

CHAPTER 4: THERMAL ANALYSIS

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Thermal Methods of Analysis

- It is a branch of analytical science where the properties of analysis are studied as they change with temperature.
- TGA: Experimental technique in which the mass of a sample is measured as function of sample temperature or time.
- The sample is typically heated at a constant heating rate (so called dynamic measurement) or held at a constant temperature (isothermal measurement)
- The results of a TGA measurement are usually displayed as a TGA curve in which mass or % mass is plotted against temperature.

TGA, Basics

Measures changes in weight in relation to changes in temperature.

The measured weight loss curve gives information on:

- changes in sample composition
- thermal stability
- kinetic parameters for chemical reactions in the sample

A derivative weight loss curve can be used to tell the point at which weight loss is most apparent

... Includes several different methods. These are distinguished from one another by the property which is measured.

- Thermogravimetric analysis (TGA): mass
- Differential thermal analysis (DTA): temperature difference
- Differential scanning calorimetry (DSC): heat difference
- Pressurized TGA (PTGA): mass changes as function of pressure.
- Thermo mechanical analysis (TMA): deformations and dimension
- Dilatometry (DIL): volume
- Evolved gas analysis (EGA): gaseous decomposition products

Often different properties may be measured at the same time:

TGA-DTA, TGA-EGA

Techniques	Quality measured
Thermogravimetric analysis (TGA)	Weight change
Differential scanning calorimetry (DSC)	Heats and temperature of transitions and reactions
Differential thermal analysis (DTA)	Temperatures of transitions and reactions

Mechanisms of Weight Change in TGA

- **Weight Loss:**

- Decomposition: The breaking apart of chemical bonds.
- Evaporation: The loss of volatiles with elevated temperature.
- Reduction: Interaction of sample to a reducing atmosphere (hydrogen, ammonia, etc).
- Desorption.

- Weight Gain:**

- Oxidation: Interaction of the sample with an oxidizing atmosphere.
- Absorption or Adsorption.

All of these are kinetic processes (i.e. there is a rate at which they occur).

TGA; Phenomena causing mass changes

Physical

Gas adsorption

Gas desorption

Phase transitions

- Vaporization
- Sublimation

Chemical

Decomposition

Break down reactions

Gas reactions

Chemisorption

(adsorption by means of chemical instead of physical forces)

TGA: Applications

- Characterization of
 - Thermal stability
 - Material purity
 - Determination of humidity
- Examination of
 - » Corrosion studies (e.g. oxidation or reactions with reactive gases)
 - » Gasification processes
 - » Kinetic processes

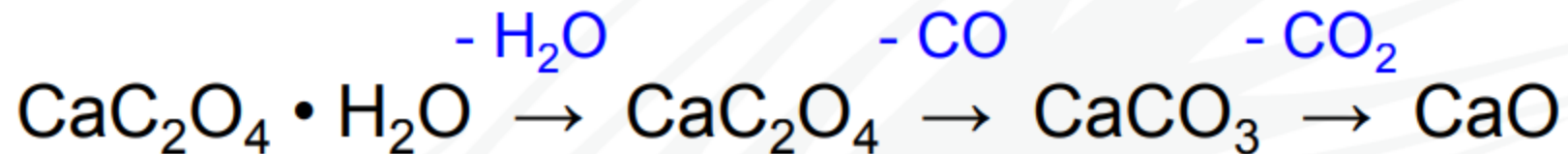
What TGA Can Tell You?

- I. Thermal Stability of Materials: **Explicate decomposition mechanism, fingerprint materials for identification & quality control**
- II. Oxidative Stability of Materials: **Oxidation of metals in air, Oxidative decomposition of organic substances in air/O₂, Thermal decomposition in inert atmosphere**
- III. Composition of Multi-component Systems: **Behaviors sufficiently different on the temperature scale can be identified and reaction mechanism formulated**
- IV. Estimated Lifetime of a Product: **Related to thermal stability**
- V. Decomposition Kinetics of Materials: **Rate of reaction, Activation Energy**
- VI. The Effect of Reactive or Corrosive Atmospheres on Materials: **Oxidation & Corrosion Studies**
- VII. Moisture and Volatiles Content of Materials: **Loss of moisture, drying, desorption**

