

# Experimental Techniques in Thermal Analysis Thermogravimetry (TG) & Differential Scanning Calorimetry (DSC)

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# Instrumentation facilities in PGRL, CHE

- 1) Simultaneous Thermogravimetry and Differential Scanning Calorimetry (SDT Q600- TA Instruments)
- 2) Autosorb iQ- Physisorption, Chemisorption, Temperature Programmed Reduction (TPR), Temperature Programmed Oxidation (TPO) & Temperature Programmed Desorption (TPD) set up (Quantachrome India)
- 3) Inductively Coupled Mass Spectrometry (ICPMS)-Trace metal concentration upto ppb levels (Agilent)
- 4) Atomic Absorption Spectroscopy (AAS) (Agilent)
- 5) Powder X-ray Diffractometer- with separate optical attachment to observe diffraction in thin films (PanAnalytical).
- 6) Field Emission Scanning Electron Microscope (TESCAN)
- 7) Nano- IR (AFM+IR) (Anasys Instrument)
- 8) Multichannel and Single Channel Voltametry (MVA) (Metrohm)
- 9) Flow Cytometer (Partec-Sysmex)
- 10) Universal Testing Machine (UTM) (Zwick/Roell)
- 11) MicroPIV

# Thermal analysis

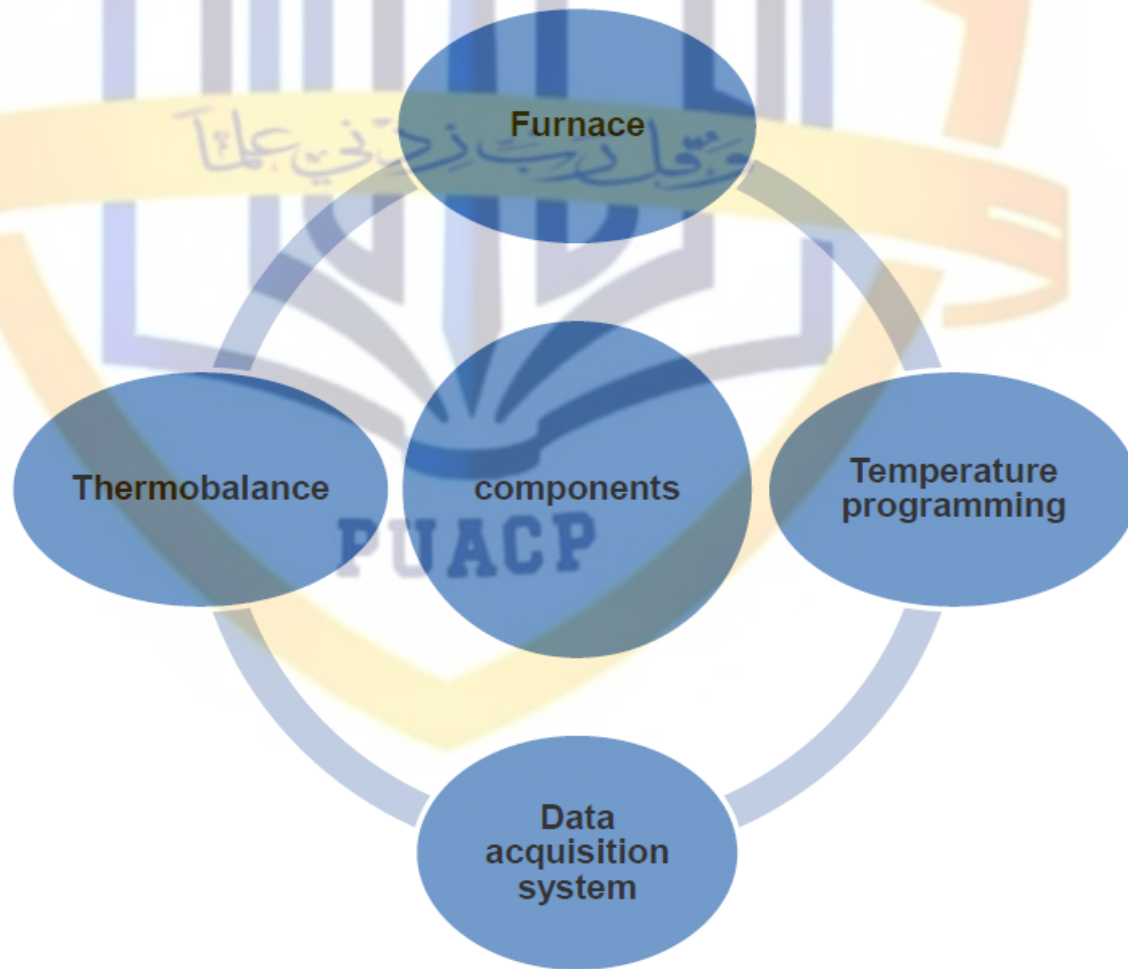
*... Includes several different methods. These are distinguished from one another by the property which is measured.*

- 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

# General conformation of Thermal Analysis Apparatus



Physical property measuring sensor, a controlled-atmosphere furnace, a temperature programmer – all interfaced to a computer

