M.Sc (Chemistry)

Thermal Analysis

Syllabus:

Theory and applications of

TGA – Thermogravimetric Analysis

DTG – Derived Thermogravimetry

DTA - Differential Thermal analysis

DSC - Differential Scanning Calorimetry

EGD - Evolved Gas Detection

TMA – Thermomechanical Analysis

Thermal Analysis Techniques

Thermo gravimetric analysis (TGA): Monitoring the change of weight as a function of temperature.

Differential Thermal analysis (DTA): Change in thermal energy as a function of temperature. (exo- or endothermic).

Differential scanning calorimetry (DSC): Change in heat as a function of temperature.

Evolved Gas Detection (EGD): Evolved Gas is detected

Evolved Gas Detection (EGA): Evolved Gas is analysis

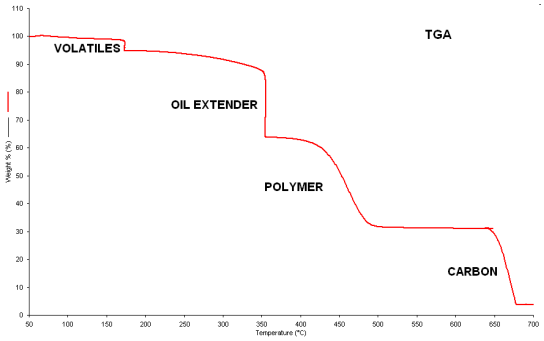
Thermomechanical analysis (TMA): Change of dimensions.

TGA – Thermogravimetric Analysis - Introduction

"TGA is a technique in which the mass of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature programme."

TGA measures the weight of a substance heated at a controlled rate as a function of temperature or time.

All materials ultimately decompose on heating, and the decomposition temperature and profile is a characteristic property of each material.



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TGA – Thermogravimetric Analysis: Example

Decomposition of calcium oxalate

Step-I

$$CaC_2O_4.H_2O \Rightarrow CaC_2O_4 + H_2O$$

MW 146 128 18

Step-II

$$CaC_2O_4 \Rightarrow CaCo_3 + CO$$

MW 128 100 28

Step-III

$$CaCo_3 \Rightarrow CaO + CO_2$$

MW 100 56 44

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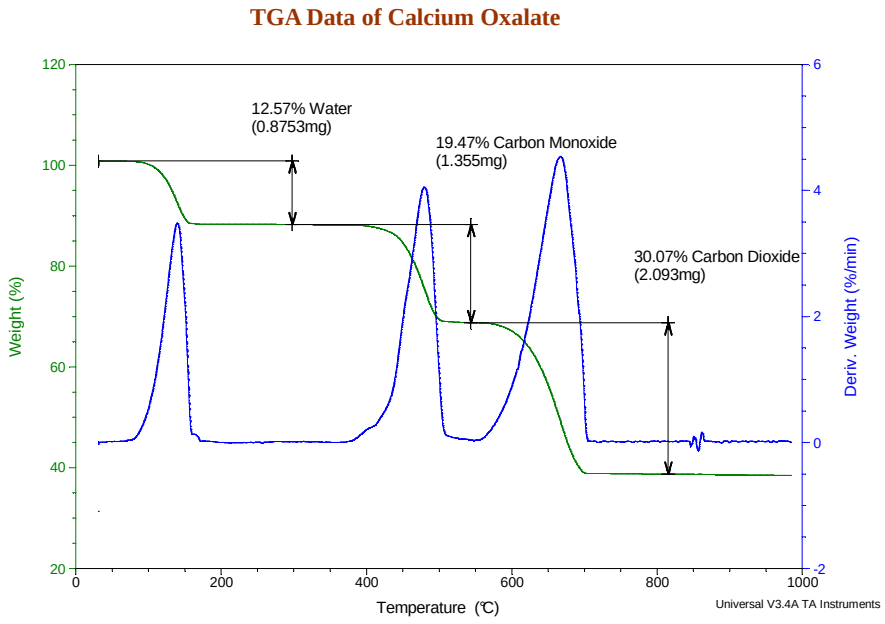
TGA – Thermogravimetric Analysis: Example



TGA – Thermogravimetric Analysis: Instrumentation

It is a thermo balance consisting of

- High precision balance
- A furnace for achieving high temperatures, e.g.., 1500 °C
- A temperature programmer
- Data acquisition system
- Auxiliary equipment to provide inert atmosphere