TGA

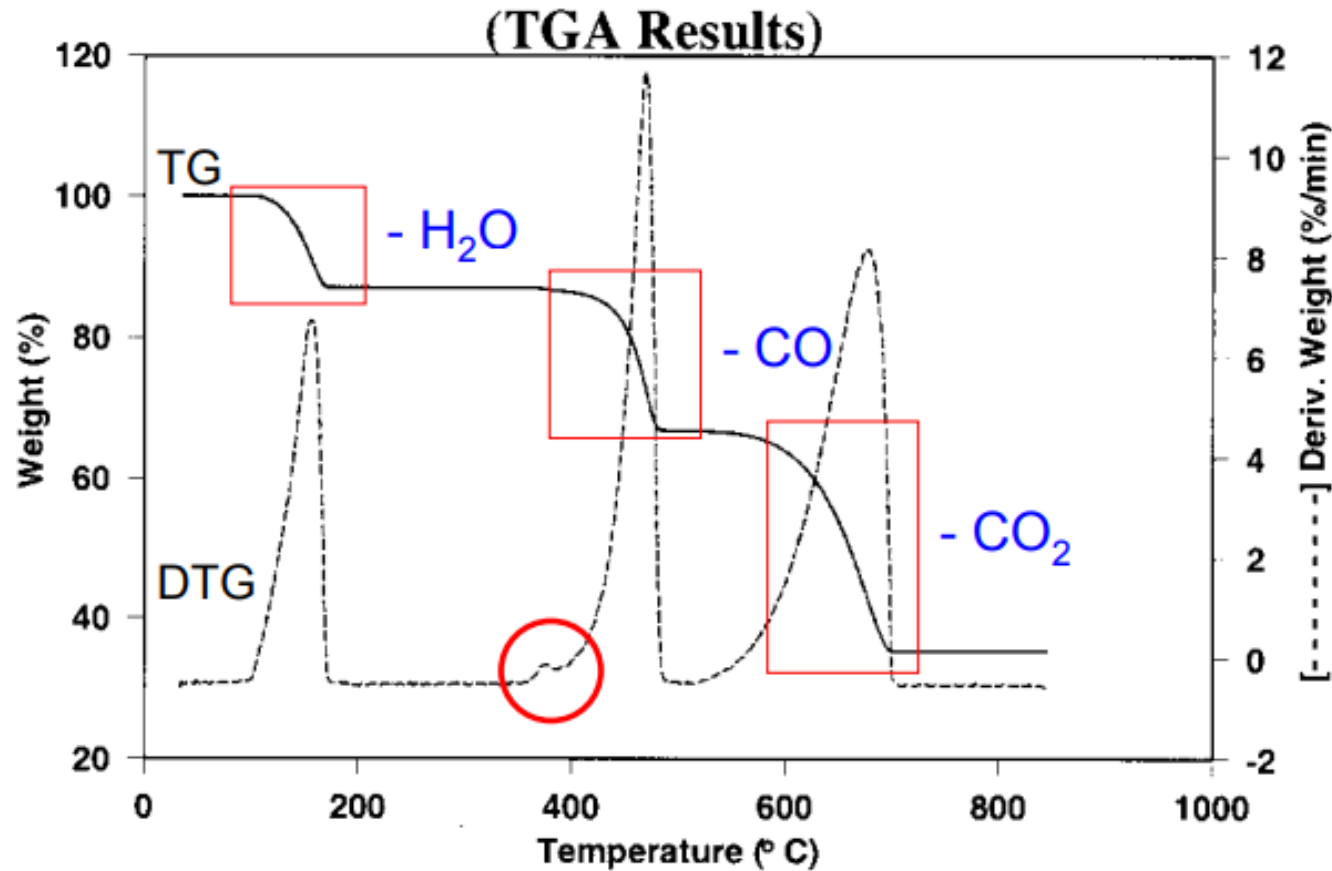
Ex. Decomposition of calcium oxalate monohydrate

- Calcium oxalate monohydrate, a standard material often used to demonstrate TGA performance.
- Exhibits three weight losses with temperature in an inert atmosphere (e.g. N₂).



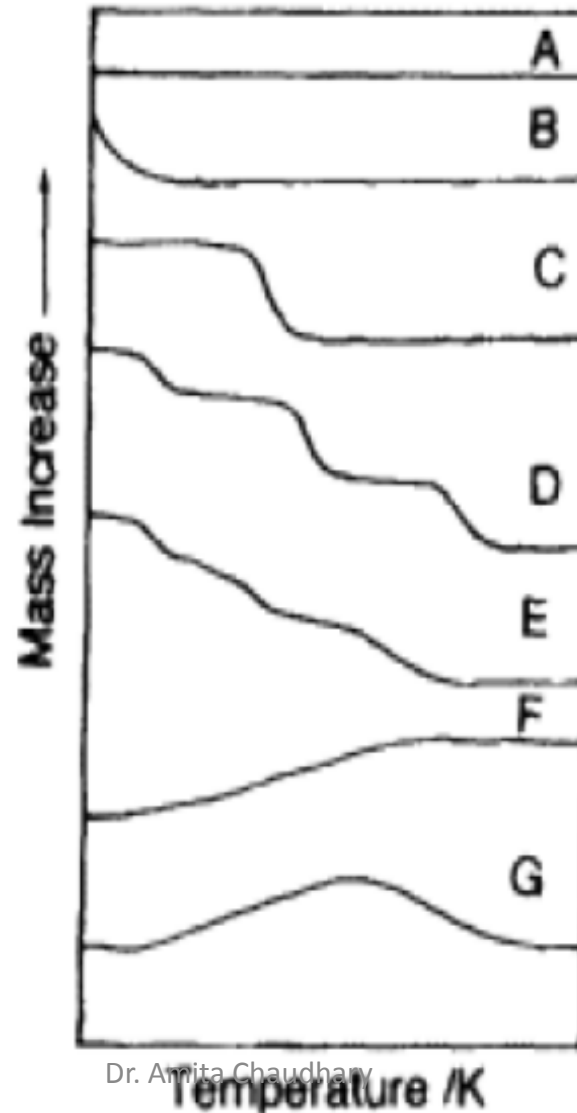
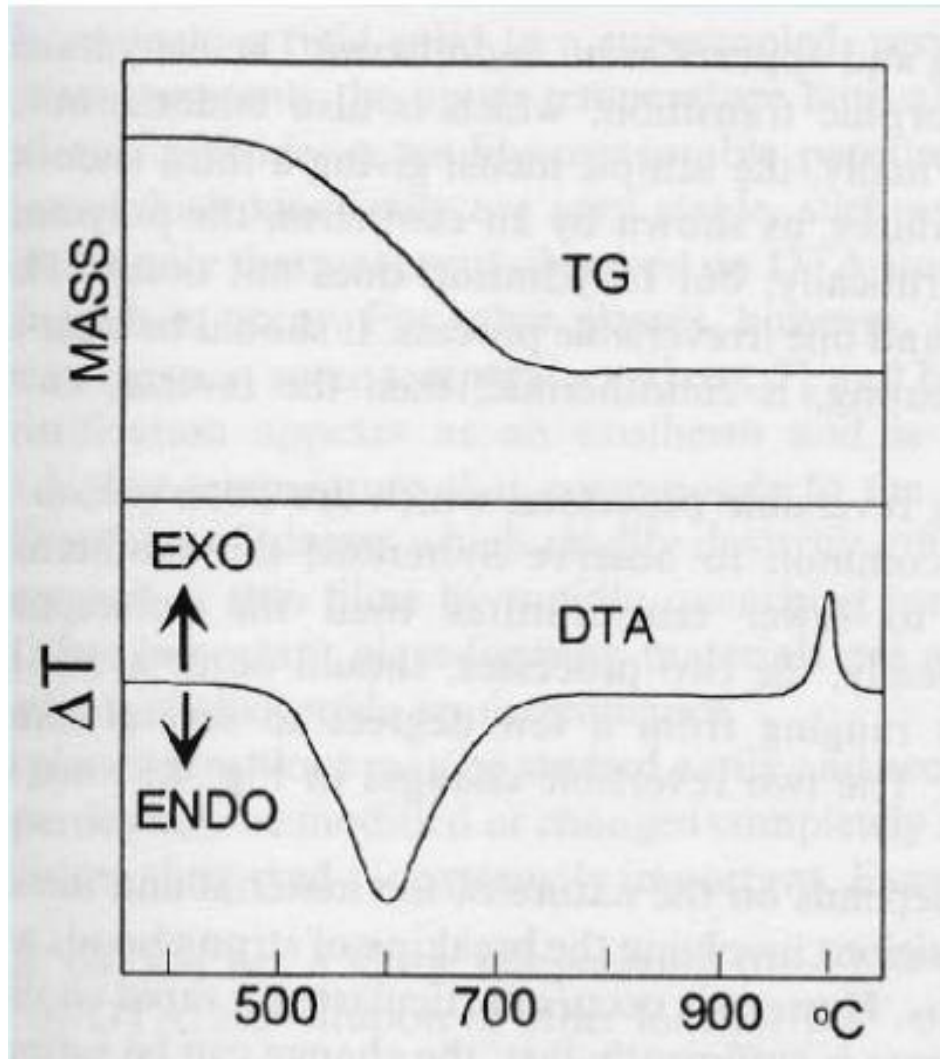
TGA

