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CONTENS:

Thermal method of analysis

DEFINATION:

Thermal method of analysis: comprise a group of techniques in which a physical property of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature programme.

Different Techniques of Thermal methods of Analysis.

Method	Abbreviation	Property Measured
Differential thermal analysis	DTA	Temperature difference
Differential scanning calorimetry	DSC	Enthalpy
Thermogravimetric analysis	TGA	Mass
Dynamic mechanical analysis	DMA	Deformation
Dielectric thermal analysis	DEA	Deformation
Evolved gas analysis	EGA	Gaseous decomposition
Thermo-optical analysis	TOA	Optical properties

History of DSC:

The technique was developed by E.S. Watson and M.J. O'Neill in 1960, and introduced commercially at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in 1963.

Thermal transitions

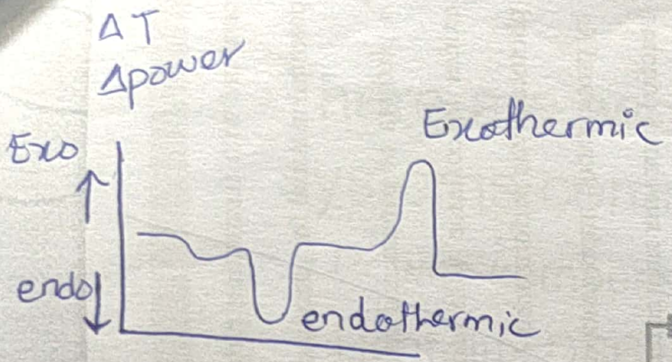
Low-molecular-weight materials change their physical state as the temperature increases; at the melting point they change visibly from a crystal to a liquid, and at the boiling point from a liquid to a vapor. Each true phase transition is defined thermodynamically by a marked change in the enthalpy. However, since changes in enthalpy can only be determined with expensive instruments, other methods are generally employed to determine the transition temperatures.

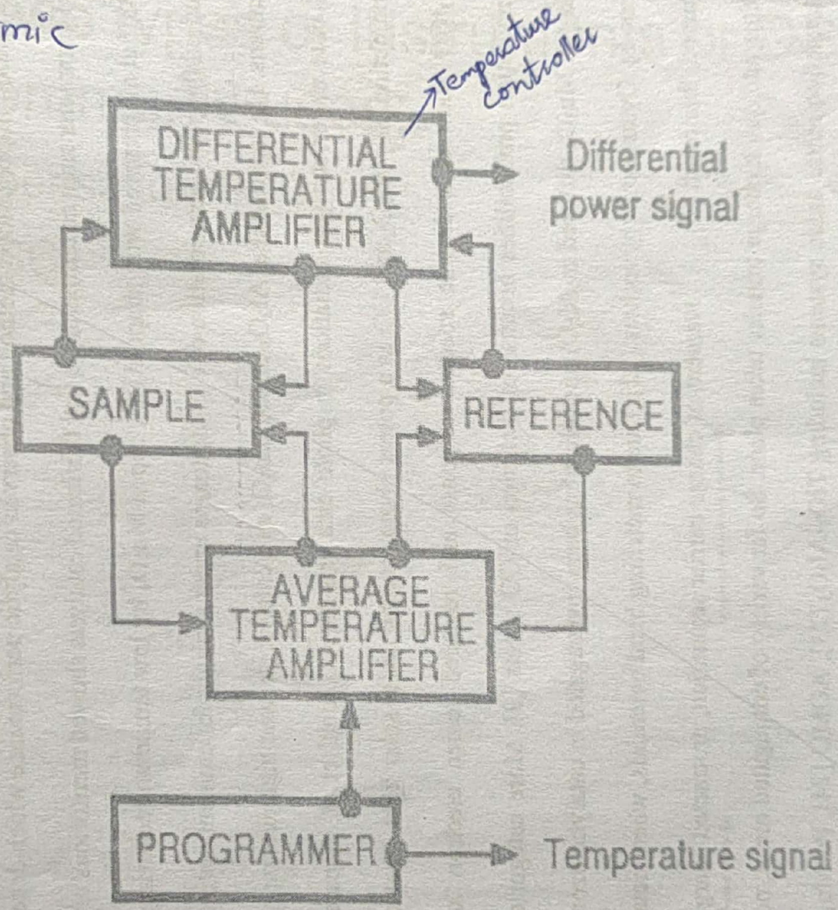
For example, in organic chemistry melting points are measured via the formation of the liquid state in the melting-point tube. This method can be used for the determination of the melting point

Principle:

- The sample and reference are maintained at the same temperature, even during a thermal event in the sample.
- The energy required to maintain zero temperature difference between the sample and the reference is measured.
- During a thermal event in the sample, the system will transfer heat to or fro from the sample pan to maintain the same temperature in reference and sample pans.

