THERMO-ANALYTICAL METHODS!

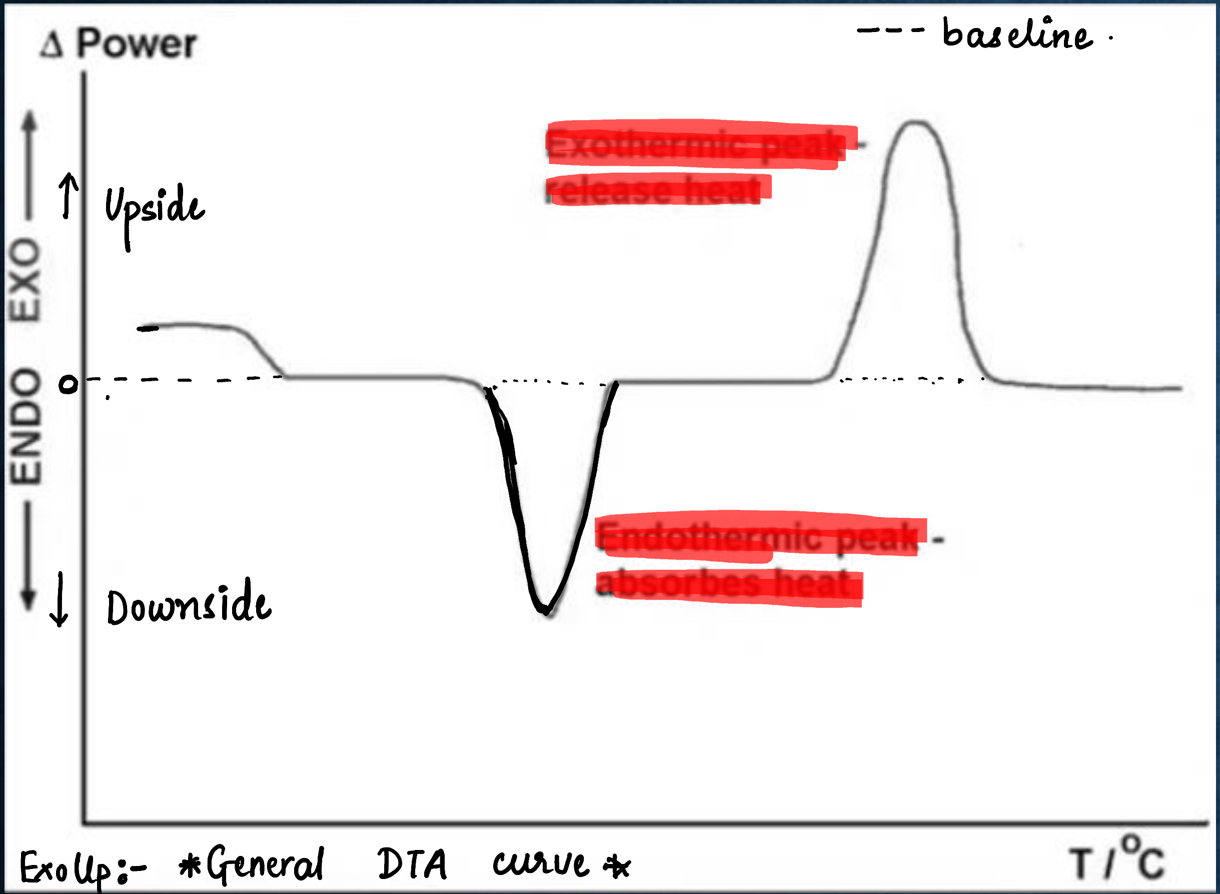
B. Differential Thermal Analysis (DTA): → 2 components → sample / Reference.

In DTA, the difference in temperature between the sample (T_S) and a suitable reference material (T_R) is recorded as a function of temperature when both are subjected it identical temperature changes.

A DTA curve is obtained when the temperature difference ($\Delta T = T_S - T_R$) is plotted against the temperature.