Ex. Decomposition of calcium oxalate monohydrate



Absolute confirmation of the decomposition process is possible when the gaseous by products are identified as they evolve, eg by mass spectrometry (MS).

Chapter 4: Thermo Gravimetric Analysis (TGA)



A: No mass change over entire range of temperature.

B: Desorption/Drying. Mass loss is large followed by mass plateau.

C: Single Stage Decomposition

D: Multistage Decomposition

E: Similar to D but either due to faster heating rates or due to no intermediaries

F: Atmospheric Reaction, Increase in mass, reactions like surface oxidation.

G: Similar to Curve F, but product decomposes at higher temperatures.

Common gaseous components originating from inorganic materials that decompose before the melting point:

H_2O , CO , CO_2 , SO_x , NO_x , Cl_2 , F_2 , CH_3OH , etc.

Also some chemical reactions in solid phase result in gaseous weight loss ex.



Factors affecting the TG curve

Heating rate
Sample size

Increases the temperature at which sample decomposition occurs.

Particle size of sample
Packing
Crucible shape
Gas flow rate

Affects the progress of their reaction

Type of thermo gravimetric analysis

Dynamic TGA - in this type of analysis the sample is subjected to conditions of continuous increase in temperature usually linear with time

Isothermal or static TGA - in this type of analysis the sample is maintained at a constant temperature for a period of time during which any change in weight are noted

Principle of TGA Operation

A TGA analysis is performed by gradually raising the temperature of a sample in a furnace as its weight is measured on an analytical balance that remains outside of the furnace. In TGA, mass loss is observed if a thermal event involves loss of a volatile component. Chemical reactions, such as combustion, involve mass losses, whereas physical changes, such as melting, do not. The weight of the sample is plotted against temperature or time to illustrate thermal transitions in the material – such as loss of solvent and plasticizers in polymers, water of hydration in inorganic materials, and, finally, decomposition of the material.

Thermo Gravimetric analysis (TGA)

Principle:

- ✓ In thermogravimetric analysis, the sample is heated in a given environment (Air, N_2 , CO_2 , He, Ar etc.) at controlled rate.
- ✓ The change in the weight of the substance is recorded as a function of **temperature or time**.
- ✓ The temperature is increased at a constant rate for a **known initial weight of the substance** and the changes in weights are recorded as a function of temperature at different time interval.
- ✓ This plot of weight change against temperature is called **thermogravimetric curve or thermogram**.

Instrumentation

- Modern TGA equipment has a sensitive balance, usually a **microbalance**, for continuously measuring sample weight, a **furnace** surrounding a sample holder, and a **purge gas system** for providing inert or reactive atmospheres.
- **A computer** generally controls the furnace and the data (weight vs. sample temperature) is collected and processed by computer.
- Several modern analytical microbalances are commercially available - **torsion balances, spring balances, and electro balances.**
- In general, the balance is designed so that a change in sample weight generates an **electrical signal proportional to the weight change.** The electrical signal is transformed into weight or weight loss by the data processing system and plotted on the y-axis of the thermal curve.