Block diagram of DSC

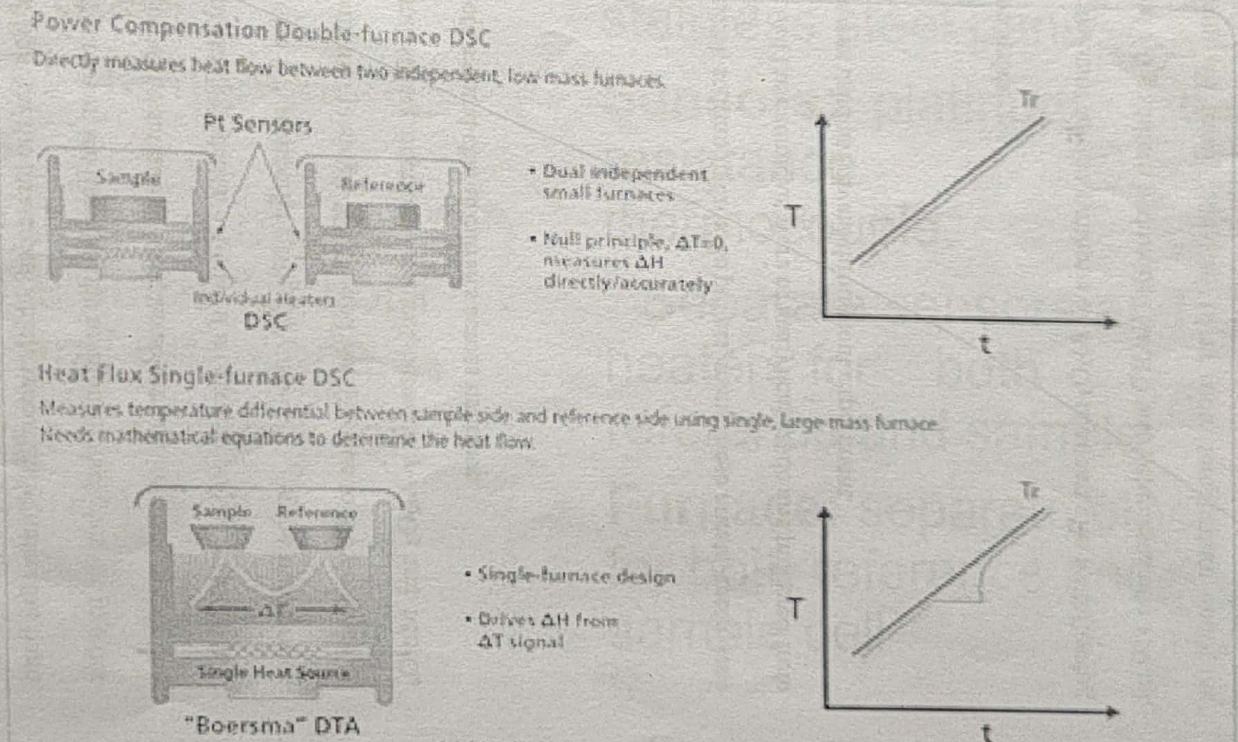




Intsrumentation:

- There are two types of Instruments or DSC systems commonly used:

1) Power-compensation DSC
2) Heat-flux DSC



Scanned with CamScanner

DSC Instruments:

1) Size and shape of sample and furnance
2) Heating Rate : ⇒ Sample & reference temperature should increase at same time.
material form which sample holder is made up of

HEAT FLUX DSC

- **Sample holder:** platinum, aluminum and stainless Steel.
- **Sensors:** Temperature sensors.