The temperature difference is due to the energy difference between the two phases of the sample under study (or between the reactant and products in case of a chemical reaction). The energy change is usually shown as enthalpy change (either endothermic or exothermic).

* Temperature difference → Dependent property → Y-axis.
  Temperature → Independent property → X-axis



Sharp endothermic → physical change
broad endothermic → dehydration
exothermic → chemical change

*Sharp endothermic peaks indicates physical changes like fusion, changes in the crystalline nature of the sample.

Broad endothermic peak indicates dehydration reaction.

Sharp exothermic peak indicates the occurrence of a chemical reaction like decomposition, etc.

- In an endothermic change (such as melting or dehydration of the sample) the temperature of the sample is lower than that of the reference material (i.e) $\Delta T = -$ ve (for endothermic process)

- In an exothermic change or process the sample temperature is higher than that of the reference material. (i.e) $\Delta T = +$ ve (exothermic process)

Initially, the DTA curve is parallel to the temperature axis till the time the sample undergoes a physical or a chemical change.
As soon as the sample attains the temperature at which the change occurs, the additional heat reaching the sample will not increase the temperature of the sample at the same rate as that of the reference material.
The temperature difference appears as a differential signal and is shown as a peak. The DTA curve returns to the baseline after the completion of the change of physical state of the sample when its temperature becomes equal to that of the reference material ie $T_S = T_R$ and $\Delta T = T_S - T_R = 0$.

Changes in weight of the sample is not a requirement for the detection of physical or chemical changes using DTA.

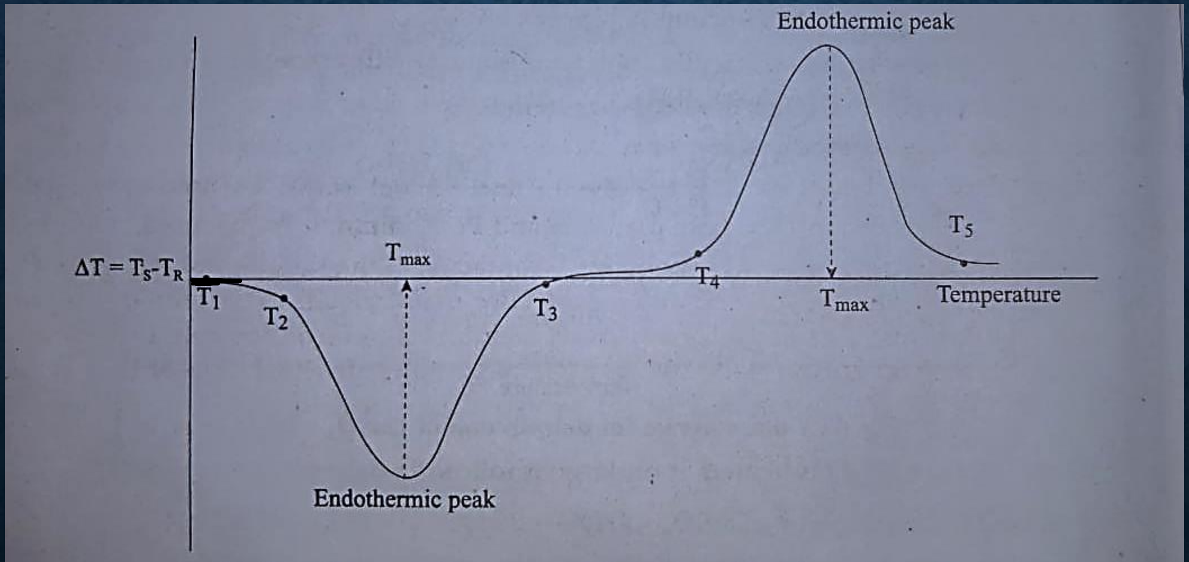


Fig. 7 : DTA curve showing endothermic and exothermic peaks

Instrumentation:

1. A sample holder.
2. A suitable thermocouple
3. A furnace with temperature programmer.
4. A differential temperature detector.
5. A recorder.
6. Atmosphere and Coolant controls.

