - In the form of wire or ribbon, if wire it should be 'wound' 'coiled-coil' fashion to accomodate differential thermal expansion.

coil fashion to accomodate thermal expansion,

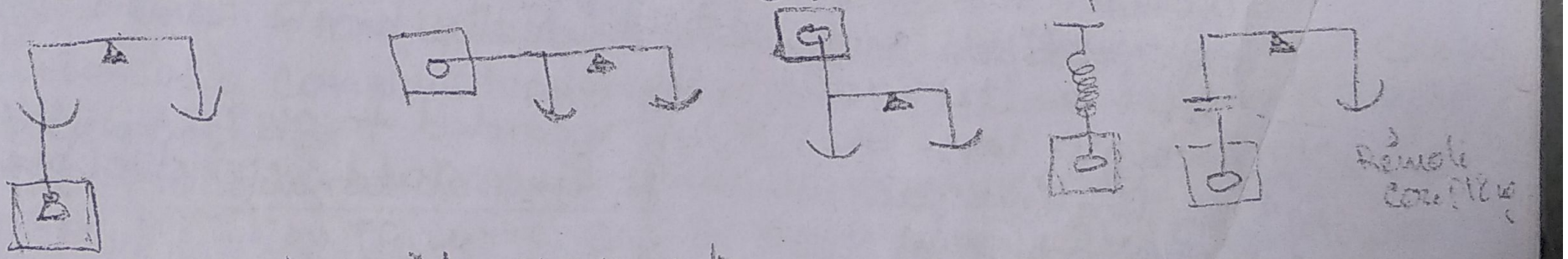
- For temp range 1100—1500°C. Platinum or Platinum-Rhodium alloy
- For temp range 1750°C. Platinum-Rhodium with 40% Rhodium
- Above 1750°C — Tungsten or Molybdenum is used,

Size of furnace (1) Low mass furnace — It cools very quickly but its linear temp. rise is very difficult to control.

(2) High mass furnace — It may hold a isothermal temp but it requires more time to achieve the required temp. It is easy to obtain large uniform hot zone in this furnace

Position of the furnace — In quartz fibre spring balance, the furnace is below the weighing system,

In beam balance several choices are possible



4. Temperature Measurement

(1) For measuring 1100°C range — Chromel or Alumel thermocouple made up of alloy of Pt and Rhodium

(2) For high temp Tungsten and Rhenium thermocouple is used

Position of Temp. measuring device — This can be done in by either of the following ways —

(i) Thermocouple is placed near the sample container (crucible) Contact with the container. Not good where two processes are employed.

(ii) The thermo couple is placed inside the sample holder but not in contact with it This is better way than (i) because small temp changes may be recorded.

(iii) The thermocouple is placed either in contact with the sample or with the sample container. This is best way of sample-temperature detection.

5. Recorder These are of two types—

(a) Time-base potentiometric strip-chart Recorder, light-beam-galvanometer, photographic paper recorders or one recorder with two or more pens — By these recorders we can check the heating rate of the furnace for linearity.

(b) X-Y-Recorder we get curves having plot of weights directly against temperature.

Note: In most of the recorders there is time, change vs temp or time but now a days % mass change vs temp or time are more popular.

temp or time are more popular.

Characteristics of Thermobalance:

A good thermobalance should have following characteristics-

(i) It should be capable of recording continuously with weight changes of the sample as a function of temperature & time.

(ii) The furnace of thermobalance should cover a wide range of temperature such as 1000, 1600 or 2400°C. Furnace should be capable of attaining temp. of 100-200c above the maximum desired working range.

(iii) The recorded temp. should ideally be the sample temperature with an accuracy better than ±1%.

(iv) weight loss should be recorded to an accuracy of ±1%.

(v) The heating rate should be linear and reproducible over the complete range of temp.

(vi) Radiation and convection currents and magnetic effect due to furnace heaters must not affect the weighing system.

(vii) The sensitivity should be in coloberation with size of the sample

(viii) Must be unaffected by the chemical attack of volatile products.

(ix) The Crucible should be located within the hot zone, and its

position must not get changed during the experiment.

(x) The balance has to be protected from furnace

(xi) It should be capable of adjusting various speeds of the chart that is being used to record mass-loss and temp. rise. and also an arrangement for recording accurate time interval.

(xii) Must have additional facility for rapid heating & cooling of the furnace to permit several TG curves to be recorded in a short span of time.