  Usually thermocouples which are same for both sample and reference.
- **Furnace:** one block for both reference and sample cell.

POWER COMPENSATION DSC

- **Sample holder** : platinum, aluminum and stainless steel pans.
- **Sensors:** platinum resistance thermocouple.

  Separate sensors and heaters for both reference and sample.
- **Furnace:** separate block for both reference and sample cell

Applications:-
① finger print region /sensor/analyse point ⇒ DTA cure for samples will always be different.
② Polymeric material To determine the characteristics of polymeric material
③ Testing purity of Drugs & other chemicals.
④ Determination of heat of reaction
⑤ Determination of stability of ligands

HEAT FLUX DSC

- The sample and the reference cells are heated at a constant rate and thermocouples are used to detect the temperature difference between sample side and the reference side using single large mass furnace
- The large single furnace which acts as an infinite heat sink to provide or absorb heat from the sample.
- The dynamic sample chamber is the environment of the sample pan compartments and the purge gas.
- Nitrogen is the most common gas , but alternate inert gas is helium or argon
- When using an oxidative atmosphere air or oxygen are the gases of choice
- The heat flux DSC is based on the change in the temperature between the sample and the

Instrument

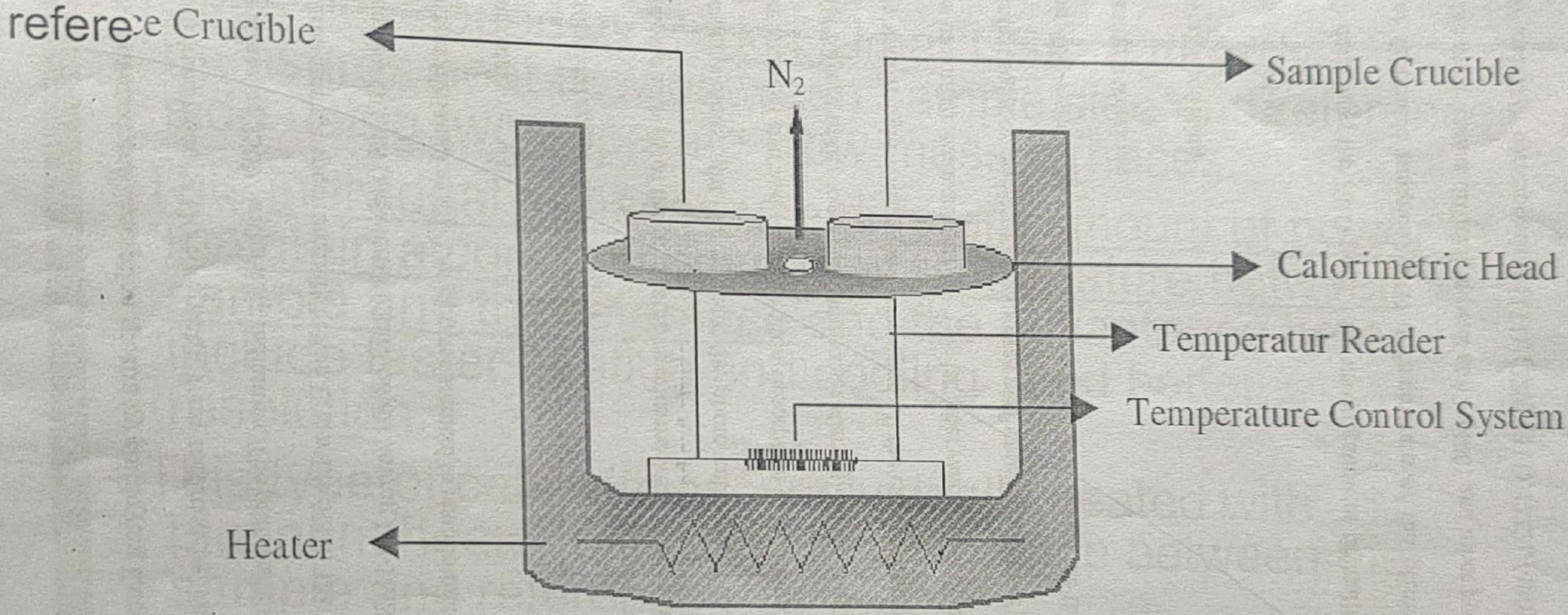


fig. Heat flux DSC

POWER COMPENSATION DSC

- Introduced in the early1960s.
