* Differential thermal Analysis. (DTA)

It can be defined as a technique in which diff. in Temperature blw sample and a reference material is recorded as a function of temperature or time, as two specimen are subjected to an environment heated or cooled at controlled rate. There is zero temperature difference if sample does not undergo any physical or chemical change. If any change occurs, ΔT will be the difference. for endothermic change, temperature of sample is lower than the reference material (α-Alumina).

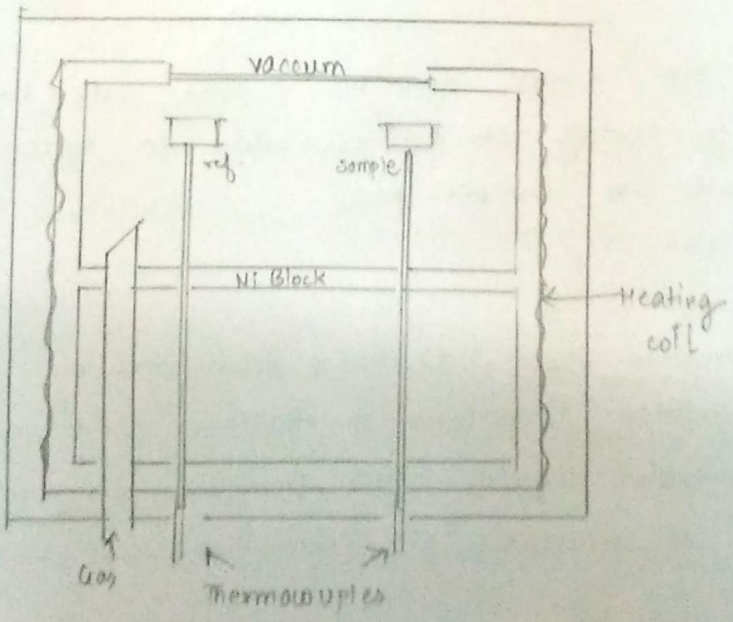
* FEATURES OF DTA APPARATUS:

i) Sample holder Assembly: It consists of a thermocouple, each for a sample and reference material., sorrounded by block to ensure even heat distribution. Sample is placed in crucible usually made of platinum, silica, nickel etc. depending upon nature of tests involved. The thermocouple is not directly connected to sample to avoid degradation & contamination.

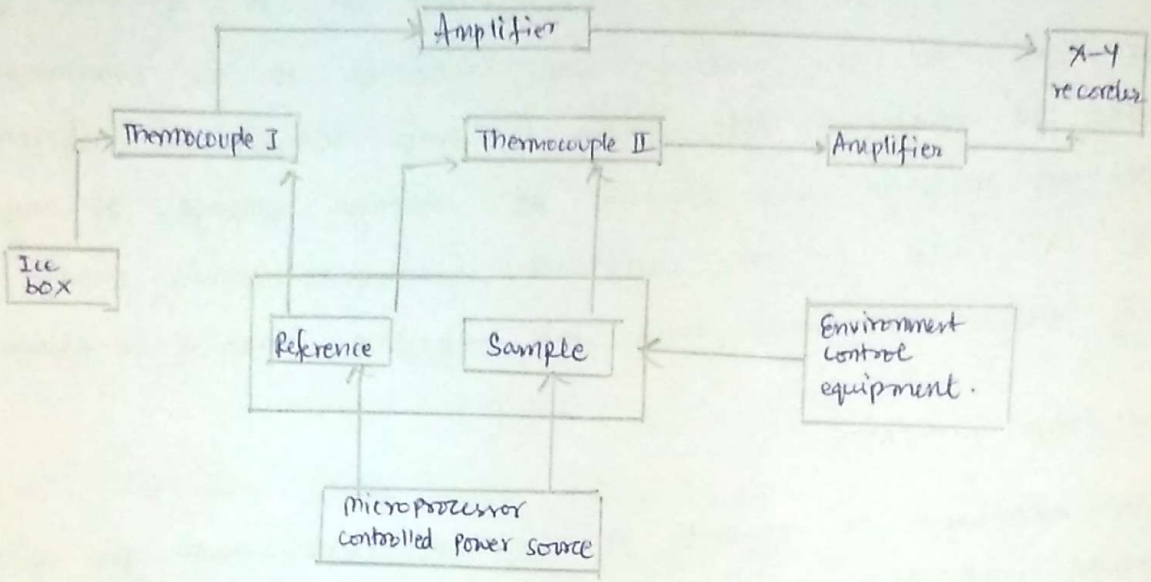
ii) furnace and Temperature programmer: The furnace should provide stable & sufficiently large hot zone and should respond quickly to temperature programmer. A temp. programmer is necessary for obtaining constant heating rates.

iii) Mebellic block: Their high ten thermal conductivity leads to smaller DTA peaks.