- Thermobalance allows for monitoring sample weight as a function of temperature
- Weight calibration using calibrated weights
- Temperature calibration based on ferromagnetic transition of Curie point standards (e.g., Ni)
- Larger sample masses, lower temperature gradients, and higher purge rates minimize undesirable buoyancy effects

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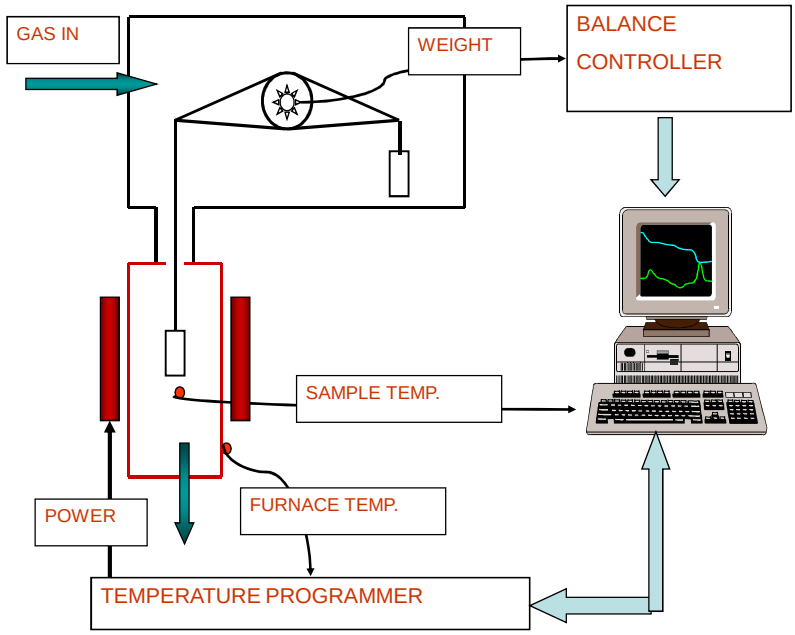
TGA – Thermogravimetric Analysis: Instrumentation.....



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TGA – Thermogravimetric Analysis: Requirements of a TG Balance

1. A thermo balance should provide accurate weight of the sample as a function of temperature. (capacity upto 1g, typical sample in mg). Its reproducibility should be very high and also highly sensitive.
2. It should operate over a wide temperature range, say from RT to 1000/1500 ^{o}C.
3. The design of thermo balance should be such that sample container is always located within a uniform hot zone inside the furnace.
4. The sample container should be such that it does not react with the sample at any given temperature.
5. The balance should not be subject to radiation or convection effects arising from the proximity of the furnace.
6. It will be advantageous if thermo balance can be coupled to a GC or IR or to QMS.

TGA – Thermogravimetric Analysis: Types of Balance

Null point balance:

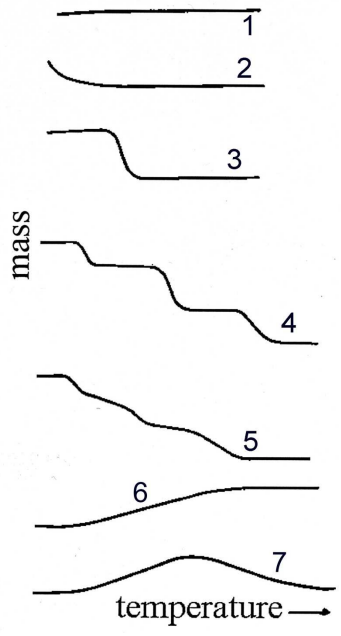
As weight change occurs, the balance beam starts to deviate from its normal position, a sensor detects the deviation and triggers the restoring force to bring the balance beam back to the null position. The restoring force is directly proportional to the weight change.

Deflection balance:

When balance arm is deflected by a change in weight, the relative illumination of photocells from light source changes due to the movement of shutter attached to the balance beam, resulting in flow of compensating current through one of the pair of photocells.

The current produced is proportional to the change in sample weight and after amplification is passed to the coil thus restoring it to its original position. There are two types of deflection balances, (i) Beam type and (ii) Cantilever type.