# 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

**Dynamic TGA**

**Isothermal TGA**



# What TGA Can Tell You?

- Thermal Stability of Materials: **Explicate decomposition mechanism, fingerprint materials for identification & quality control**
- Oxidative Stability of Materials: **Oxidation of metals in air, Oxidative decomposition of organic substances in air/O<sub>2</sub>, Thermal decomposition in inert atmosphere**
- Composition of Multi-component Systems: **Behaviors sufficiently different on the temperature scale can be identified and reaction mechanism formulated**
- Estimated Lifetime of a Product: **Related to thermal stability**
- Decomposition Kinetics of Materials: **Rate of reaction, Activation Energy**
- The Effect of Reactive or Corrosive Atmospheres on Materials: **Oxidation & Corrosion Studies**
- Moisture and Volatiles Content of Materials: **Loss of moisture, drying, desorption**

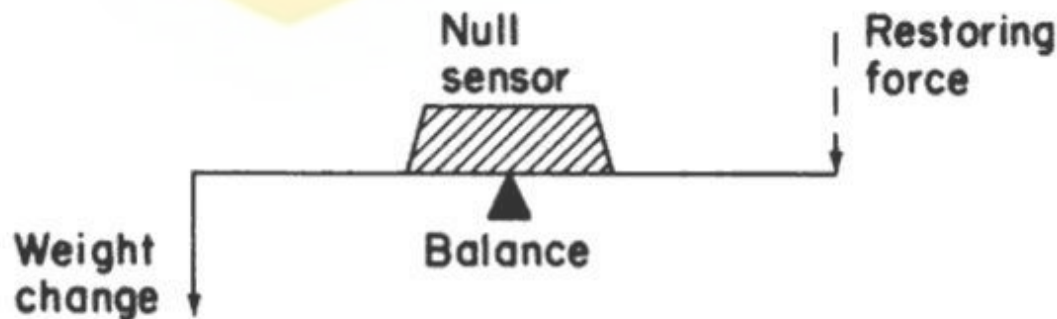
# Mechanisms of Weight Change in TGA

- 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: How the balance works

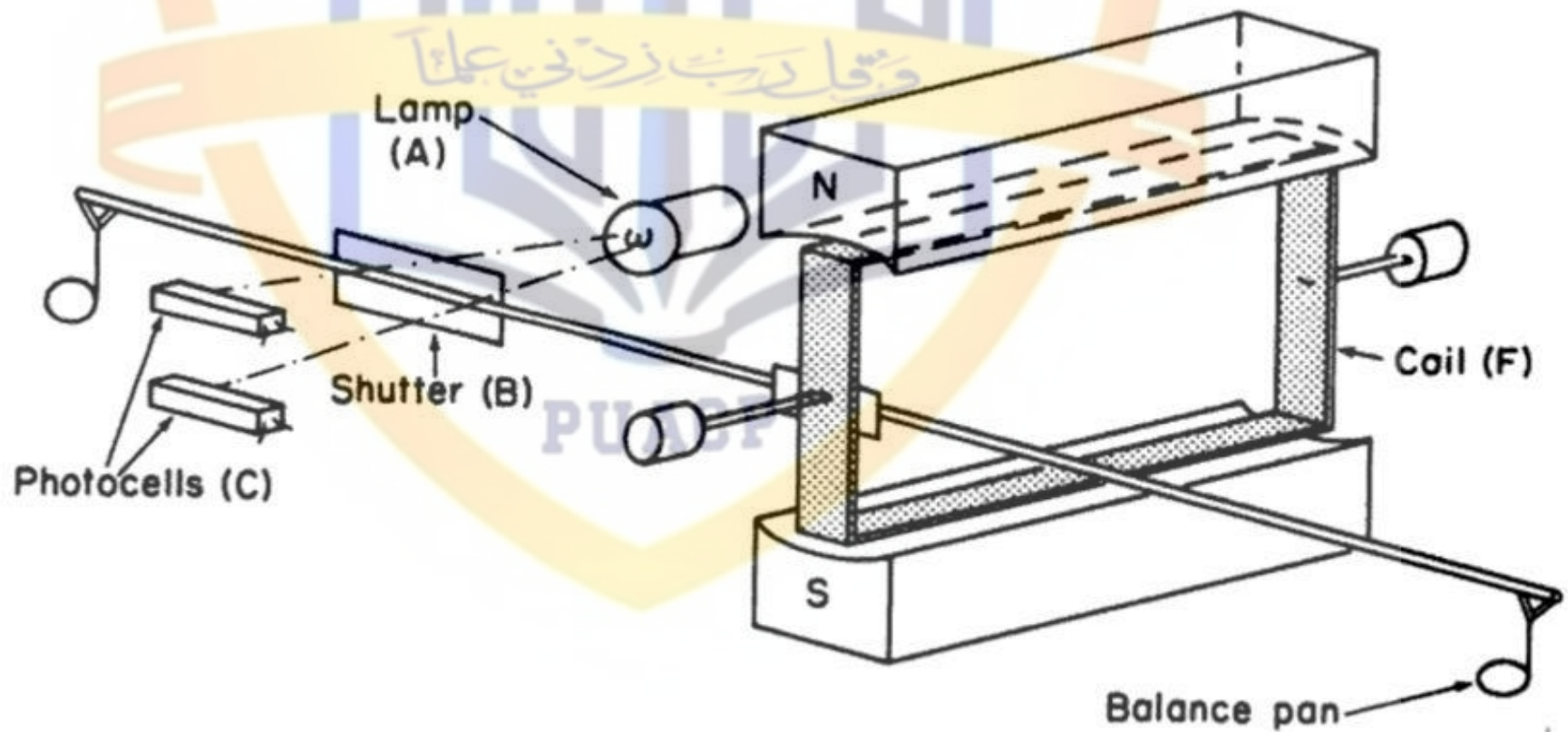
- The balance operates on a null-balance principle. At the zero, or “null” position equal amounts of light shine on the 2 photodiodes.
- If the balance moves out of the null position an unequal amount of light shines on the 2 photodiodes. Current is then applied to the meter movement to return the balance to the null position.
- The amount of current applied is proportional to the weight loss or gain.