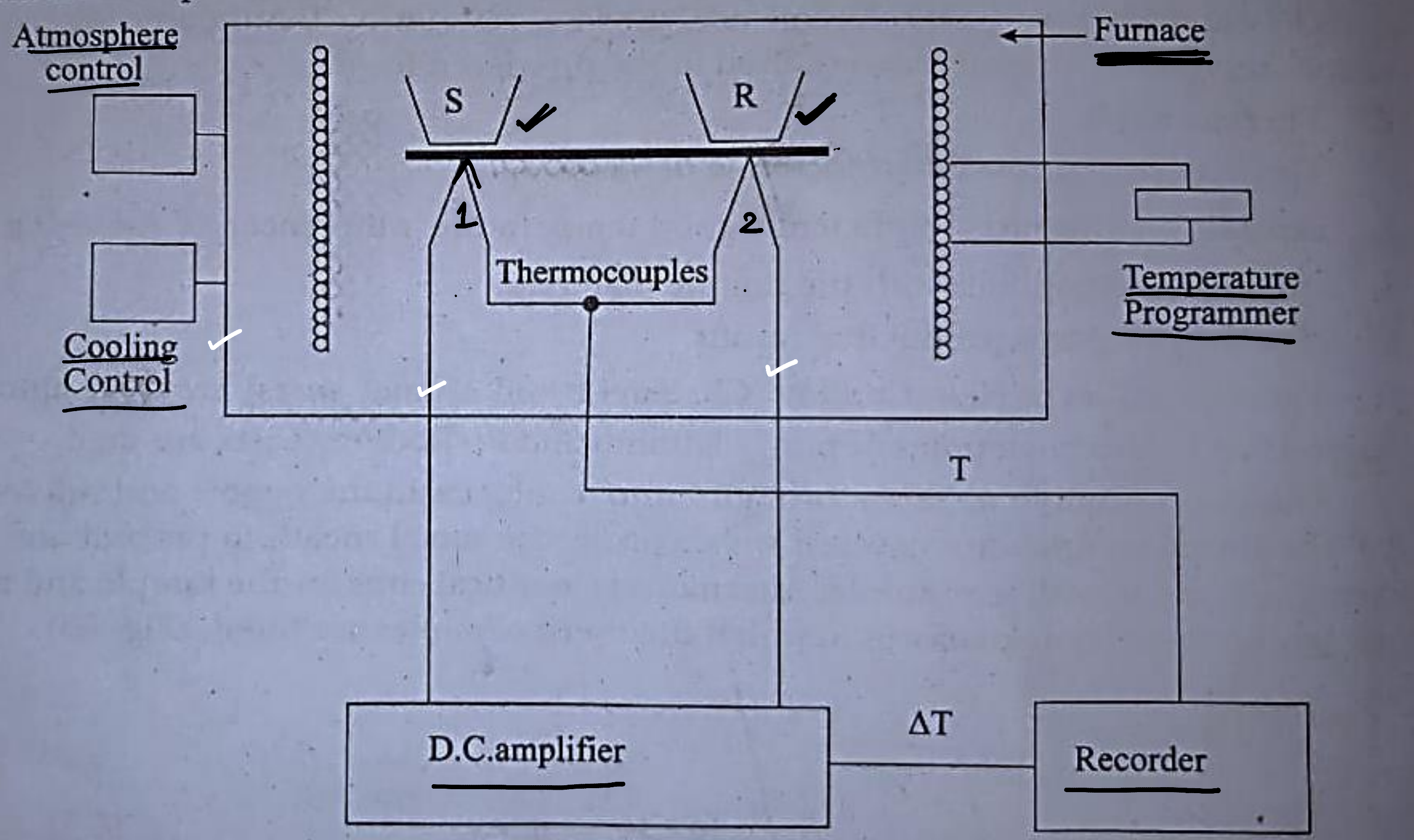


Fig. 9 : DTA assembly

1. Sample Holder:

⊛{ Ni, Stainless steel, Pt → metallic
 Glass, Quartz, Silica, Alumina → non-metallic

Nickel, Stainless steel and Platinum alloys are used as sample holder materials.
Glass, Quartz, Vitreous Silica, Sintered Alumina are used for preparing non-metallic sample holders.