Applications

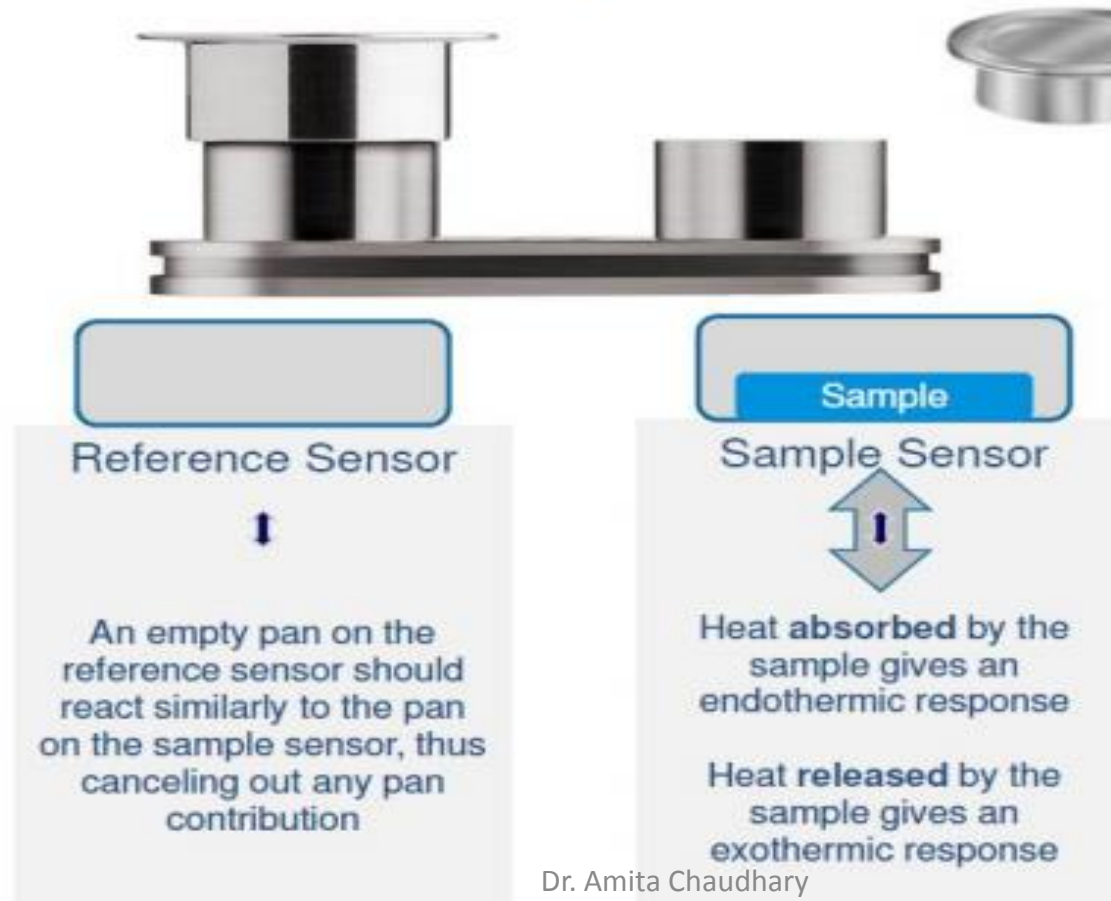
Principle uses of TGA include measurement of a material's thermal stability and its composition. Typical applications include:

- Filler content of polymer resins
- Residual solvent content
- Carbon black content
- Decomposition temperature
- Moisture content of organic and inorganic materials
- Plasticizer content of polymers
- Oxidative stability
- Performance of stabilizers
- Low molecular weight monomers in polymers

Differential Scanning Calorimetry (DSC)

What does a DSC measure?

A DSC measures the difference in heat flow rate ($\text{mW} = \text{mJ/sec}$) between a sample and inert reference as a function of time and temperature



DSC- Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) relies on the measurement of the difference between the heat flow vs. temperature relation of the sample and the heat flow vs. temperature relation of a standard. There are many types of calorimeters and the criteria for their classification.

The **classification of these devices** can be made in respect of:

- **Ranges of temperature and pressure range** – high temperature/pressure and low temperature/pressure;
- **Type of the test process** – to measure the heat of mixing, heat capacity;
- **Thermodynamic conditions** – adiabatic, non-adiabatic;
- **Sample weight change during the measurement** – open (with the exchange of mass), closed (no mass transfer).