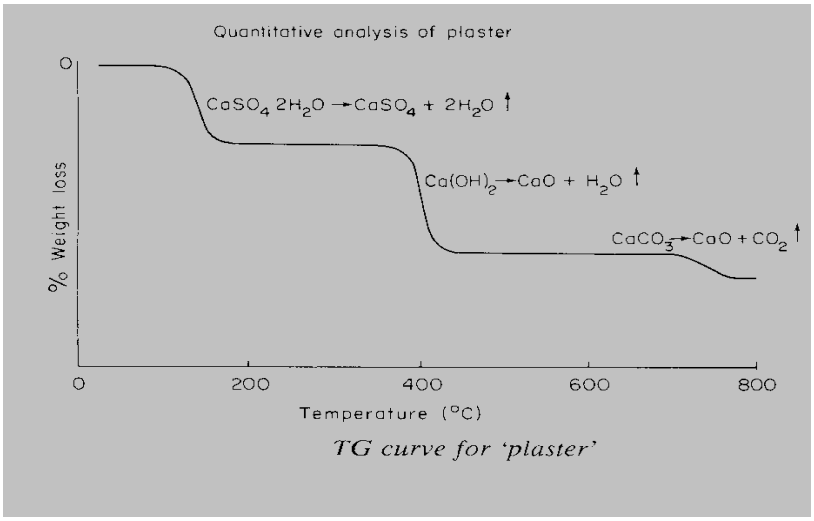
TGA – Thermogravimetric Analysis: Typical TG Curves



1. no change
2. desorption/drying (rerun)
3. single stage decomposition
4. multi-stage decomposition
5. as 4, but no intermediates or heating rate too fast
6. atmospheric reaction
7. as 6, but product decomposes at higher temperature

TGA – Thermogravimetric Analysis: Applications – Quantitative Analysis

Plaster contains gypsum ($CaSO_4 2H_2O$), lime $Ca(OH)_2$ and chalk $CaCO_3$.



TG curve for 'plaster'

TGA – Thermogravimetric Analysis: Applications – Quantitative Analysis...

- Ca, Sr and Ba are precipitated as monohydrated oxalates.
- In the first step,

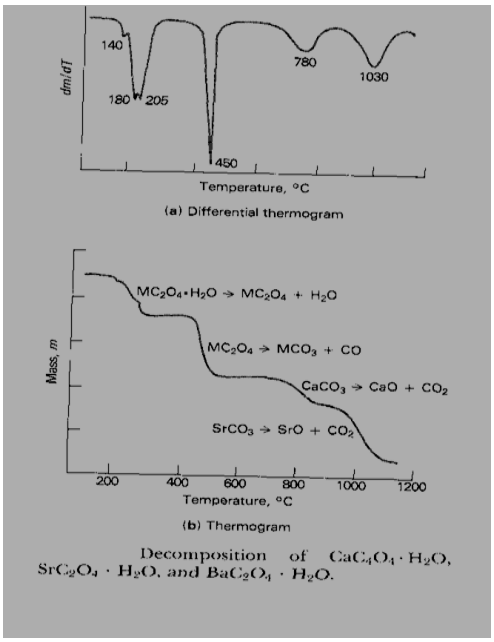
H_2O is removed from all the three oxalates

- In 2nd step,

carbonates are formed by losing CO

- In 3rd step,

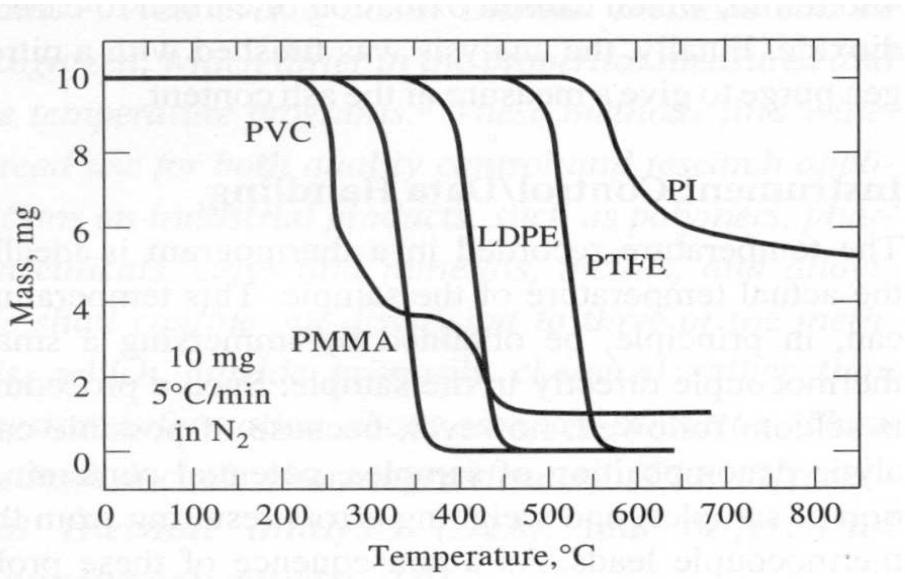
stable oxides are formed by losing CO_2



Decomposition of $CaC_2O_4 \cdot H_2O$, $SrC_2O_4 \cdot H_2O$, and $BaC_2O_4 \cdot H_2O$.