*A 'Null point' balance*

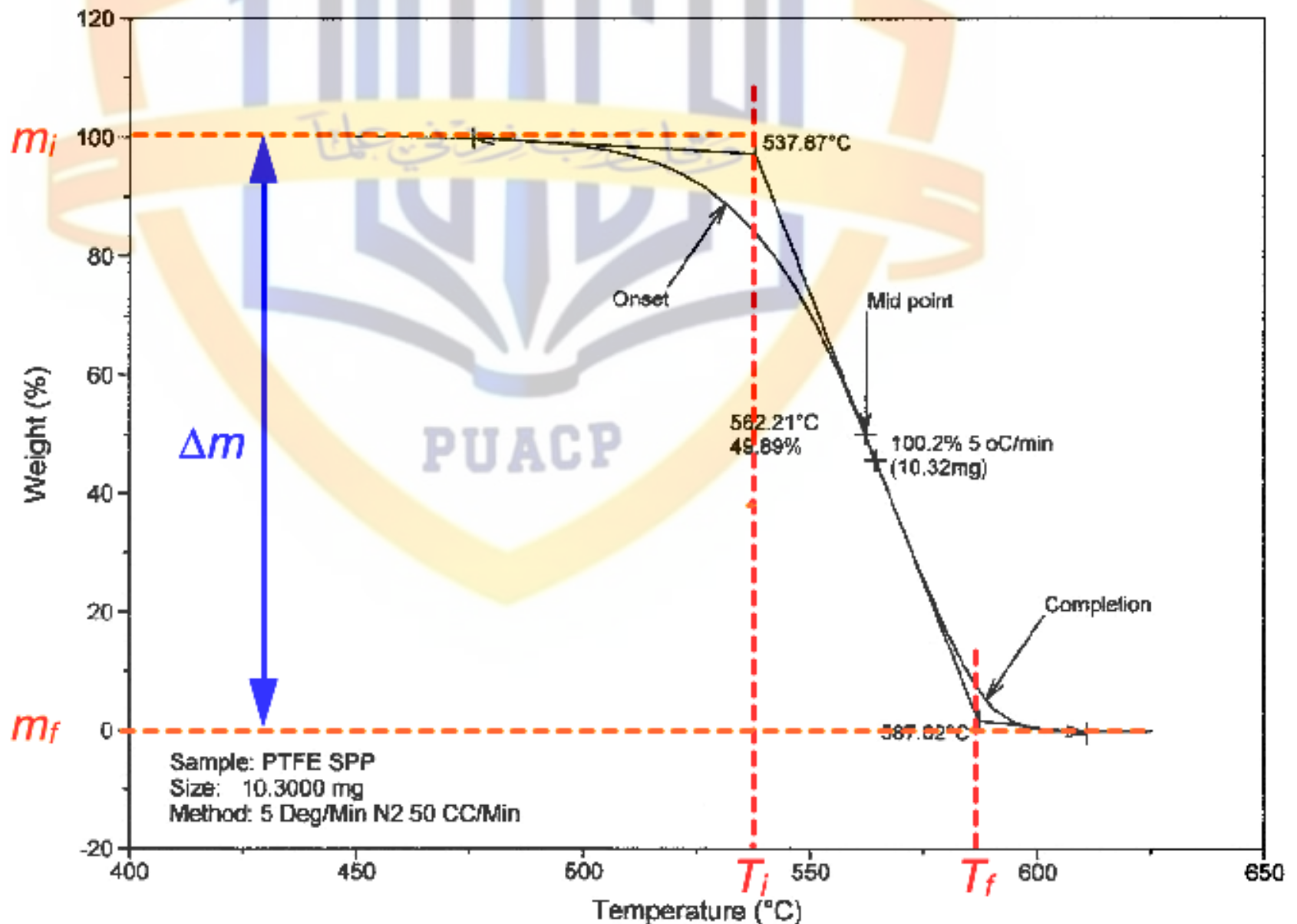


## TGA: How the balance works.....contd.



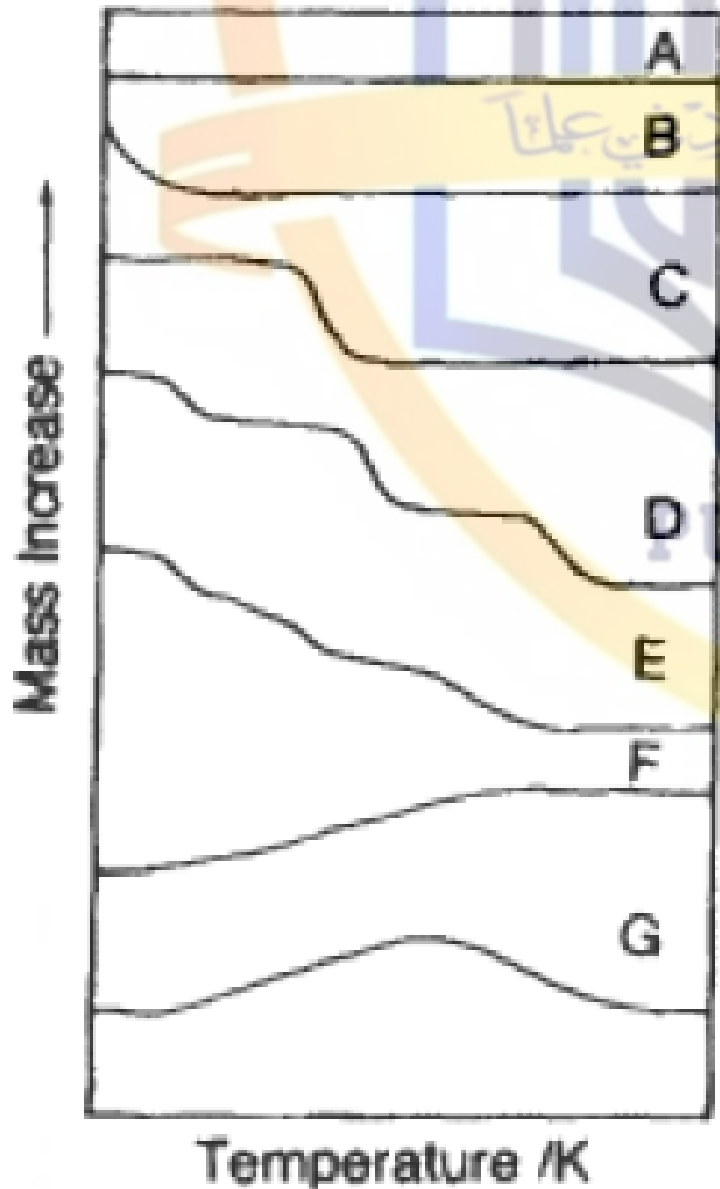
*The balance head unit for a particular **thermobalance***