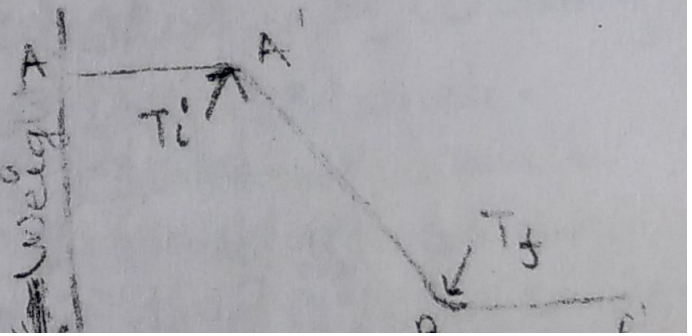
Thermogram:- The plot of weight against temperature or, time produced by thermogravimeter is called Thermogram.

Thermogravimetric Curve or TG Curve

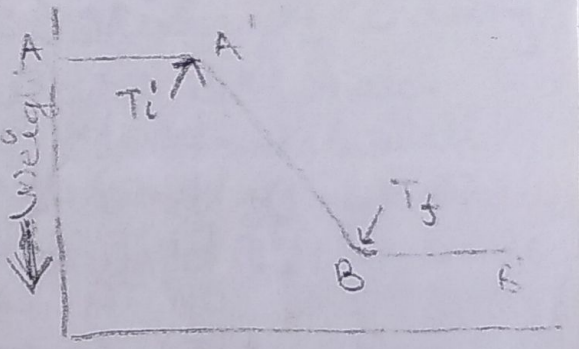
- Weight should be plotted on the ordinate with weight decreasing downwards and Temp.(T) or time (t) on abscissa increasing from left to right.
- If plotted the % of the total weight, then theoretical weight loss for the various stages of decomposition is indicated directly on TG Curve.

INFORMATIONS FROM THERMOGRAMS

Following informations from TG curves may be noted — (i) Horizontal portions indicates the



loss for the various stages of decomposition is indicated directly on TG curve.



INFORMATIONS FROM THERMOGRAMS

Following informations from TG curves may be noted — (i) Horizontal portions indicates the region where there is no weight change means material is thermostable (means no change in properties on heating) e.g. Curve AA' is perfectly horizontal means the compound is stable up to temp Ti'e

This information of thermostability for substances like alloys, building materials, packing materials, polymers and high pressure valves is important to the engineers for their safe uses.

(ii) The curved portions like A'B' shows weight losses and also that how much weight is lost by heating the sample up to a given temp. From this inorganic Chemists determine the composition of a compound and also the reaction involved in the decomposition

(iii) The Procedural decomposition Temperature (Pdt). This is indicated by Ti on TG curve can be determined. It is the lowest temperature at which the cumulative mass change reaches a magnitude that the thermobalance can detect.

(iv) Final Temperature (T_f) is the temp. at which the cumulative weight change first reaches its maximum value corresponding to the complete reaction. Indicated by T_f on TG curves.

(v) Reaction Interval The diff. between T_f & Ti that is ($T_f - T_i$) is reaction Interval

⇒ These physical properties can be used in the identification of a chemical compound. e.g. If $CaCO_3$ is heated above 250°C it loses 44% of its weight and the evolved gas, collected and identified as CO_2 which confirms the reaction of decomposition $CaCO_3 \rightarrow CaO + CO_2$

Factors Affecting Thermograms Factors affecting thermograms are classified in two groups -

[A] Instrumental Factors - (or Thermobalance Factors)

(a) Heating Rate - Temperature of decomposition is higher at faster rate of heating and low at slower rate of heating e.g.

(i) Decomposition of polystyrene in Nitrogen (for 10% decomposition)
375°C decomposition temp when rate of heating 1°C/minit.
394°C decomposition temp when rate of heating 5°C/minit

(ii) Decomposition temp of Complex $[Co(NH_3)_4(H_2O)(CN)Co(NH_3)_4CN](ClO_4)_4$
151°C when the heating rate 5°C/min
159°C when the heating rate 10°C/min
& 161°C when the heating rate 15°C/min

• There is decomposition temp. change with the change of heating rate but mass-losses remain unchanged.

• Heating Rate has little effect on Reversible Reactions

• Rate of heating also affects position of Intermediate compounds

heating rate but mass-losses remain unchanged.