TGA – Thermogravimetric Analysis: Applications – Polymers

• Conditions of polymer degradation, metal oxidation, identify polymers

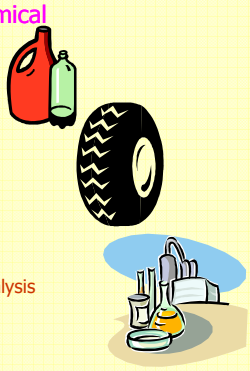


TGA – Thermogravimetric Analysis: For a wide variety of applications

• Thermal stability range of materials

Polymer / Rubber / Chemical

Melting
Degree of Crystallinity
Glass transition
Processing conditions
Curing / crosslinking
Oxidative Stability (OIT)
Isothermal crystallization
Specific Heat (Heat Capacity)
Kinetics studies
Moisture/volatiles content
Compositional analysis
Combustion/decomposition analysis
Softening
Material strength / modulus
Expansion/contraction



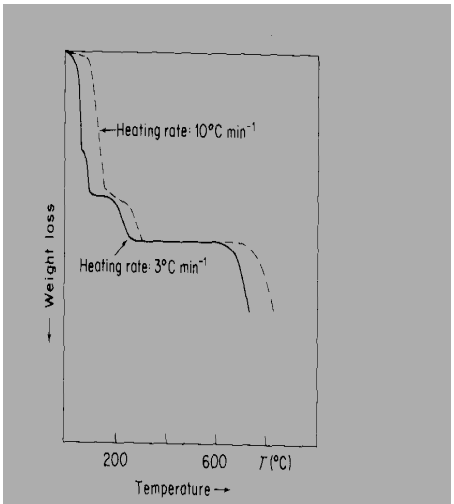
Pharmaceutical

Polymorphism
Moisture content
Purity
Packaging
Crystallinity / Amorphous phase studies
Coating analysis
Powder characterization
High throughput testing (HyperDSC)

Life Sciences

Protein melting / unfolding
Protein denaturation
Characterization of lyophilized protein
Metabolic heat generation

TGA – Thermogravimetric Analysis: Factors affecting TGA curves

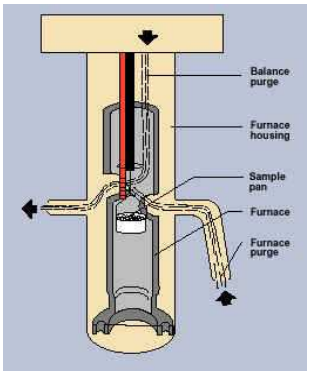


$CuSO_4.5H_2O$ heated in air in a platinum crucible

- Experimental conditions can alter the onset as well as the end of decomposition.
- Shape/sharpness of curves change with heating rate.
- Experimental conditions should be known for comparison of curves from different sources.
- Change of atmosphere influences the decomposition.
- Oxidation takes place in air, while decomposition takes place in its absence.

TGA – Thermogravimetric Analysis: Gas Flow Rates

- High flow purge rates ? Not recommended, specially for vertical TGA balances due to more turbulence) :
- Better controlled atmosphere (inert) specially at higher temperatures
- Typical purge gas flow rate for small furnace : 60 ml/min for a vertical TGA , but can be increased up to 500 ml/min (even 1000 ml/min) in case of horizontal models, to rapidly purge the furnace without the use of vacuum.



TGA – Thermogravimetric Analysis: Sources of Error

1. Buoyancy effect of sample container

- It is nothing but apparent gain in weight when an empty, thermally inert crucible is heated.

Modern instruments take care of these factors. A blank run with an empty crucible is always preferable.