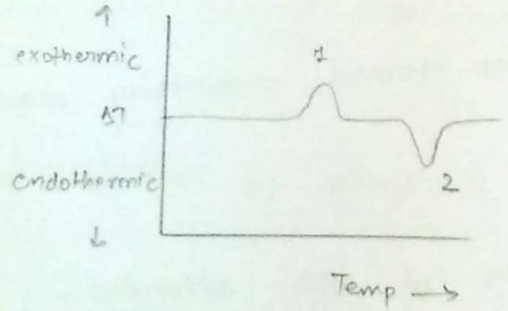
Schematic diagram of DTA apparatus.



* Block diagram of DTA Apparatus.



* Representation of DTA data : A plot of ΔT against temp. or time is made, if Temp. varies linearly with time. Peak 1 is exothermic peak and peak 2 is endothermic peak. Peak is sharp endothermic peak signifies fusion process and broad endothermic peak signifies dehydration. Physical changes results in endothermic curves and chemical changes results in exothermic pe curves.



NOTE : The shape of DTA ~~*~~ peak does not change with weight or heating rate. Lowering the heating rate is equivalent to reducing the weight & both results in sharper peaks.

* APPLICATIONS :

1> It provides information about a) phase transformation 2) structure inversion 3) dehydration 4) oxidation or reduction 5) decomposition 6) formation of crystalline structure 7) transition in crystalline structure 8) reactions due to impurities 9) volatilization of liquids.

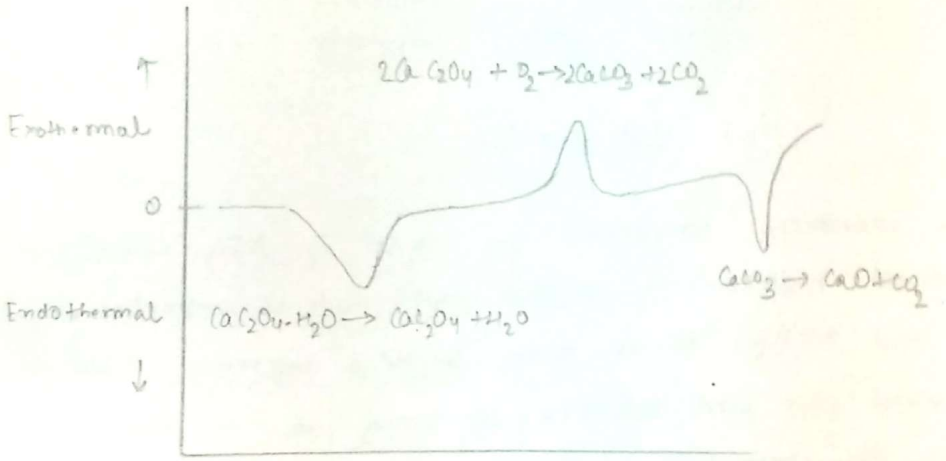
Peak area is given as:

$$(A) = \int_{T_1}^{T_2} \Delta T \cdot dt = \frac{m \cdot \Delta H}{g \cdot k} = K' m \Delta H .$$

where ΔH = enthalpy change for rxn involved.
g = geometrical factor of apparatus
k = thermal conductivity of sample.

Information that can be gathered from peak area:
i) mass of Analyte if K' & ΔH are known.
2) ΔH if m & K' are known.

ii) Differential thermogram for calcium oxalate monohydrate in flowing air (O_2) atmosphere is shown. (8°C/min rate). It contains two minima and a maxima. Minima indicates decomposition and maxima indicatjon oxidation.



If this graph is obtained under inert atmosphere conditions, then there will be three minimas. Because rxn. occuring will be $CaCO_3$ (s).
$CaC_2O_4 \rightarrow CaCO_3 + CO$, which is endothermic rxn.

iii) It is used for determining melting & boiling pts for organic comp.

iv) in study & characterization of polymers. Its DTA curve gives information about transitions occuring during heating of polymer.
T_G (Gloss Traction Temperature) which is a characteristic for polymer is defined as temp. at which constituent particles of polymer begins to have translatory motion.

v) For Qualitative Analysis of polymer mixture. In its DTA curve, each peak represents melting point of one of polymers.

* Differential scanning Calorimetry (DSC).

In DSC, the energy necessary to establish a zero temp. diff. between a sample and a reference is measured as a function of Temp. In endothermic transitions, the energy absorbed by the sample is compensated by the energy input to sample.

Instrumentation :