# Analysis of TGA data



Draw tangents of the curve to find the onset and the offset points

# Classification of TGA Curves



**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.

# Calcium Oxalate Decomposition



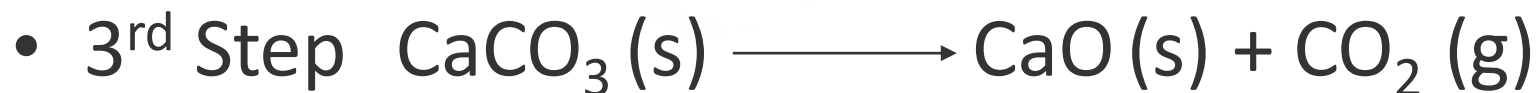
*Calcium Oxalate Monohydrate*

*Calcium Oxalate*



*Calcium Oxalate*

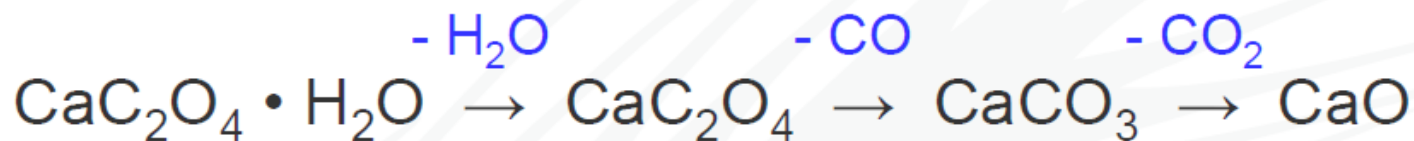
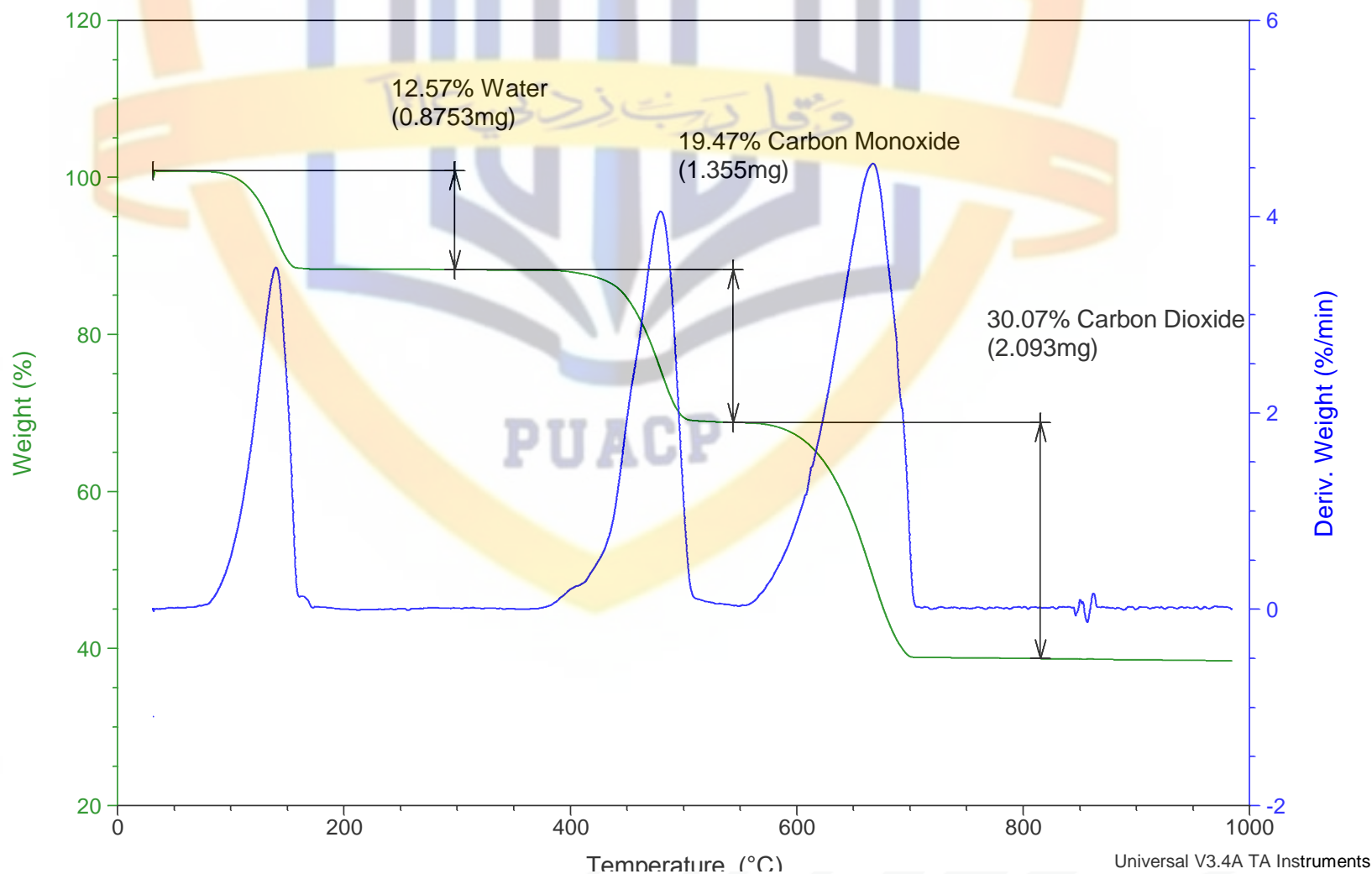
*Calcium Carbonate*