The density of gases decreases with increasing temperature :

e.g. Air :	25°C	1.29 mg/ml
	225°C	0.62 mg/ml
	425°C	0.41 mg/ml

TGA – Thermogravimetric Analysis: Sources of Error

2. Furnace and temperature effects

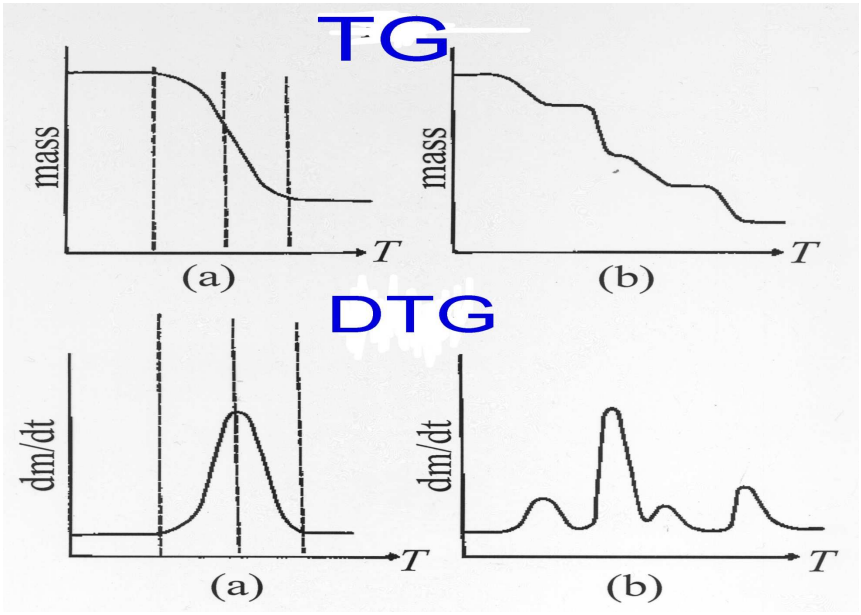
- Heat from the furnace may cause convection.
- Magnetic and inductive interaction between certain samples and winding of the furnace.
- Thermocouple calibration

3. Other effects

- Turbulence in the gas flow.
- Temperature measurement effects.
- Placement of the thermocouple.
- Quantity of sample used for analysis.
- Packing of the sample
- Container materials. Mostly Pt, Alumina crucibles are used.
- Gas flow to evacuate the decomposition products.

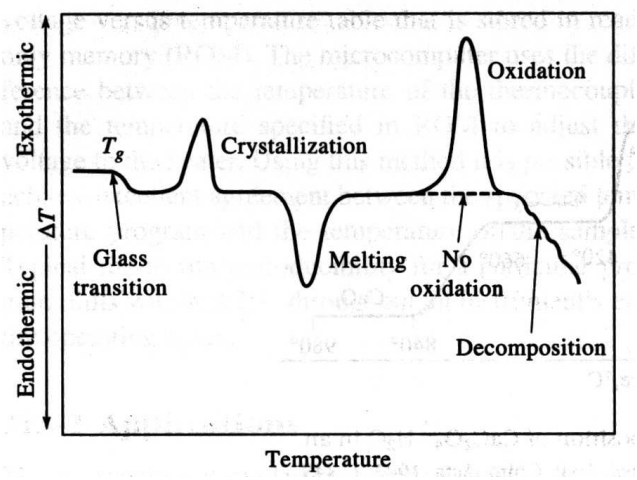
DTG – Derived Thermogravimetry

plots change in mass with temperature, dm/dt, and resolves changes more clearly.

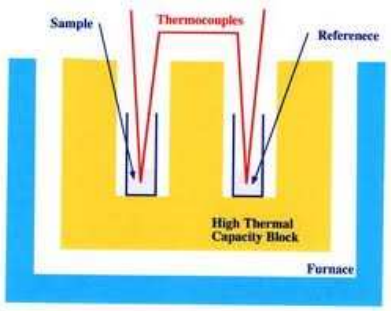


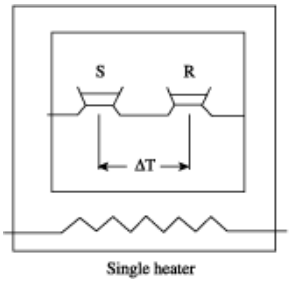
DTA – Differential Thermal Analysis: Introduction

the temperature difference between a sample and an inert reference material, $\Delta T = T_S - T_R$, is measured as both are subjected to identical heat treatments



DTA – Differential Thermal Analysis: Instrumentation

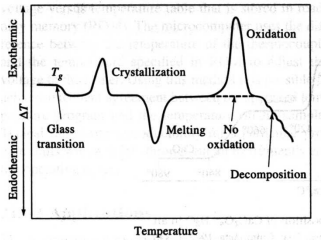




Single heater

•There is a constant temperature difference ΔT between S and R since they have different heat capacities.