- Heating Rate has little effect on Reversible Reactions
- Rate of heating also affects position of Intermediate compounds on TG curves e.g. $NiSO_4 \cdot 7H_2O$
  - TG curve shows one curve break corresponding to $NiSO_4 \cdot H_2O$ when the heating rate is 2.5°C/min.
  - TG curve shows four breaks corresponding to $NiSO_4 \cdot 6H_2O$, $NiSO_4 \cdot 4H_2O$, $NiSO_4 \cdot 2H_2O$ and $NiSO_4 \cdot H_2O$ when the heating rate is 0.6°C/min.

⇒ Thus the detection of intermediate compounds by TG method depends upon the heating rate.

(b) Effect of furnace Atmosphere. There is marked influence of the furnace atmosphere on the TG curve e.g. decomposition of $CaCO_3$ take place at much higher temp. if CO_2 rather than N_2 is used as the surrounding atmosphere.

- Nature of the surrounding gas must be constant throughout the experiment in Thermobalance, mostly Vacuum condition is used. But the other common atmospheres in TG are—

(i) Static air: Air from the atmosphere is allowed to flow through furnace

(ii) Dynamic air: Compressed air from the cylinder is passed through the furnace at measured rate.

(iii) Inert Atmosphere Oxygen free nitrogen is used as inert environment.

(c) Sample Holder The geometry of sample holder can change the slope of TG curve.

- Shallow dish is preferred because in it there is a rapid gaseous exchange between the sample and the surrounding atmosphere.
- When the atmosphere is totally the gas involved in the reaction, the geometry of the sample holder has no effect on the slope of TG curve. e.g. decomposition of $CaCO_3$ is not affected in the atmosphere of CO_2 the gas evolved but in the atmosphere of dynamic N_2 atmosphere shape of TG curve depends upon the shape of sample holder

[B] Sample Characteristics

(a) Weight of the Sample • If higher amount of sample is used there is deviation from linearity as the temp. rise, in the case of fast exothermic reaction. eg formation of CO during decomposition of Calcium oxalate to Calcium Carbonate.

- To detect the presence of intermediate Compound, small sample is preferred eg 18 mg $CuSO_4 \cdot 5H_2O$ do not show break corresponding to $CuSO_4 \cdot 3H_2O$ while 0.426 mg sample do so in TG curves.

(b) Sample Particle Size • various particle size of sample alter the

break corresponding to $CuSO_4 \cdot 3H_2O$ while 0.426 mg sample do so in TG curves.

(b) Sample Particle Size • various particle size of sample alter the reaction rate and hence the shape of the curve with smaller particle size decomposes earlier while greater particle size decomposition proceed at higher temp.

(c) Heat of Reaction • Heat of reaction will change the difference between the sample temp. and furnace temp. For exothermic, sample temp. lead the furnace temp. and for endothermic sample temp lag behind the furnace temp.

(d) Compactness of the Sample A compressed sample will decompose at higher temperature than a loose sample

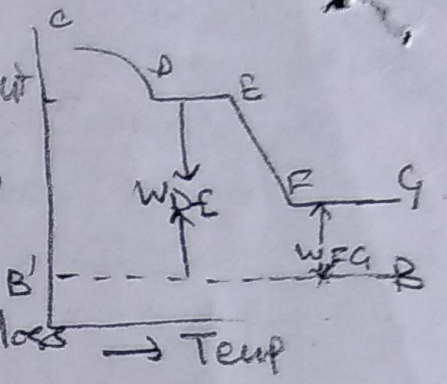
(e) Previous History of the Sample Previous history means eg. $Mg(OH)_2$ prepared by precipitation method has different decomposition temperature than that from naturally occurring material. It means that one must be sure about the source or method of formation of the sample

Applications of TGA

Some special application are

1. Automatic thermogravimetric Analysis

- Consider the Thermogram, in this first the thermobalance is operated to get base line BB'
- Substance to be determined is precipitated by suitable precipitant and then transfered to the Crucible, heating is started and the weight-loss curve is recorded (Thermogram)

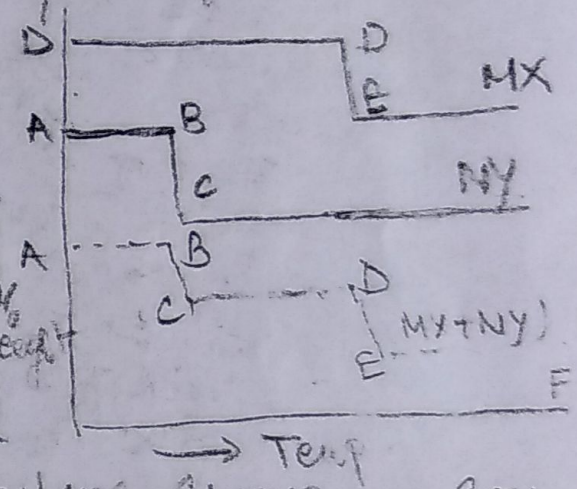


- In the thermogram there are two horizontal levels, DE and FG, corresponding to weight W_{DE} and W_{FG} (Thermostable state) by appropriate gravimetric factor W_{DE} & W_{FG} is converted in to the mass of the metal ion.