*Calcium Carbonate*

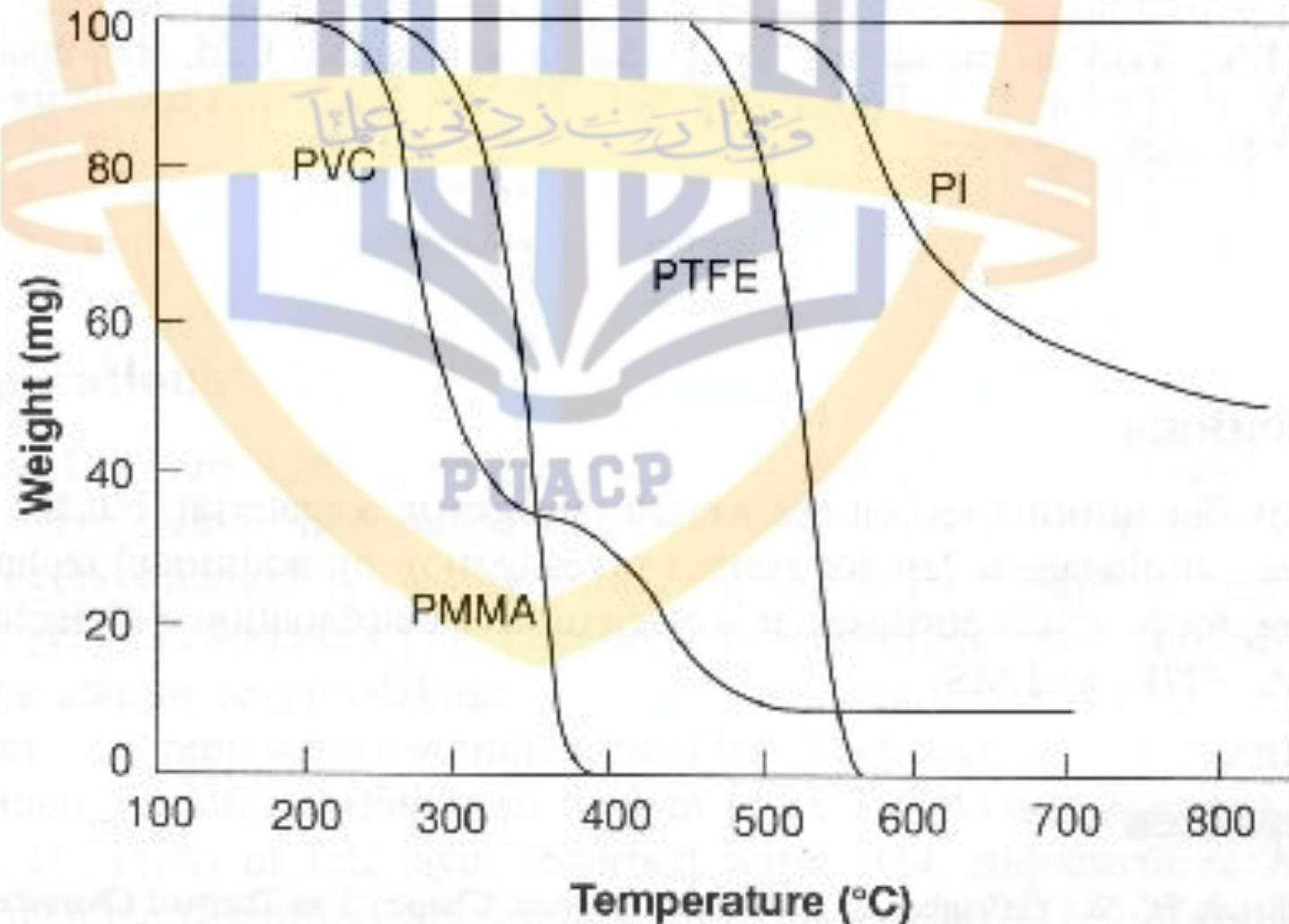
*Calcium Oxide*

# TGA of Calcium Oxalate Monohydrate





# Thermal degradation profile of common polymers



**Inert atmosphere: Depolymerization or Carbonization**

**Air Atmosphere: Oxygen in air active ingredient in degradation**

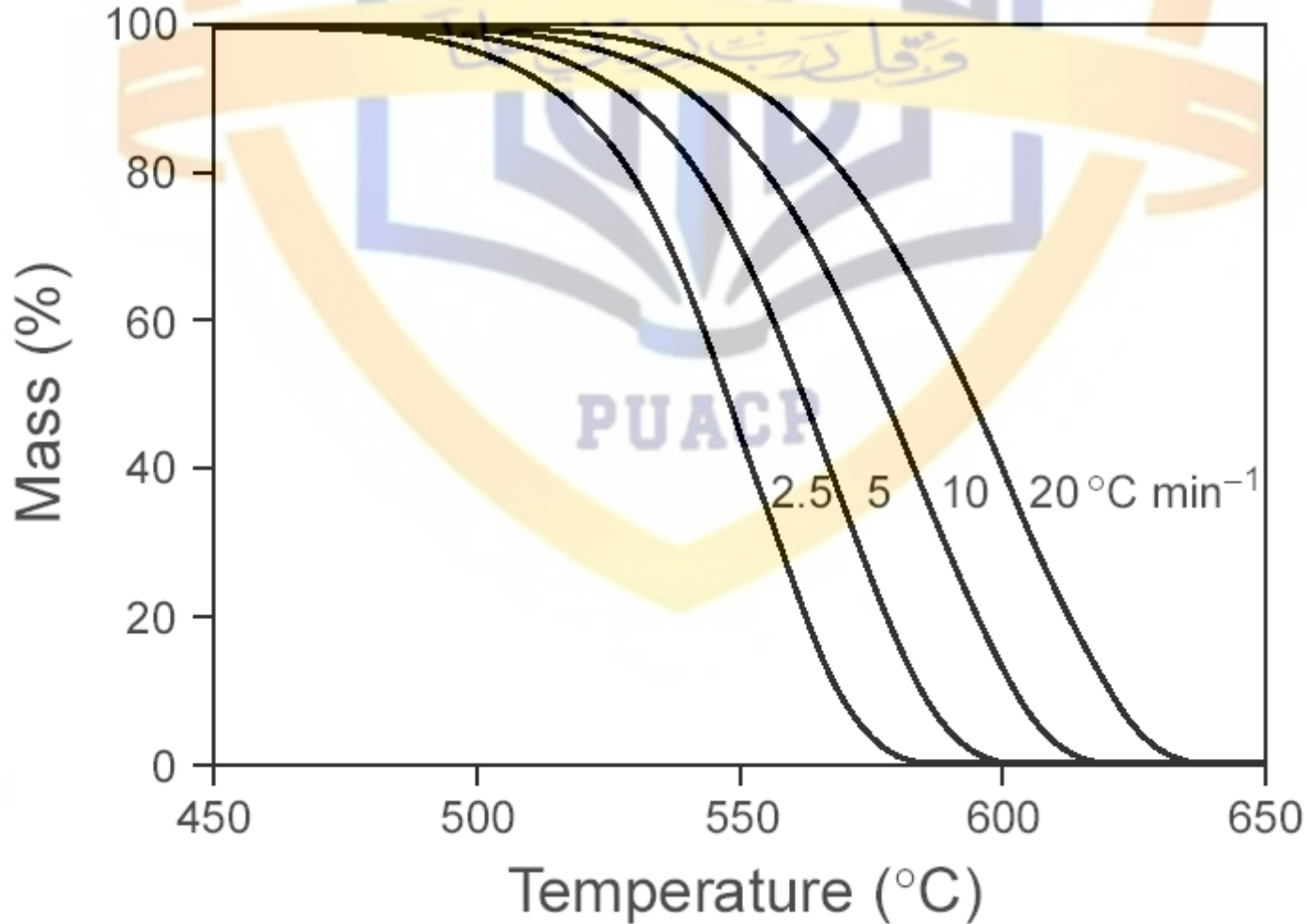
# TGA Curves are not '*Fingerprint*' Curves