- It was developed by Perkin Elmer USA. It directly measures heat flow between sample side and reference side using two separate , low mass furnaces.
- This individual furnaces use different amount of power to maintain a constant change of temperature between sample and the reference and the advantages here include faster heating and cooling , and better resolution.
- This type of cell, with two individually heated with platinum heater monitors the difference between the sample and reference .
- Platinum resistance thermometers track the temperature variations for the sample and reference cells.
- Holes in the compartment lids allows the purge gas to enter and contact the sample and reference .

Instrument

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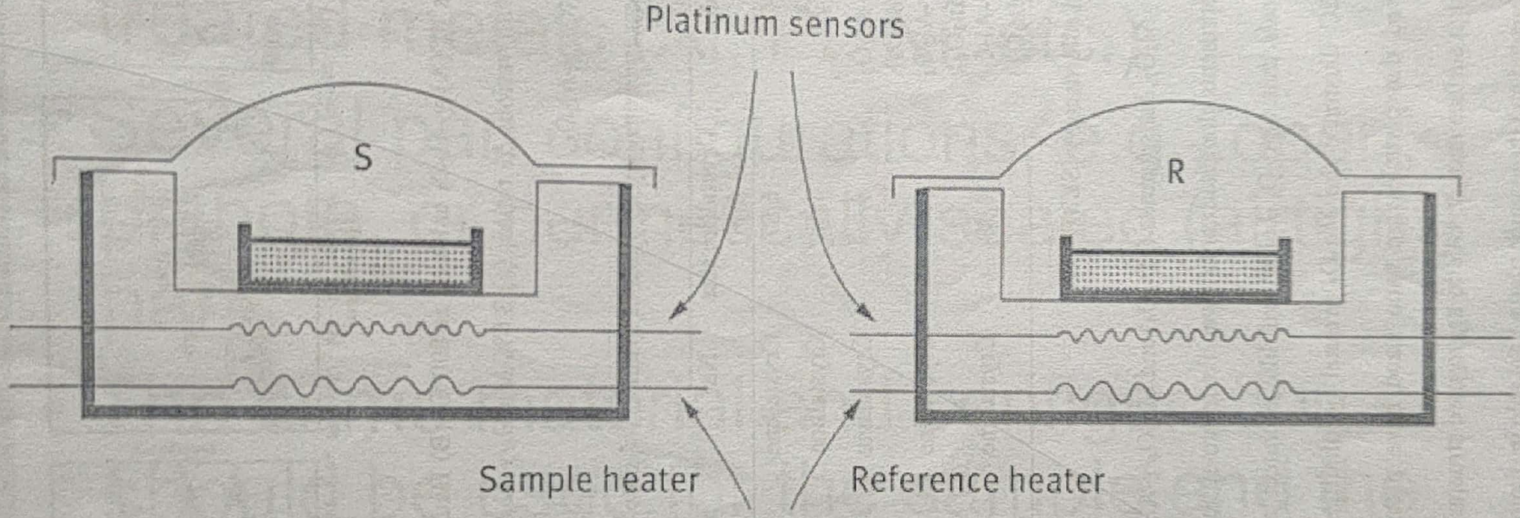
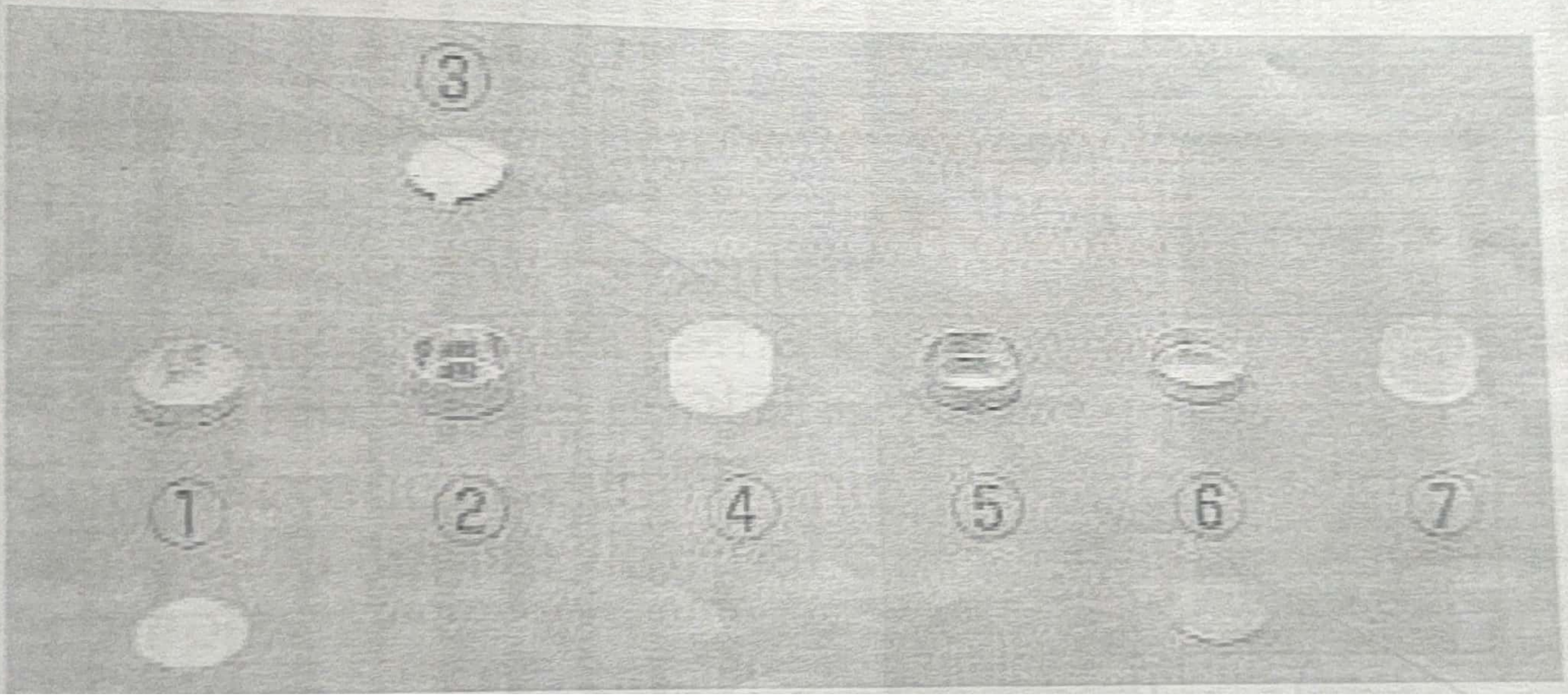