⇒ This method is quite rapid, entire operation require 12 min.

For binary mixture

- Procedure as above is repeated with individual components MX & NY and also the mixture of MX and NY
- From the curve it is clear that component MY decomposes from D to E where NY decomposes from B to C which corresponds to the same temperature as that on initial Component Curve. Therefore from the mixture curve we can determine the amount of NY determining the value of BC and also MX from DE (dotted)



⇒ It is clear that analysis of binary or ternary mixtures may

→ Temp

Component curve. Therefore from the mixture curve we can determine the amount of NY determining the value of BC and also MX from DE (dotted)

⇒ It is clear that analysis of binary or ternary mixtures may be carried out by one simple operation with reasonable accuracy.

2. Evaluation of Gravimetric Precipitates - To determine the correct drying temperatures of precipitates e.g.

(a) Lithium is precipitated as triple periodate $KLiFeIO_6$. Duval showed that it is unsuitable for TG analysis as this compound shad constant decrease in weight from 40°C – 947°C. It mean no drying temp for this ppt.

(b) For salicylaldoxime

- Duval found no plateau (thermostable part) on TG curve shaw no drying temp for the ppt. (drawback was very fast heat rate shown by Borrel & Paris)
- Borrel & Paris found 135°C as minimum drying temp.
- Kettach confirmed 150°C as most suitable drying temp. of ppt irrespective of the moisture content.

3. Evaluation of Suitable Standards

- Duval from TG studies confirmed that following substances [illegible] as standard [illegible]

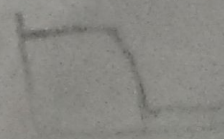
Magnesium Ammonium Chloride, ammonium bicarbonate and ammonium fluoride.

- He also confirmed that following compounds are most suitable for preparing standard solutions. —
Lithium sulphate monohydrate, Sodium dichromate dihydrate, Sodium Cobaltinitrite, Hydrazinium Chloride, Hydrazinium sulphate, Ascorbic acid and methylglucamine.
- He confirmed that it is advisable not to heat the compound above the definite temp e.g.
EDTA (109°C); Urea (165°C); NaF (850°C); $Ni(NO_3)_2 \cdot 6H_2O$ (50°C)
$KHCO_3$ (125°C); $NiSO_4 \cdot 7H_2O$ (100°C)

4. Testing of purity of Sample — Thermobalances can be used to determine the purity of the sample and also the nature of impurity e.g.
- The unusual weight loss in TG curve of calcium oxalate at 105°C reported by Kettach was not due to the loss of absorbed water but was due to some impurities
- In an experiment Kettach while running thermograms of different sample of $CaCO_3$ found weight loss due to adsorbed water and subsequent loss of CO_2 by the original sample. There was no further weight change in any sample up to 1300°C except one, which showed marked weight change at 1080°C. On examination it was confirmed that this weight loss was due to the presence of the impurities of $CaSO_4$ in the sample.

the impurities of $CaSO_4$ in the sample.

5. Curie Point Determination • Curie-Point is the temp at which a ferromagnetic substance lose their magnetism.
• Using a range of standard materials, an accurate calibration curve of the furnace can be produced. As -
• suitable caliberation standards are placed in the sample pan of the balance and a large permanent magnet is placed below the pan, sample will experience an downward attraction leading to an apparent increase in weight. At curie-point the loss of ferromagnetism will be reflected by an apparent loss of weight, enabling the temperature experienced by the balance pan to be accurately known. On the TG curve, the temp at which the thermogram shad a decrease in weight is the curie Temperature of the substance.
• This technique can also be used to study thermal effects on induced magnetism and the effect of heat on ferromagnetic materials.



2020/8

Organic Compounds Some organic compound decomposition reactions are studied by DTA and TG techniques e.g.