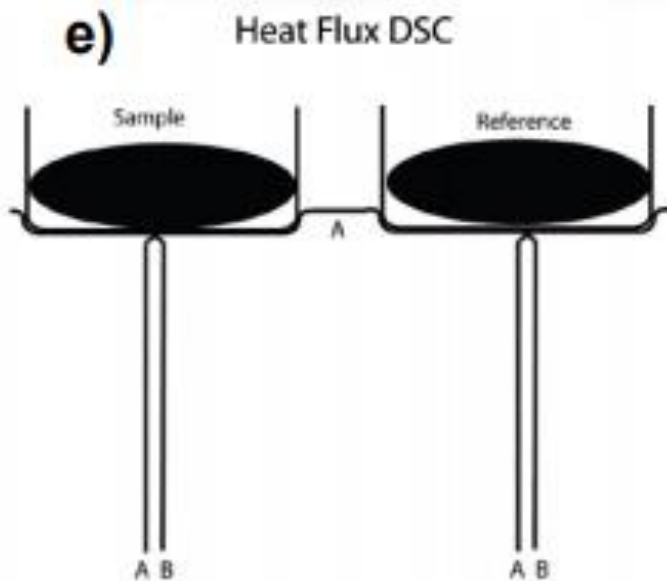
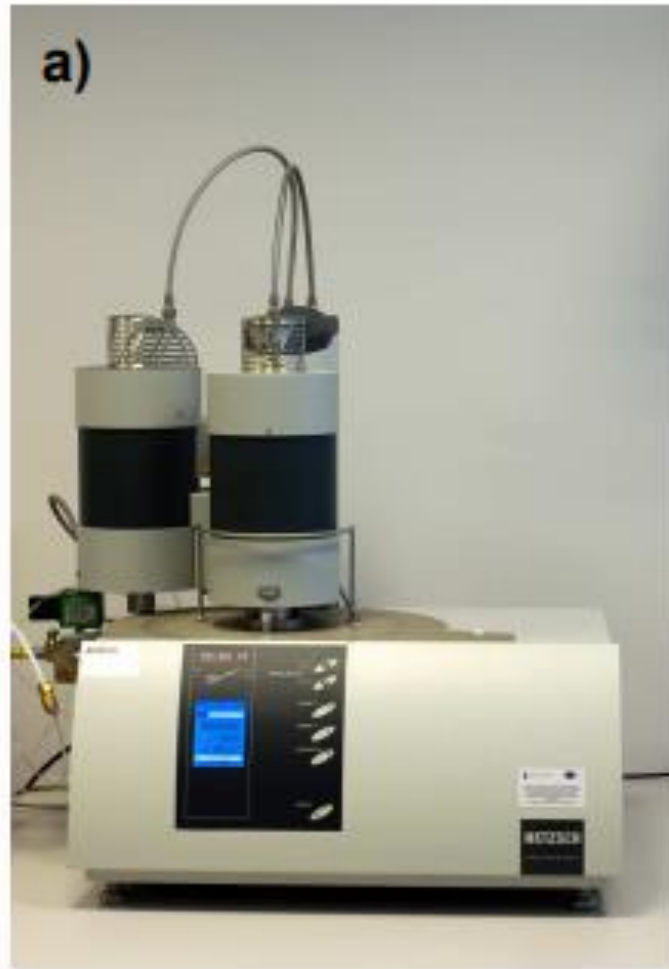
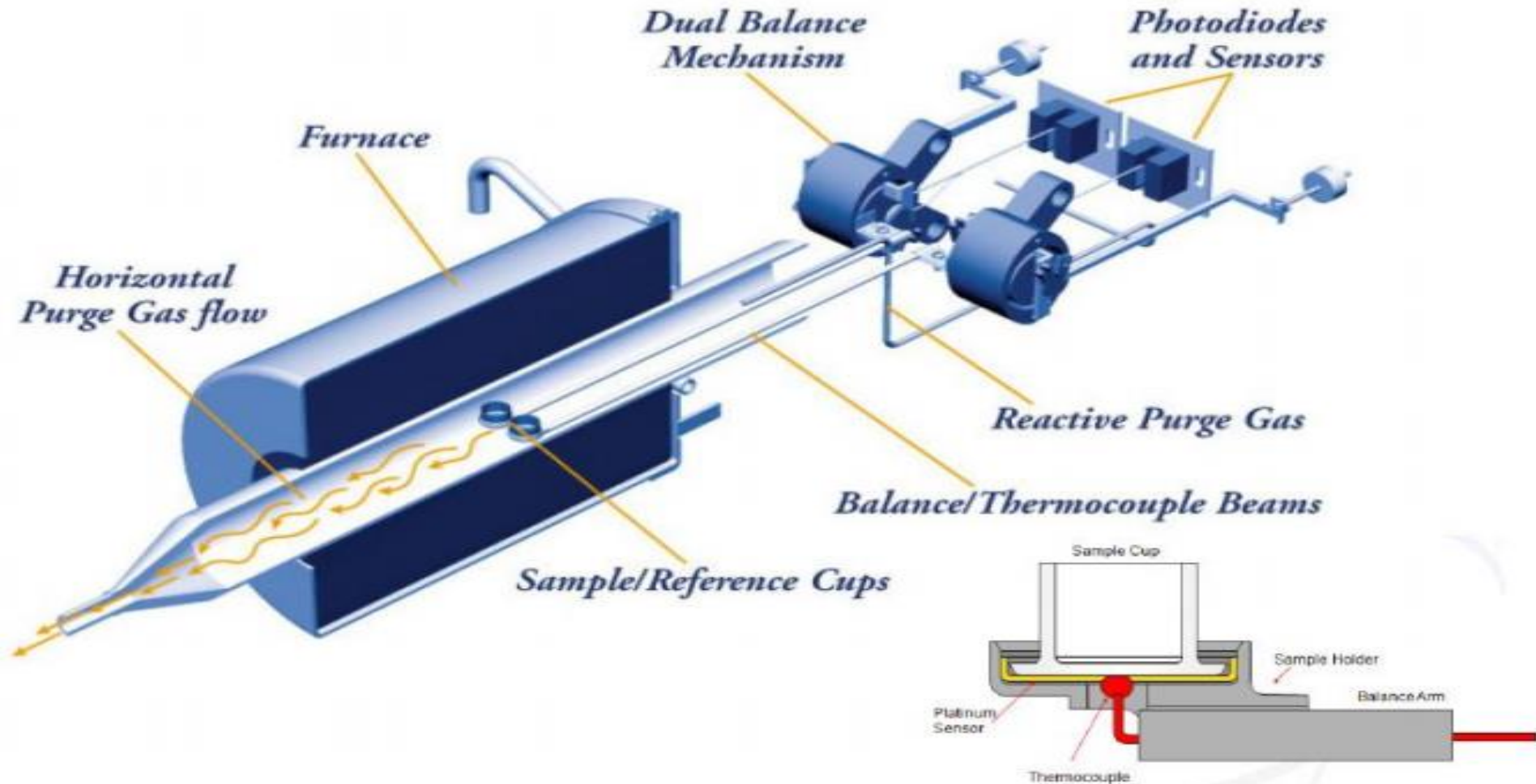