The reference material used in DTA should have the following properties:

a. It should not undergo any chemical changes like decomposition or dehydration in the operating temperature range.
b. It should not react with the sample holder and the thermocouple.
c. Its thermal conductivity and heat capacity should be similar to that of the sample.

[redacted] - reference for inorganic samples.
[redacted] - reference for organic samples.

Both the sample and the reference material should be used in powdered form.

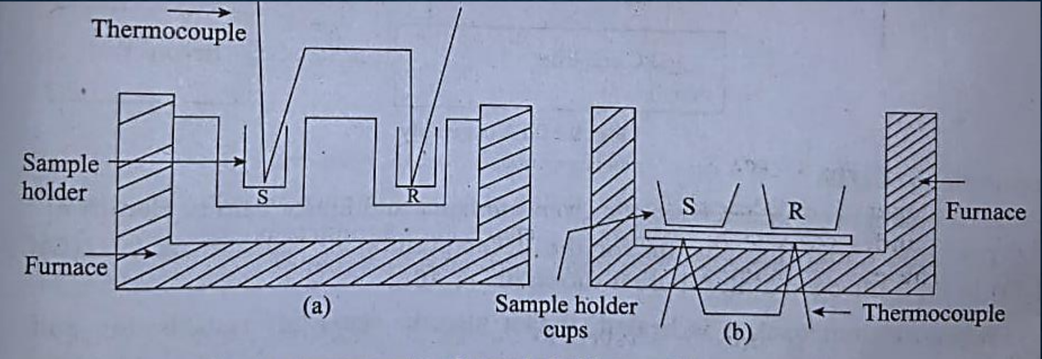


Fig. 8 : Arrangement of sample holders and thermocouples

2. Thermocouple: (choice of thermocouple depends upon the temperature).

The choice of a good thermocouple depends on its

a. Capability to produce a sufficiently good temperature difference. $\Delta T = T_S - T_R$
b. Chemical compatibility with the sample material.
c. Capability to give reproducible results.

Thermocouples of [redacted]

Thermocouples wires are brought into contact with the sample and reference. The thermocouple are covered with a [redacted] any possible chemical reaction with the sample. Alternatively, identical cups for the sample and reference may be supported on a platform to which the thermocouple are fitted.

3. Furnace with temperature programmer: (depends upon the temperature used for experiment).

A tubular furnace is used in DTA. It should be uniform, hand wound are not uniform and are not useful. • Machine wound are uniform. • Grooved muffled cores and time biflar winding is preferred. • The entire length of the differential thermocouple should be shielded.

The furnace is prepared by winding nichrome wire on a porcelain support -can be used upto 1200^{0}C.
Kanthal wire is wound on alumino-silicate -can be used upto 1200^{0}C- 1400^{0}C.
Pt-Rhodium alloy wire is wound on alumina support- can be used upto 1600^{0}C- 1800^{0}C.
Refectary material like Rhenium and tungsten in inert gas or vacuum- can be used upto 2100^{0}C.

A heating rate of 10-20^{0}C per minute is maintained.

The heating rate generally influences the DTA curves, as higher the heating rate, sharper the peaks.

The furnace provided with the temperature programmer to maintain a linear temperature rise. The temperature programmer should be capable of giving a wide range of heating rates e.g. 1-50^{0}C per minute.
On-off type controllers are not used because switching off or on or full power, considerable noise may occur particularly at temperatures above 700°C.

4. Differential temperature detector:
The thermocouple serves as the temperature sensor.
The Voltage signal produced depends on the temperature different, ΔT between the two junctions of the thermocouple.

5. Recorder:
The recorder incorporates the amplifier to magnify the signals coming from the temperature sensor (T) and the differential temperature sensor (ΔT) of the thermocouple. The electric signals are recorded on a twin pen recorder. If faster charts speeds are used, DTA peaks get flattened out.