(i) Malonic acid shows phase transition in the region 70°C, melting at about 140°C and decomposition above 150°C

$$HOOC-CH_2-COOH \longrightarrow CO_2 + CH_3COOH$$

(ii) Glycine melts with decomposition, in the region of 220°C.

(iii) L-Glutamic acid, has three stages of decomposition in air as

(a) L-Glutamic → Pyrrolidone-α-carboxylic acid + one mole water at 175°C

(b) Pyrrolidone-α-carboxylic acid → Pyrrole + one mole of water

(c) Pyrrole ⟶ All gaseous products zero weight

Glass Technology

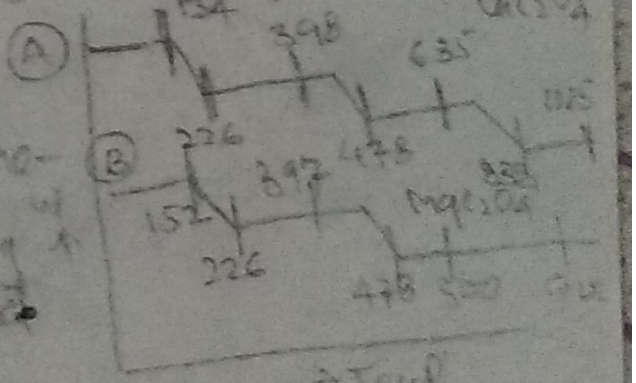
- If a mixture of 85% SiO_2 + 15% Na_2CO_3 when used in DTA and TG analysis in combination, then endothermic DTA peaks at about 97.5°C, 560°C and 780°C correspond to weight changes on the TG curve.
- Positions of the above peaks are affected by the ratio of the components in the mixture, the relative grain size and other factors.

Building Materials It is the study of ternary compounds in

other factors.

Building materials - It is the study of ternary compounds e.g. Ca4Al6SO16 and the formula Ca4Al6SO16 was confirmed by X-ray curves obtained by heating a mixture of alumina & gypsum in a thermobalance over a range of 900 to 1400°C. The following observations were recorded -

- At about 1050°C, the mixture starts losing weight and at 1250°C, the weight loss stops.
- At 1400°C, the mixture again looses weight, the rate of weight loss at this temp. is about 1/30 of that gypsum at the same temperature and partial pressure of SO3
- The weight loss at 1250°C corresponds to 3% of an amount equivalent to one mole of SO3 per mole of Al2O3
- X-rays diffraction pattern of the product shows that this is 90% and weight loss confirms the proposed formula, $Ca_4Al_6SO_{16}$



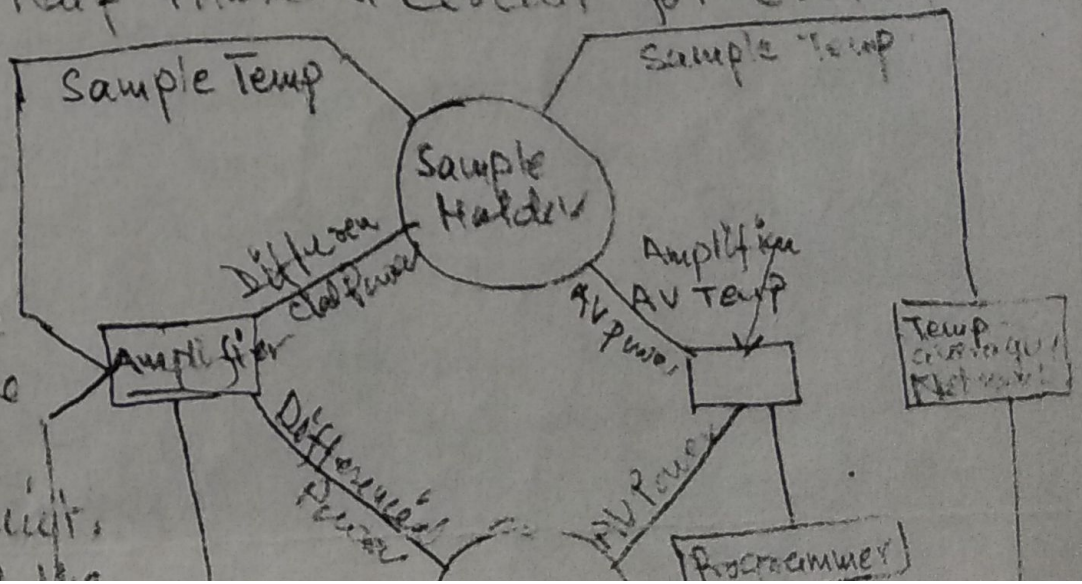
Analysis of Mixture - Calcium and magnesium oxalate can be determined by igniting at two temperatures. At 500°C the $CaCO_3$ and MgO are stable while at 900°C both metals exists as simple oxides. The weights of a mixed precipitate at these two temperatures will permit calculation of both

Differential Scanning Calorimetry (DSC)

- In DSC a zero temperature difference between a substance and a reference material is developed. It is recorded as a function of temp or time when the substance & reference material, both heated or cooled at a predetermined rate.
- The abscissa indicate the transition temp.
- The area of peak measures the total energy transfer to or from the sample.