Fig. 1. Photos of the DSC Instrument: a) overview, b) Cross-sectional of DSC, c) the DSC sample carrier; d) DSC crucibles; e) DSC sample carrier cross section

DSC-TGA: Instrument Design

DSC-TGA (SDT): Instrument Design



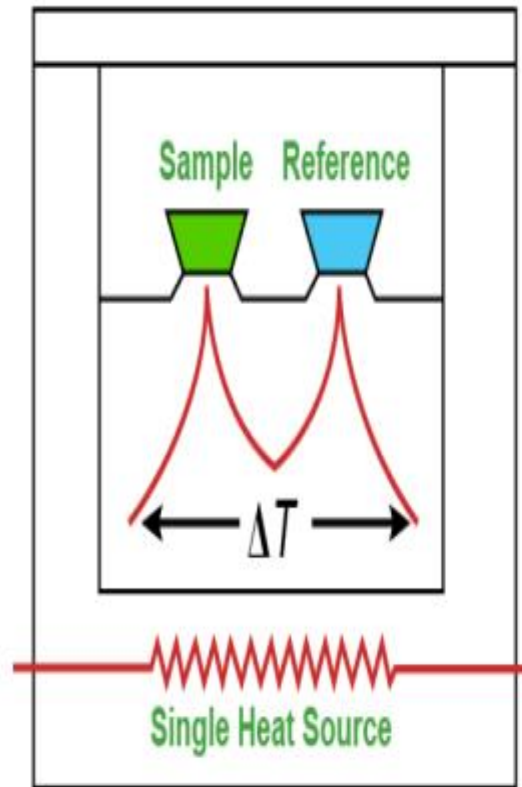
Type of DSC

Among the differential scanning calorimeters, two types of devices :

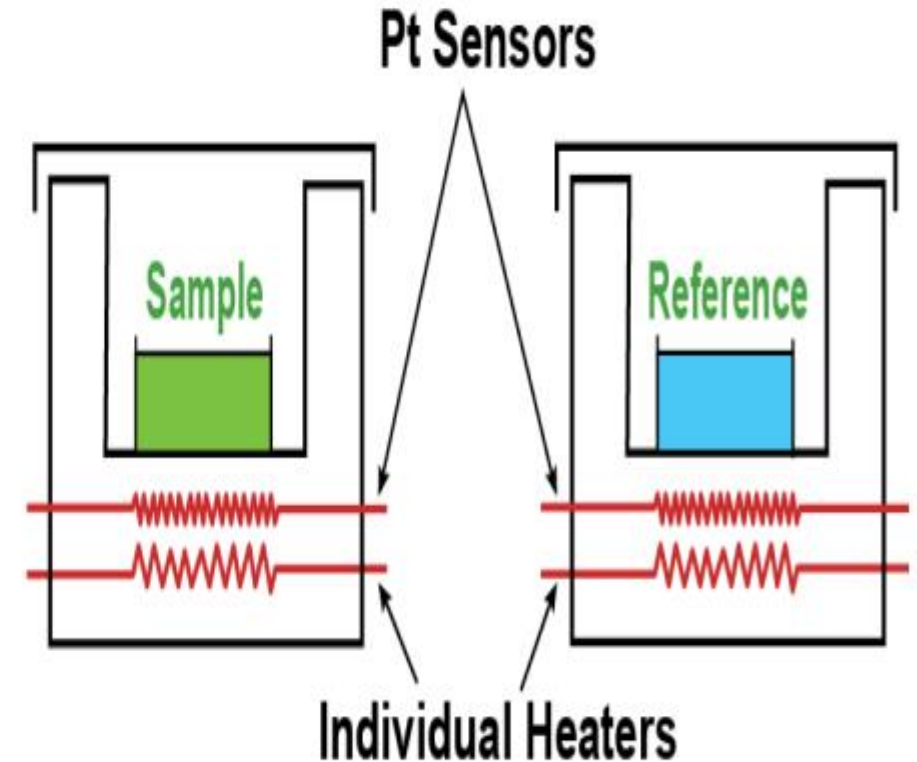
- **Flow (heat flux DSC):** In the case of heat flux differential scanning calorimeters, directly measured signal is a change in temperature between a test sample and a reference sample (Fig1a,b,c,e). This difference is proportional to the flow of the heat flux between the two samples and is automatically converted to the value of the heat flux using special software.
- **Compensation (power compensation DSC):** It consist of two identical and isolated heaters located in the same temperature (in one heater a tested sample is placed and in the other - a reference sample). Temperature changes during the phase transformation or the reaction in the sample are compensated by varying the electrical energy supplied to the heater which is directly proportional to the heat absorbed during the process .

Types of DSC

There are two different types of DSC: *Heat-flux DSC* in which heat flux remains constant and *Power differential DSC* in which power supply remains constant.



Heat Flux DSC:
Quantitative DTA



Power Compensated DSC:
Measures Enthalpy Change,
Compensates heat release or
gained during thermal event

The result of calorimetric measurements is a DSC curve shown as the temperature/ time dependence on the heat flux (per time unit).