•But when the sample undergoes an endo (exo) thermic change ΔT becomes different.



<10 mg of sample (s) and inert reference (r) are contained in Al pans each with thermocouple, held in heating block, with thermocouple.

DTA – Differential Thermal Analysis: Instrumentation…

Sample holder:

sample and reference cells (Al)

Sensors:

- Pt/Rh or chromel/alumel thermocouples
- one for the sample and one for the reference
- joined to differential temperature controller

Furnace:

- alumina block containing sample and reference cells

Temperature controller

- controls for temperature program and furnace atmosphere

DTA – Differential Thermal Analysis: Typical results from DTA

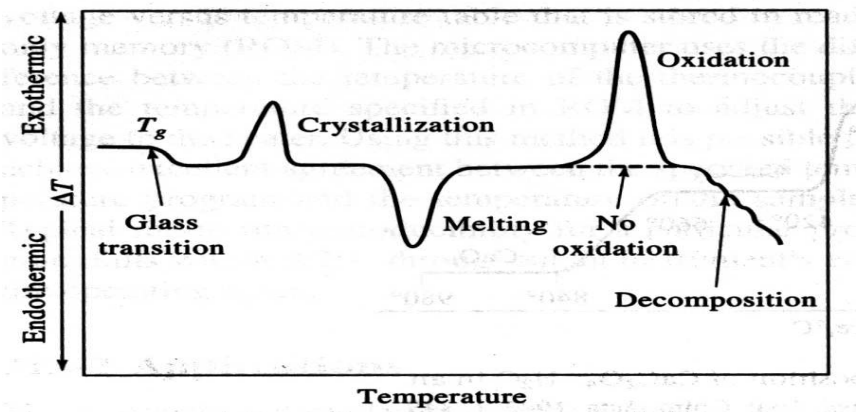
Analysis of a polymer shows several features due to physical and chemical changes, including:

glass transition: glassy, amorphous polymer becomes flexible

crystallization of amorphous polymer into microcrystals is exothermic.

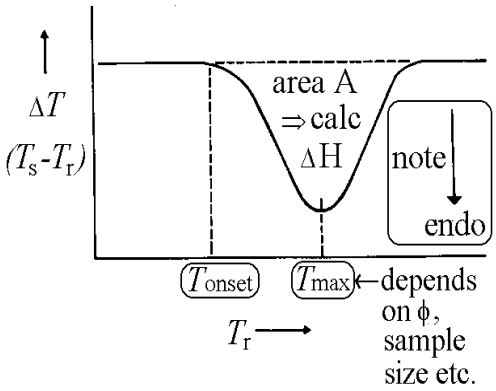
oxidation peak would be absent in N_2 atmosphere

DTA of polymer



DTA – Differential Thermal Analysis: Applications

- To construct phase diagrams and study phase transitions.
- To find ΔH



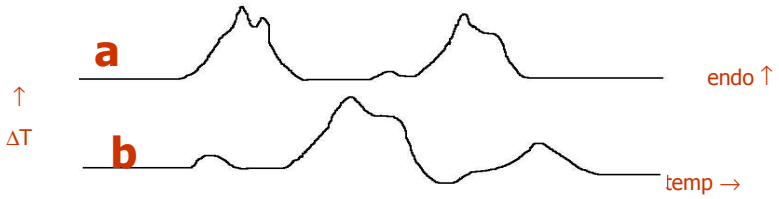
peak area (A) = ± K. ΔH.m

m- mass of sample
ΔH- heat of reaction
K –constant which depends upon sample geometry as well as thermal conductivity. K varies with the temperature, hence instrument has to be calibrated at each temperature

- To find the heat of fusion of the sample
- To determine M.Pt., B.Pt., decomposition temperatures of organic compounds

DTA – Differential Thermal Analysis: Applications

- To fingerprint substances



DTA of (a) butter and (b) margarine

butter

margarine

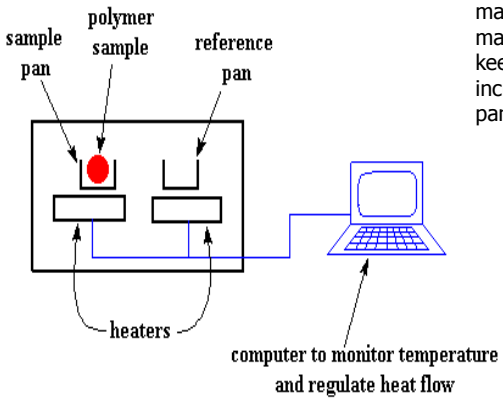
DSC – Differential Scanning Calorimetry: Introduction

DSC is a thermal analysis method where differences in heat flow into a substance and a reference are measured as a function of sample temperature, while both are subjected to a controlled temperature program.