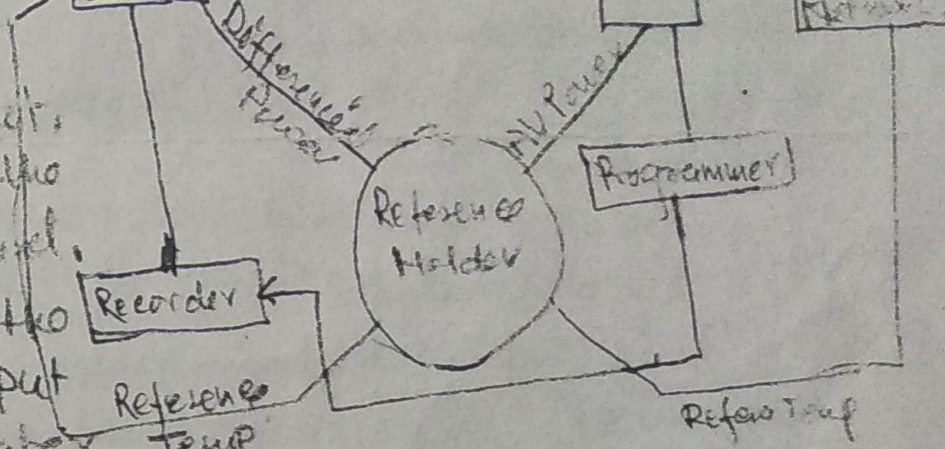
Instrumentation

- Instrument works on the temp. Control to two similar specimen-holders in the sample holding assembly.
- In its left half, there is a circuit for differential temperature control while in its right-half there a circuit for average temp. control.
- In the average temp. control circuit an electrical signal, which is proportional to the temp of the sample and reference holders, is generated through the programmer.
- In differential temp. control circuit,



programmer.

- In differential temp. Control circuit, signals representing the temp. of the sample and the reference compared.
- If no reaction is taking place in the sample, the differential power in put to the sample and reference heater is almost zero. But if the reaction is taking place a differential power is fed to the heaters (Attitude)
- The integral of the peak so obtained gives the thermal energy change of the sample



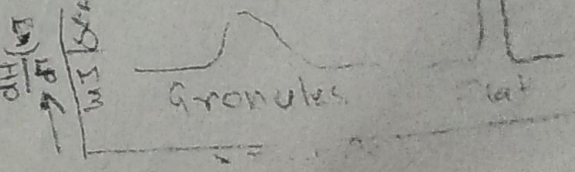
(Block Diagram of DSC Instrument)

Sample DSC may analyse liquids and solids in the form of Powder, crystals granules or foil.