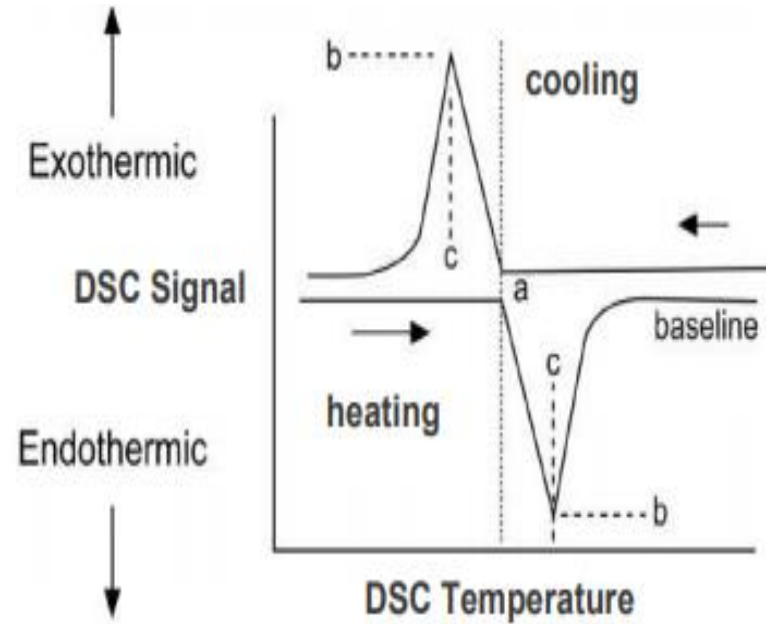
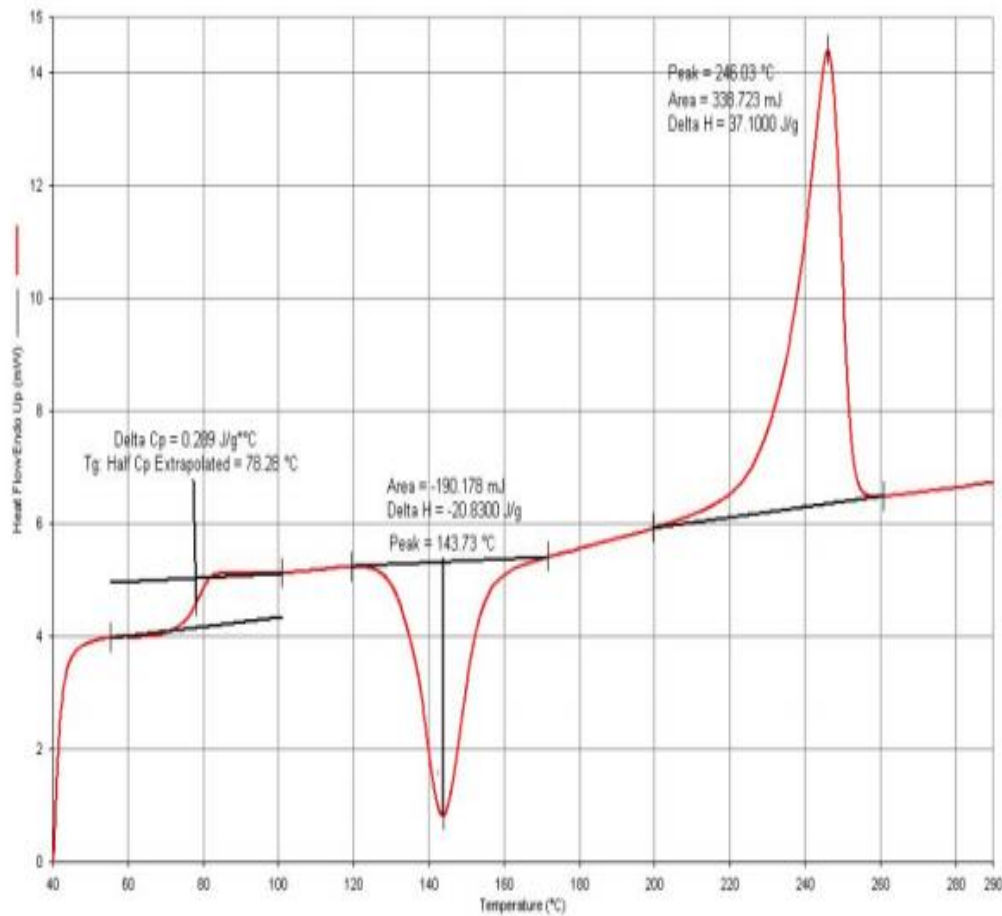


Fig. 2. DSC curves of heating and cooling cycles for pure metal: a - onset temperatures (phase transformation), b - peak signals, c - peak temperatures

- An endo- and exothermic peaks are recorded on these curves (Fig. 2), which result from the temperature differences between a tested sample and a reference sample, showing negative or positive deviations from the so called “baseline”, which is recorded at the time when no transformations/ reactions occurs in the sample.
- The differences are caused by phase transformations and chemical reactions occurring in the material.
- If the temperature of a tested sample during the phase transformation/chemical reaction is lower than the reference temperature, the heat is absorbed. The situation is registered as the endothermic peak.
- Conversely, when the sample temperature is higher and there is separation of the heat, then this is marked as the exothermic effect



In this sample of PET (Polyethylene terephthalate) the first transition undergoes is seen at 78 °C, and is known as the glass transition temperature (T_g). At this transition, the polymer changes from a relatively hard, glassy solid, to a softer, more flexible or rubbery material. This is observed as a deflection in the heat flow profile, and not as a distinct peak as in the other transitions. The second transition, occurring at 144 °C, is the crystallization point. As the temperature is increased to this point, the polymer structure gains enough flexibility to rearrange from the amorphous glassy state generated by the rapid quenching, into a lower energy crystalline state. This lower energy state thus evolves heat, which is seen as a negative peak on the graph above. Finally, as the heat is continued to increase, the PET melt point is reached. The DSC temperature can then be rapidly quenched to produce a fully amorphous polymer, or slowly lowered to produce a crystalline