The basic difference between DTA and DSC

DSC- calorimetric method, energy differences measured.

DTA- temperature differences measured.



The polymer sample means there is extra material in the sample pan. Having extra material means that it will take more heat to keep the temperature of the sample pan increasing at the same rate as the reference pan.

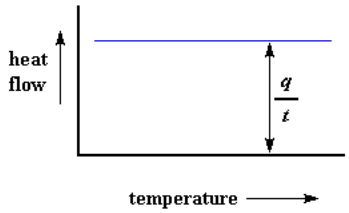
Plot :

Temperature on the *x*-axis

Heat output on the *y*-axis

DSC – Differential Scanning Calorimetry: Introduction

heat absorbed by the polymer against temperature



Heat flow is going to be shown in units of heat, *q* supplied per unit time, *t*.

The heating rate is temperature increase *T* per unit time, *t*.

$$\frac{\text{heat}}{\text{time}} = \frac{q}{t} = \text{heat flow}$$

$$\frac{\text{temperature increase}}{\text{time}} = \frac{\Delta T}{t} = \text{heating rate}$$

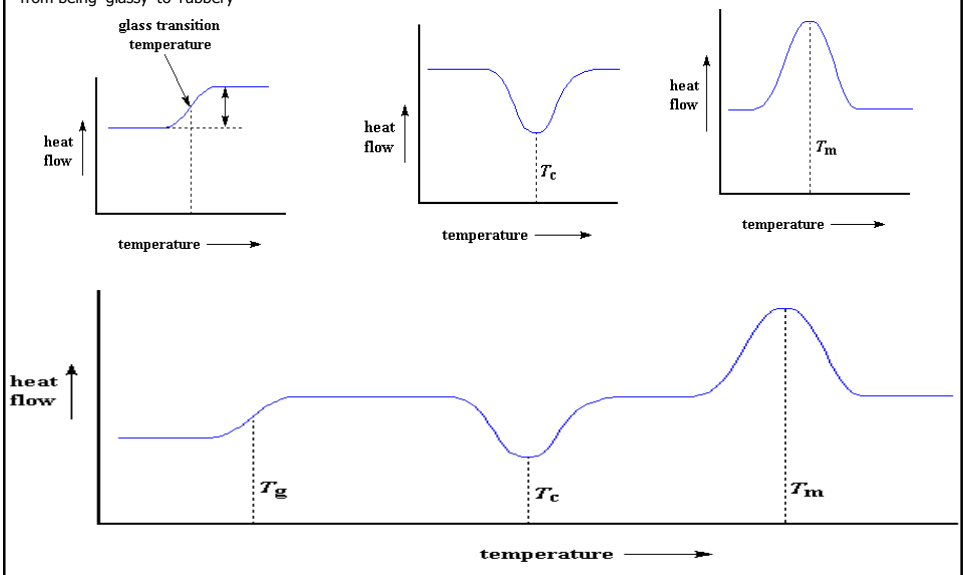
divide the heat flow *q/t* by the heating rate *T/t*. We end up with heat supplied, divided by the temperature increase

$$\frac{\frac{q}{t}}{\frac{\Delta T}{t}} = \frac{q}{\Delta T} = C_p = \text{heat capacity}$$

when you put a certain amount of heat into something, its temperature will go up by a certain amount, and the amount of heat it takes to get a certain temperature increase is called the *heat capacity*, or C_p

DSC – Differential Scanning Calorimetry: Introduction

Tg is the critical temperature at which the material changes its behavior from being 'glassy' to 'rubbery'

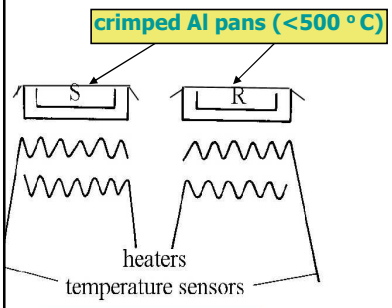


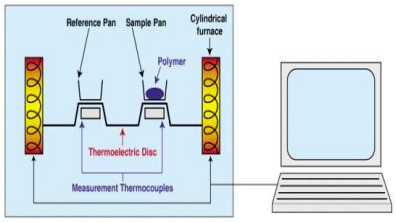
The entire DSC plot, right before your very eyes!