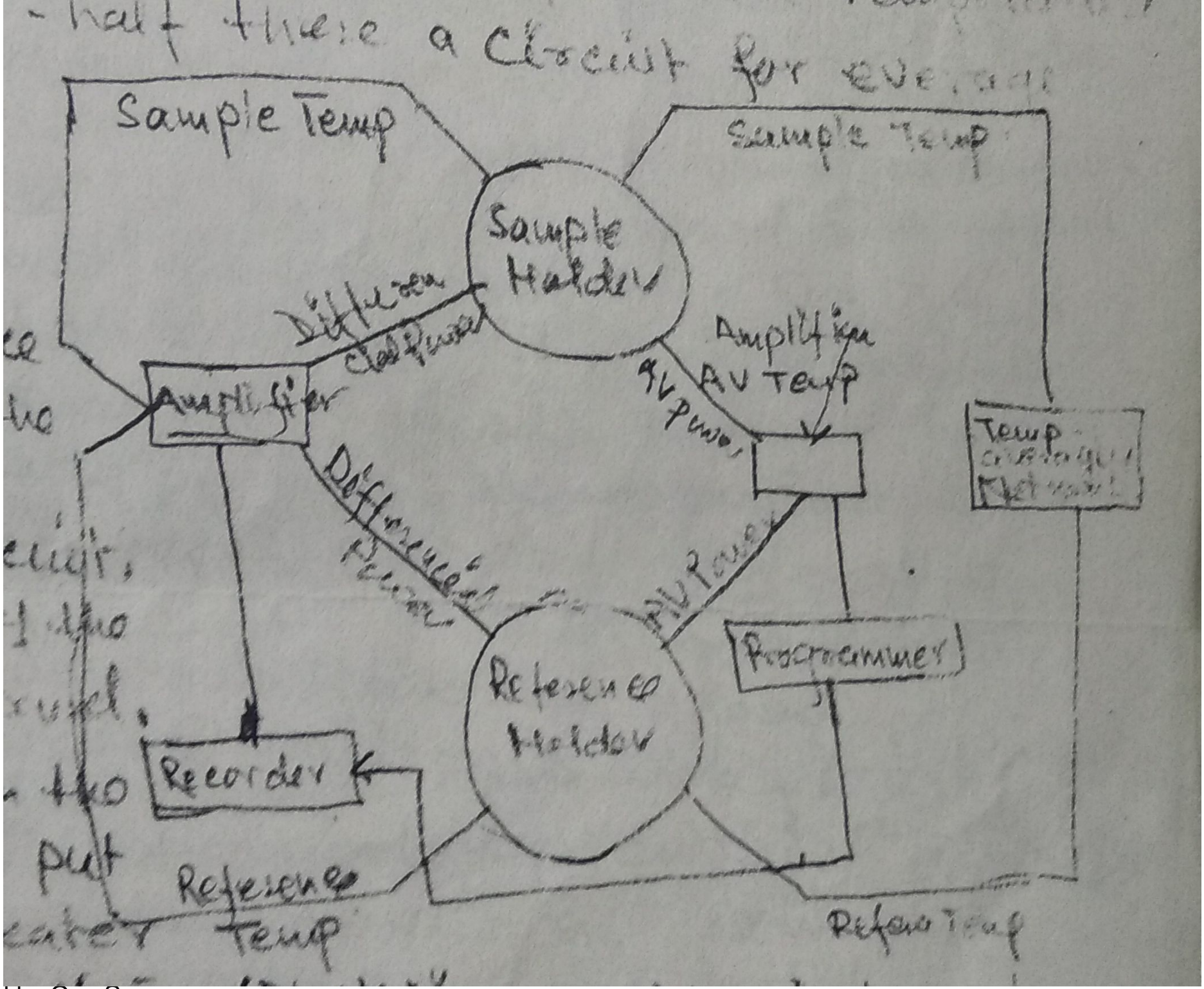
Reference Material An inert material like alumina is also used. Some time an empty pan with lid is also used.

Generally, DSC measurements are carried out in environment. The optimum rate recommended for [illegible] is [illegible] ml/min

Factors Affecting DSC Curves 1. Sample Shape: The shape of the sample has little effect on the quantitative nature of DSC but has more effect on qualitative aspect e.g

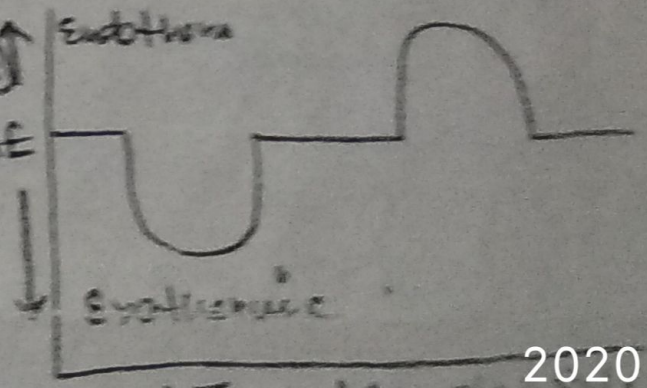


- Normally, sample is in the form of a disc film or powder spread out to be uniform



2. Sample Size : About 0.5 to 10 mg is usually sufficient
- Smaller samples enable faster scanning give better shaped peaks with good resolution and provide better contact with the gaseous environment.
- With large samples, smaller heats of transitions may be measured with greater accuracy.