6. Atmosphere and Cooling Coolants:
A facility for flushing the sample and the reference assembly with a selected gas is provided. There is also a cooling facility to cool the assembly to ambient for low temperature DTA work. Any gas sent to such a low temperature assembly must be completely dried before use to prevent gas condensation problems.

❖ FACTORS AFFECTING THE DTA CURVE:

1. Dynamic gaseous atmosphere
2. Static gaseous atmosphere.

The various factor affecting the DTA curve are as follows:

1. Environmental factors.

The DTA technique is more sensitive to the gaseous environment around the sample.
Reaction of the atmospheric gases with the sample may also produce extra peaks in the curve.
In DTA, two types gaseous environment are used,
Static gaseous atmosphere: The atmosphere of the sample is changing in concentration chemically due to the evolved gases and physically due to convection current.
Dynamic gaseous atmosphere: Gases are swept in a controlled manner.

2. Instrumental factors.

High thermal conductivity → sharp exothermic
Poor thermal conductivity → sharp endothermic

If material has
high thermal conductivity- sharp exothermic peaks and flat endothermic peaks are obtained eg. Metals.
Poor thermal conductivity- sharp endothermic peaks and flat exothermic peaks are obtained eg. Ceramic.
The size of the holder and the amount of sample should be as small as possible for better resolution.

The thickness of the thermocouple wires affects the intensity of peaks, shape of peaks and the baseline.
If the wires used are thick- more distortion of peak heights and peak temperature may take place.
If thinner wires are used- less distortion of peak heights and peak temperature may take place. But the resistance is high and may be unstable in impedance matching.

thick → more distortion in peak height/T.
thin → less distortion in peak height/T.

3. Sample Characteristics:
Physical
Packing density.
Particle size
• Peak area decreases with increase in size.
• Peak T shifts to higher values with increase in size.
• Completion T decreases with decrease in size.
• Degree of crystallinity.
• Amount of sample influence peak area.
• As wt of the sample increases peak intensity and temperature.
• In order to maintain the heat capacity nearly constant during heating, the sample is generally mixed with diluents. Generally, diluents affects the area, temperature and even resolution of the DTA peaks.

peak area ↓ = ↑ in size
peak temp ↑ = ↑ in size.
peak temp ↑ = ↑ weight of sample

Chemical:

- The chemical reactivity of the sample, the sample holder, thermocouple material, the ambient gaseous environment and added diluents greatly alter the DTA peaks.
- Therefore, one should make every effort to select these materials as inert chemically as possible with the sample.

APPLICATIONS OF DTA:

every sample → peculiar DTA curve.

1. DTA Curves are characteristic for a given substance and hence help to identify it.
2. The thermal stability of oxalates, carbonates, oxides and metal complexes can be studied.
3. The purity of organic materials like polymers, oils, fats and pharmaceuticals can be determined by DTA.
4. The heat of reaction of chemical reactions and phase changes can be determined as the peak area is a linear function of the heat of the reaction.
5. DTA is used for identification and quantitative analysis of inorganic and organic materials.

TGA → change in mass

DTA → difference in temperature.

DSC

Thermometric Titration.

c. Differential Scanning Calorimetry:

In DSC the heat flow is measured and plotted against temperature of furnace or time to get a thermogram. This is the basis of Differential Scanning Calorimetry (DSC). Differential scanning calorimetry (DSC) is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

It is used for determination of melting point, Crystallization, Glass Transition, O.I.T. (Oxidative Induction Time-It is a standardized test performed in DSC that measures the level of stabilization of the material tested. The time between melting and onset of decomposition in isothermal conditions is measured), Polymorphism, Purity, Specific Heat, Kinetic Studies, Curing reactions(The process in which an adhesive undergoes a chemical reaction and becomes a solid by forming a bonded joint), Denaturation (A process pertaining to change in the structure of a protein from regular to irregular arrangement of polypeptide chains)

Thank you!

Thank You