DSC – Differential Scanning Calorimetry: Instrumentation

Power compensation device

– better resolution; faster heating and cooling rates. *s and r heated by separate heaters to keep same temperature, as T is changed linearly.*





Sample holder

- Al or Pt pans

Sensors

- Pt resistance thermocouples
- separate sensors and heaters for the sample and reference

Furnace

- separate blocks for sample and reference cells

Temperature controller

- differential thermal power is supplied to the heaters to maintain the temperature of the sample and reference at the program value

First control circuit, the average temperature control unit, provides the x axis: average temperature of s and r as a function of time.

The second control unit, differential temperature circuit, provides a signal proportional to the difference in power input (mW) to the 2 furnaces.

EGD/EGA – Evolved Gas Detection & Analysis

technique in which the nature and/or amount of volatile product(s) released by a substance subjected to a controlled temperature program is determined

Evolved Gas Detection (EGD): Single preselected component of evolved gas is sensesd

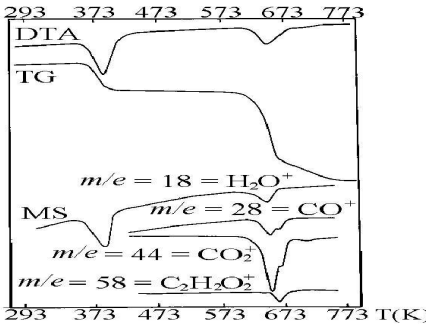
Evolved Gas Detection (EGA): absolute identity of evolved gas is analyzed

By combining appropriate analyzer to a thermogravimetric system for performing either EGA or EGD

The TG-MS combination is used for EGA

The TG-FID (Flame Ionization Detectors) is used for EGD

e.g. using a jet separator interface to a ms; or using intermittent gc sampling coupled to DSC. Given are TG-DTA-MS curves for decomposition of hydrated *Co(C4H406)* 2.5 H20 in Ar, with heating rate 2.5 °C min^{-1}



TMA – Thermomechanical Analysis - Introduction

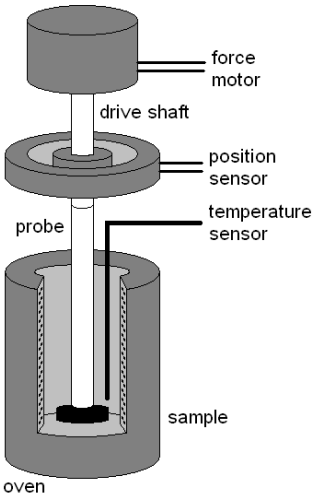
TMA involves the measurement of mechanical properties such as volume (dilatometer) expansion, contraction, extension or penetration of materials as a function of temperature.

TMA technique is useful in the study and assessment of mechanical properties of materials for the temperature rante -100°C to 1000°C.

Useful in assessing the polymer and metal properties

solids, liquids or pasty materials analysis

TMA – Thermomechanical Analysis - Instrumentation



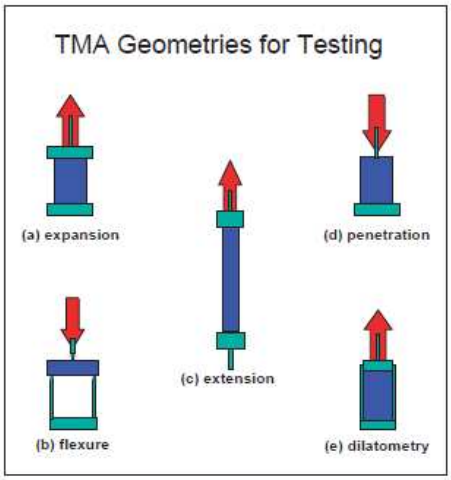


Figure 1. Testing geometries used in the TMA are similar to those used in standard mechanical testing: (a) expansion which is used for both compression and CTE studies, (b) flexure or three-point bending, (c) extension or tensile, (d) penetration and (e) dilatometry or bulk.