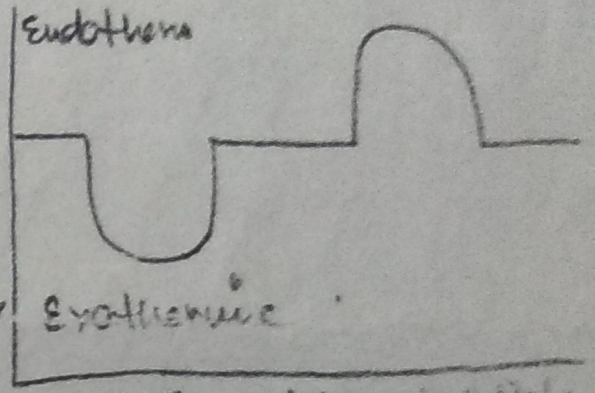
Principle : DSC involves the heating of the sample and an inert reference in parallel. For power Compensation DSC, the two are heated quite separately with separate electrical heaters.
- Heaters are programmed to ensure that the temp. of both sample and the reference advance at exactly the same rate.
- When endotherms or exotherms occur in the sample, the power to the heater will need to be varied in order to maintain $\Delta T = 0$. The thermogram shows the difference in power supplied to the heaters (ΔE) and the Temp. Change of the sample



- Thermocouples are used to sense the differential heat flow (supply) to the sample and standard.
- The peaks for endotherms and exotherms

$\Delta T = 0$. The thermogram shows the difference in power supplied to the heaters (ΔE) and the Temp. change of the sample

- Thermocouples are used to sense the differential heat flow (supply) to the sample and standard.
- The peaks for endotherms and exotherms reversed in direction for DTA relating to DSC.



Applications

- In this method, by measuring the power difference, we can get direct measurement of enthalpy changes, hence it is a good tool for thermodynamic measurements.
- TG can be used to detect changes in weight with changes of temperatures and also it can be used to detect phase changes.
- DSC can be used for all the applications of DTA
- ~~It this~~ small size of the sample is used in this Techniques.

Disadvantage Due to small sample size thermograms are often complex and thus difficult to interpret fully.

Thermomechanical Analysis (TMA) These techniques are based on the measurement of mechanical properties such as expension, contraction, extension or penetration of materials as a function of temperature. TMA curves obtained in this way are characteristics of the sample.

In this technique ~~assessment~~ measurements over the temperature range from $-100^{\circ}C$ to $1000^{\circ}C$ may be made. Study of a polymeric material based upon linear expansion measurements.

Instrumentation. TMA analyser contains probes for accurately measure both temperature of the sample, and very small movements of a probe in contact with the surface of the sample.

Analyser, uses a quartz probe containing a thermocouple for temperature measurement, and is coupled to the core of a linear variable differential transformer (LVDT). Small movements at the sample surface are transmitted to the core of the LVDT and converted in to an electrical signal.

In this way a sample ranging from a few μm to cm thickness may be studied with sensitivity to movements of a few μm. For studying different mechanical properties the detailed construction of the probe will vary as shown in the fig.

~~Appli~~ Principle Measurement of the effect of heat on the mechanical properties of a sample e.g. expension, compression, penetration and extension.

Probes fitted with thermocouples to measure the

extension.

Quartz probes fitted with thermocouples to measure the temperature, and follow the movement of the sample. Linked transducers i.e. a linear variable density transformer to sense the probe movement and produce a related electrical signal. Sample furnace, programmers and various output devices.

Applications. 1. Mainly used in the study of mechanical properties of polymers used for their characterization as well as to assess its mechanical utility.

2. This is an important technique in application of quality control.

3. The ability to study small specimens gives the technique a distinct advantage over more traditional methods of mechanical testing of sample size is limited.

4. Its range of heating for mechanical properties is -100°c-1000°c.

Disadvantage: Information is restricted largely to mechanical properties and cannot easily be related to actual composition of the sample.

DYNAMIC MECHANICAL ANALYSIS (DMA)

This is most sensitive thermal analysis or thermal analytical technique for detecting transitions associated with the movement of polymer chain.

- The technique involve measuring the resonant frequency and mechanical damping of a material forced to flex at selected amplitude.
- Mechanical damping is the amount of energy dissipated by the sample as it oscillates, while the resonant frequency defines Young's (elastic) modulus or stiffness.
- Loss modulus and ratio of loss modulus to elastic modulus can be calculated from the raw frequency and/or damping data.
- Modulus and frequency, as well as damping, change more dramatically than heat capacity or thermal expansion during transitions.
- DMA is helpful in determining the effectiveness of reinforcing agents and fillers used in thermoset resins.