DSC Heat Flow

$$\frac{dH}{dt} = C_p \frac{dT}{dt}$$

$$\frac{dT}{dt} = \text{Heating Rate}$$

$$\frac{dH}{dt} = \text{DSC heat flow signal}$$

$$C_p = \text{Sample Heat Capacity} \\ = \text{Sample Specific Heat} \times \text{Sample Weight}$$

Heat flows into the sample as a result of either Heat flows out of the sample as a result of either

- Heat capacity (heating)
- Glass Transition (T_g)
- Melting
- Evaporation
- Other endothermic processes

- Heat capacity (cooling)
- Crystallization
- Curing
- Oxidation
- Other exothermic processes

DSC measurements can be made in two ways: by measuring the electrical energy provided to heaters below the pans necessary to maintain the two pans at the same temperature (power compensation), or by measuring the heat flow (differential temperature) as a function of sample temperature (heat flux). The DSC ultimately outputs the differential heat flow (heat/time) between your material and the empty reference pan. Heat capacity may be determined by taking the ratio of heat flow to heating rate. Thus,

$$C_p = \frac{q}{\Delta T}$$

where C_p is the material's heat capacity, q is the heat flow through the material over a given time, and ΔT is the change in temperature over that same time.

Enthalpy of Transition

- The area under the peaks in the curve can be use to calculate the enthalpy of transition.
The enthalpy of transition can be expressed as

$$\Delta H = KA$$

Where, ΔH = Change in Enthalpy

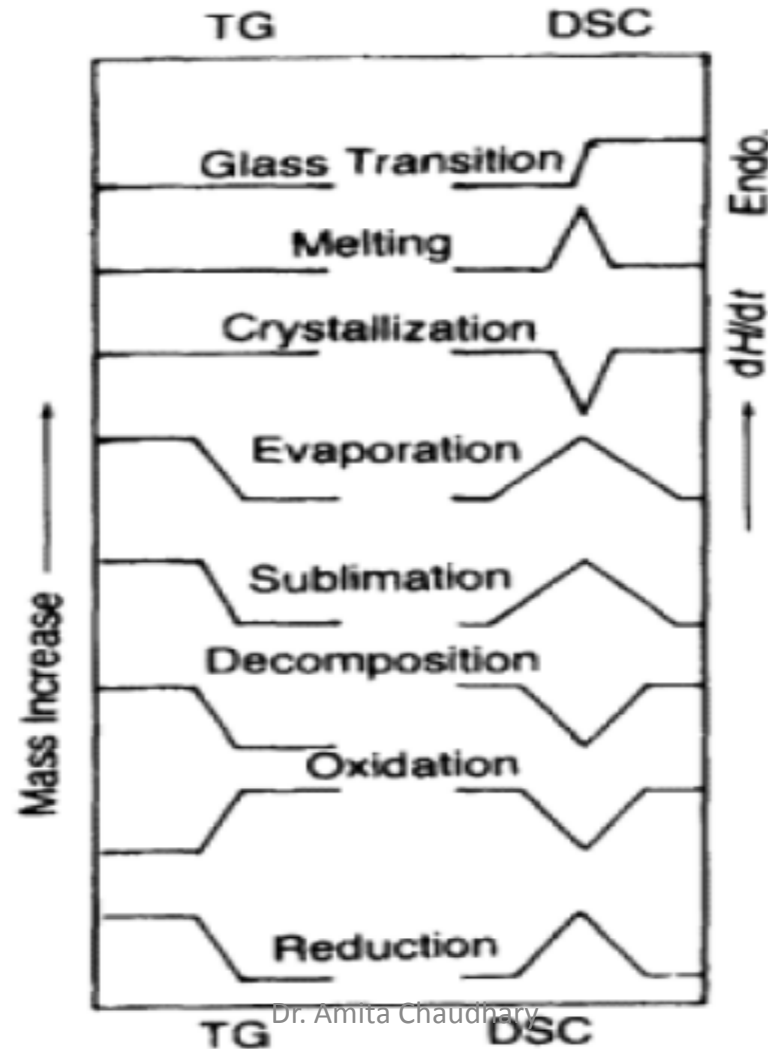
K= calorimetric Constant

A= Area under the peak (by integration of peak)

- Area under the peak is directly proportional to the heat evolved or absorbed in a reaction.
- Height of the peak represents the rate of reaction.

Interpretation of curves

Comparison of TG-DSC for variety of physicochemical processes



Applications

Common usages of DSC include investigation, selection, comparison, and end-use performance evaluation of materials in research, quality control, and production applications. DSC is commonly used to measure a variety of properties in both organic and inorganic materials, from metals and simple compounds to polymers and pharmaceuticals. The properties measured include:

- Glass transitions
 - Phase changes
 - Melting
 - Crystallization
 - Product stability
 - Cure/cure kinetics
 - Oxidative stability
 - Heat capacity and heat of fusion measurements
- Polymers
 - Identification
 - Melt Point
 - Glass Transition Point
 - Degree of Crystallization
 - Cross-Linking Characterization
 - Composites
 - Characterization of Blends
 - Examination of Epoxy Cure
 - Organic Additives
 - Oxidative Stability of Antioxidant Formulations
 - Heat Capacity
 - Purity
 - Quality Control
 - Cure quality of epoxies and epoxy composites.
 - Crystallization in pharmaceutical compounds.
 - Melting point depression.