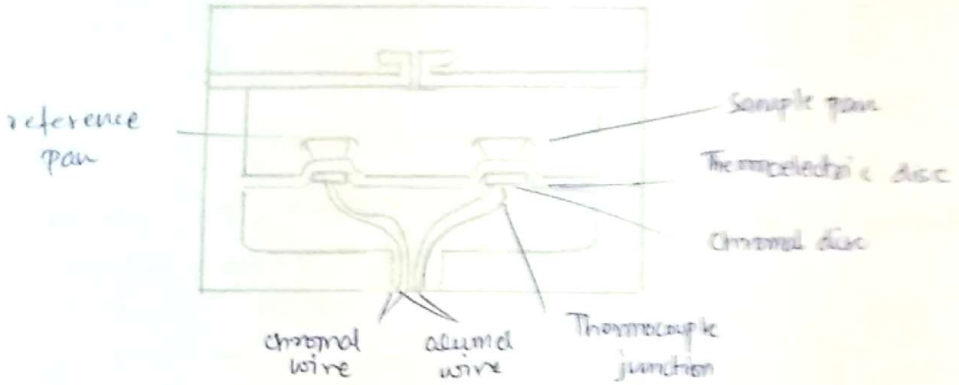
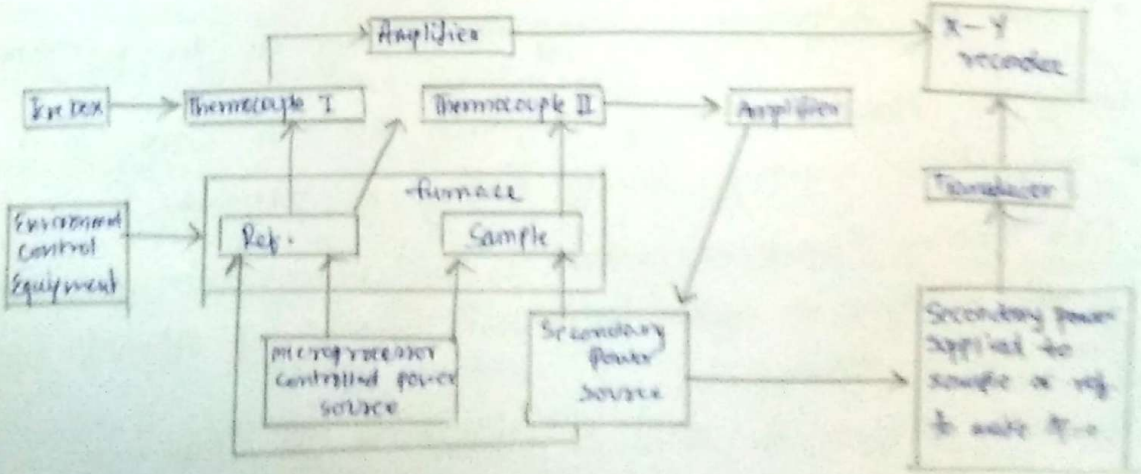


Fig 1: Heat flux DSC.

It consists of identical components to that of DTA except that it contains individual heaters. A metallic disk (made of constantan alloy) is means of heat transfer to or from sample & reference. A sample, contained in metal pan and reference, an empty pan is placed on the metallic disks. The chromel and alumel wire attached with chromel wafers forms thermocouples which directly measures sample temperature. The required energy or heat, then flows through metallic disk.

* Block diagram of DSC apparatus.



NOTE: The peak Area of DSC thermogram is given as:

$$A = k' m \Delta H \propto m \Delta H.$$

for DSC curve, ΔH is plotted against identical temp. of sample & ref.

* APPLICATIONS:

i) In analysis of a blend of synthetic fibres.

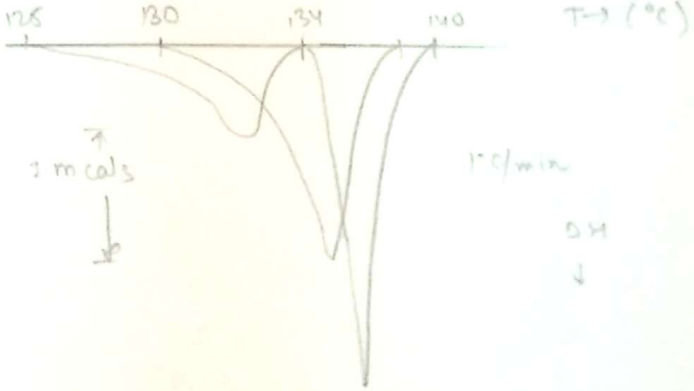
ii) In analysis of a blend of polymers. eg. Both Polyethyl terephthalate (PET) and acrylonitrile-butadiene-styrene have a blend mixture which can be separated by DSC & can also be evaluated.

iii) In determination of enthalpy of transition such as enthalpy of crystallisation, fusion etc.

iv) In determination of melting, boiling & decomposition points for organic compounds.

v) to determine purity of drug samples.

fig shows DSC curve for phenacetin for diff. purity.



* Difference between DSC and DTA. (most important).

DTA	DSC
* The temp. of sample is compared with that of reference material w.r.t furnace temperature.	The heat energy supplied on a variable rate so as to establish zero value of ΔT.
* In DTA curve, ΔT is plotted against T_c (furnace Temp.)	In DSC, ΔH is plotted against identical temp. of two.
* It proves provides calorimetric accuracy in temp. range -190°C → 1600°C.	It provides calorimetric accuracy in temp. range -190° → 750°C.
* Area under peak is complex function of Δ and heat capacity.	Area under peak is directly related to ΔH.
* No secondary power source is required.	* Secondary power source is required for supplying heat so that $\Delta T = 0$.