Fig. Power compensated DSC

Sampling:

- Accurately-weigh samples (~3-20 mg)
- Small sample pans (0.1 mL) of inert or treated metals (Al, Pt, Ni, etc.)
- Several pan configurations, e.g., open, pinhole, or hermetically-sealed (airtight) pans
- The same material and configuration should be used for the sample and the reference
- Material should completely cover the bottom of the pan to ensure good thermal contact

Small sample masses and low heating rates increase resolution



Reference material

An inert material like alumina is generally used. An empty pan with lid is also used if the sample weight is small.

- With sample weight it is necessary to use reference material , because the total weight of the sample and its container should be approximately the same as the total weight of the reference and its containers .
- The reference material should be selected so that it posses similar thermal characteristics to the sample .
- Most widely used reference material is alpha alumina

Keiselguhr is another reference material normally used when sample has a fibrous nature

Typical DSC curve

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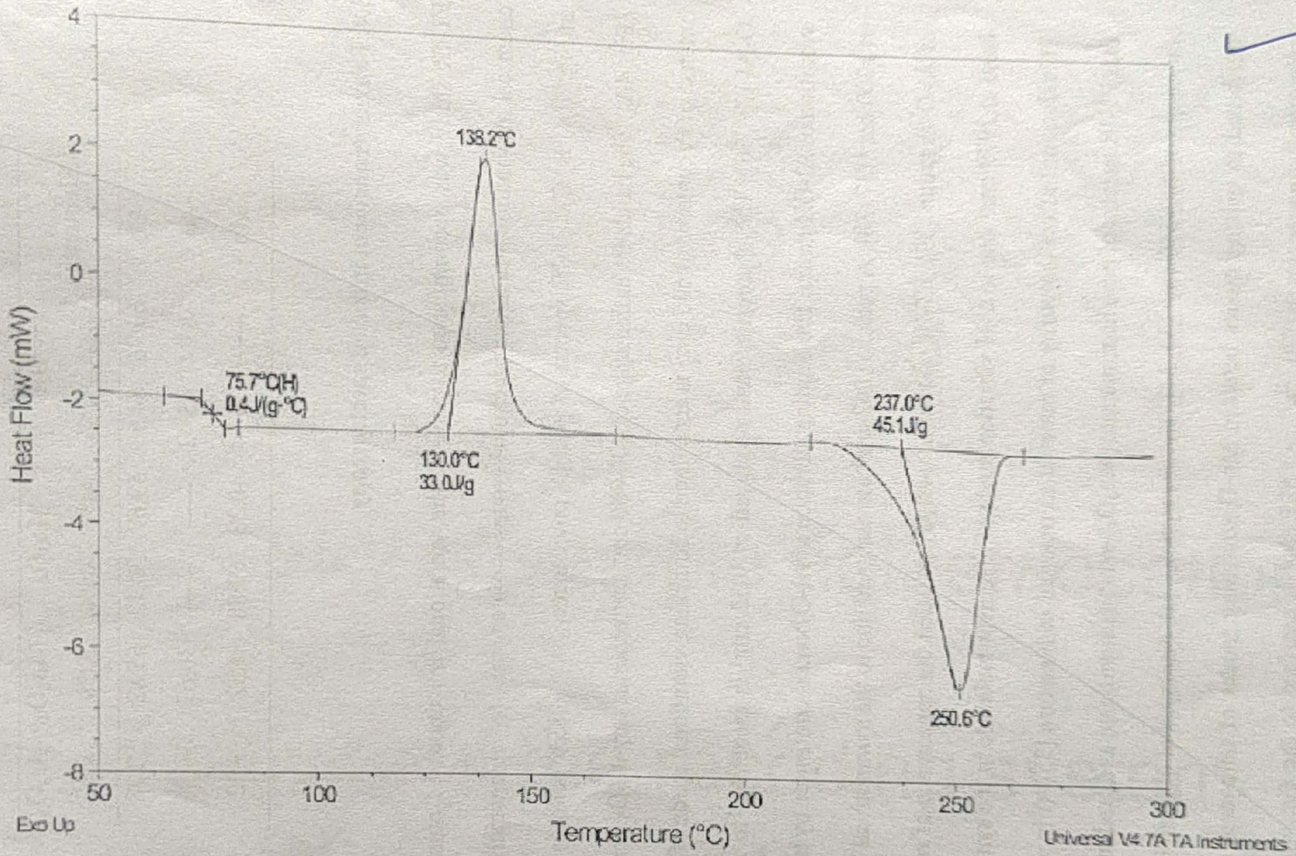

DSC Scan of Polyethylene Terephthalate: Heat Flow versus Temperature

Factors affecting DSC curve

1-Instrumental factors

a- Furnace heating rate

b- Recording or chart speed

c- Furnace atmosphere

d- Geometry of sample holder/location of sensors

e- Sensitivity of the recoding system

f-Composition of sample containers

Cont....

2-*Sample characteristics*

a- Amount of sample

b- Nature of sample

c- Sample packing

d- Solubility of evolved gases in the sample

e- Particle size

f- Heat of reaction

Advantages:

- Rapidity of the determination
- Small sample masses
- Versatility
- Simplicity
- Applicable
- Study many types of chemical reactions
- No of Need calibration over the entire temperature for DSC

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Disadvantages:

- Relative low accuracy
- Not be used for overlapping reactions.
- Difficulties in test cell preparation in avoiding evaporation of volatile Solvents
- Does not detect gas generation

APPLICATIONS

- Purity determination of sample directly
- Detection of polymorphism
- Quantification of polymorph
- Detection of meta stable polymorph
- Detection of isomerism
- Stability / compatibility studies
- Percentage crystallinity determination
- Lyophilisation studies
- Finger printing
- Choosing better solvent