Because most events that occur in a TGA are kinetic in nature (meaning they are dependent on absolute temperature and time spent at that temperature), any experimental parameter that can effect the reaction rate will change the shape / transition temperatures of the curve. These things include:

- **Pan material type:**
  - Alumina Pans: Inert till 1700°C
  - Platinum Pans: Good thermal conductivity, but not always inert due to its catalytic activities
- **Ramp rate:** suitable heating rate to detect overlapping reactions
- **Purge gas:** Protective Gas for balance, Purge gas or reactive gas for the furnace
- **Sample mass:** Low mass: Resolution limit of microbalance,  
High mass: Pronounced thermal gradients

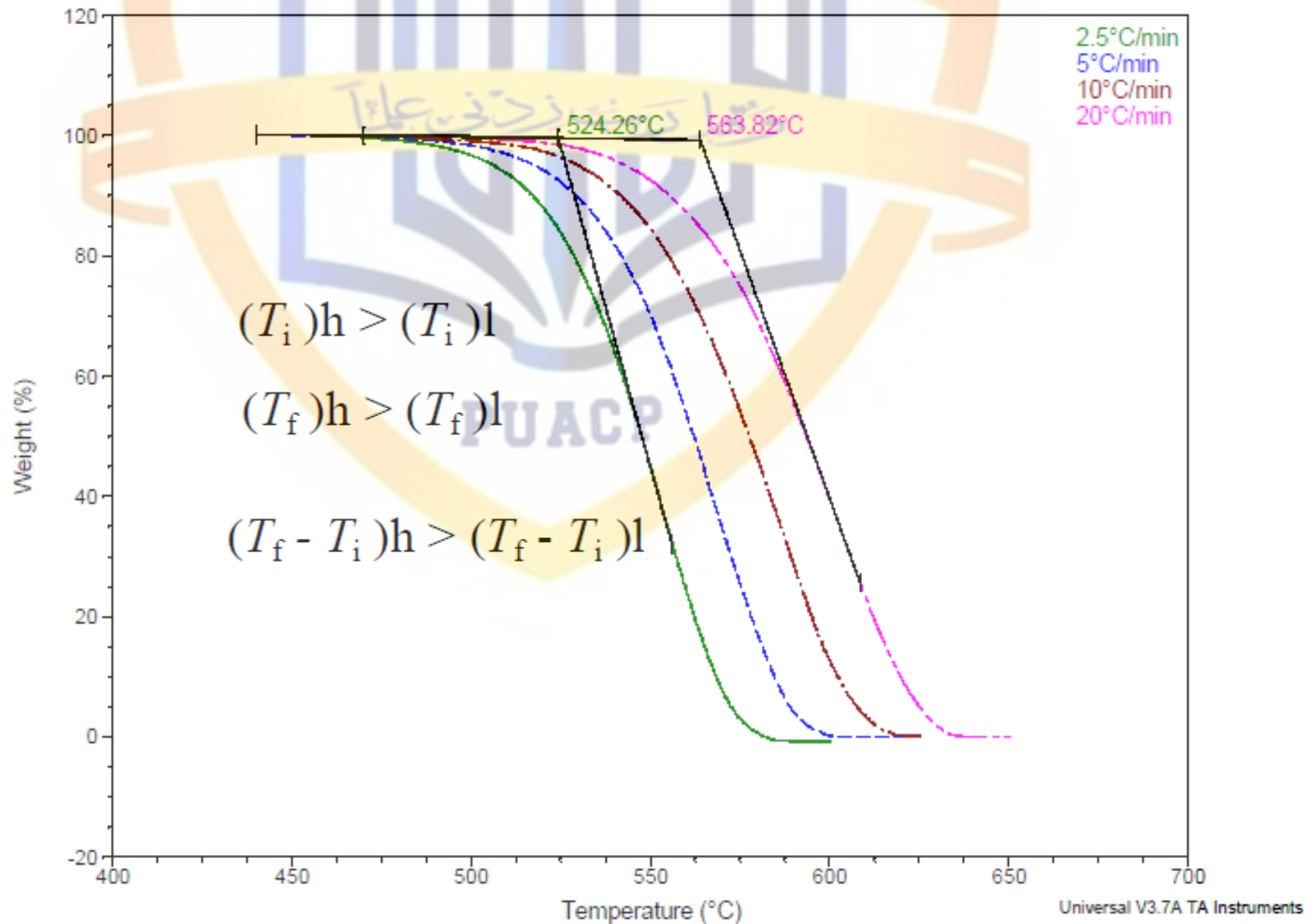
# Effect of heating rate

10 mg samples of PTFE, heated at 2.5, 5, 10 and 20 °C/min



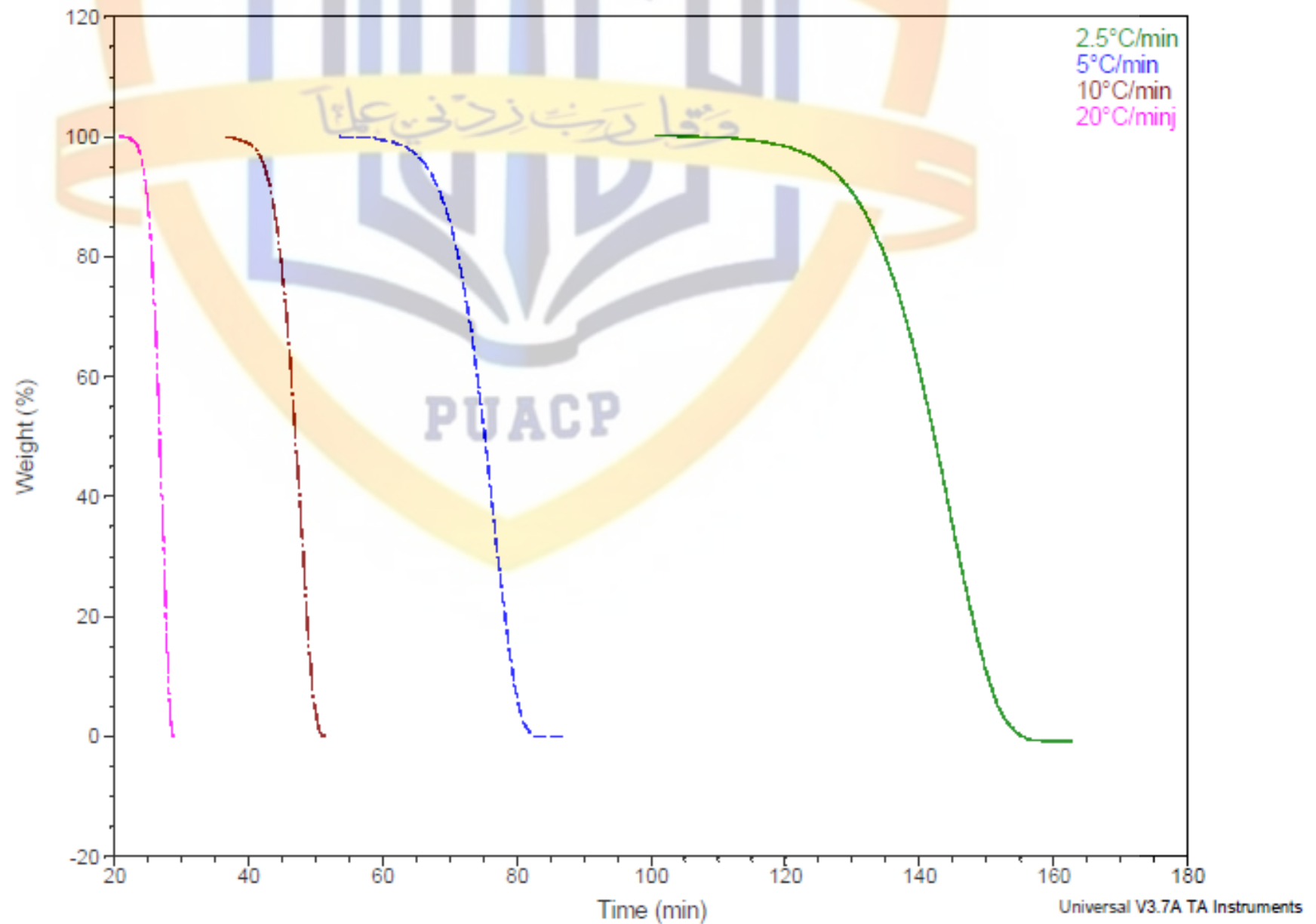
Slow heating     $\longleftrightarrow$     approach thermal equilibrium  
Fast heating     $\longleftrightarrow$     generates thermal lag

# Shift in onset with Heating Rate



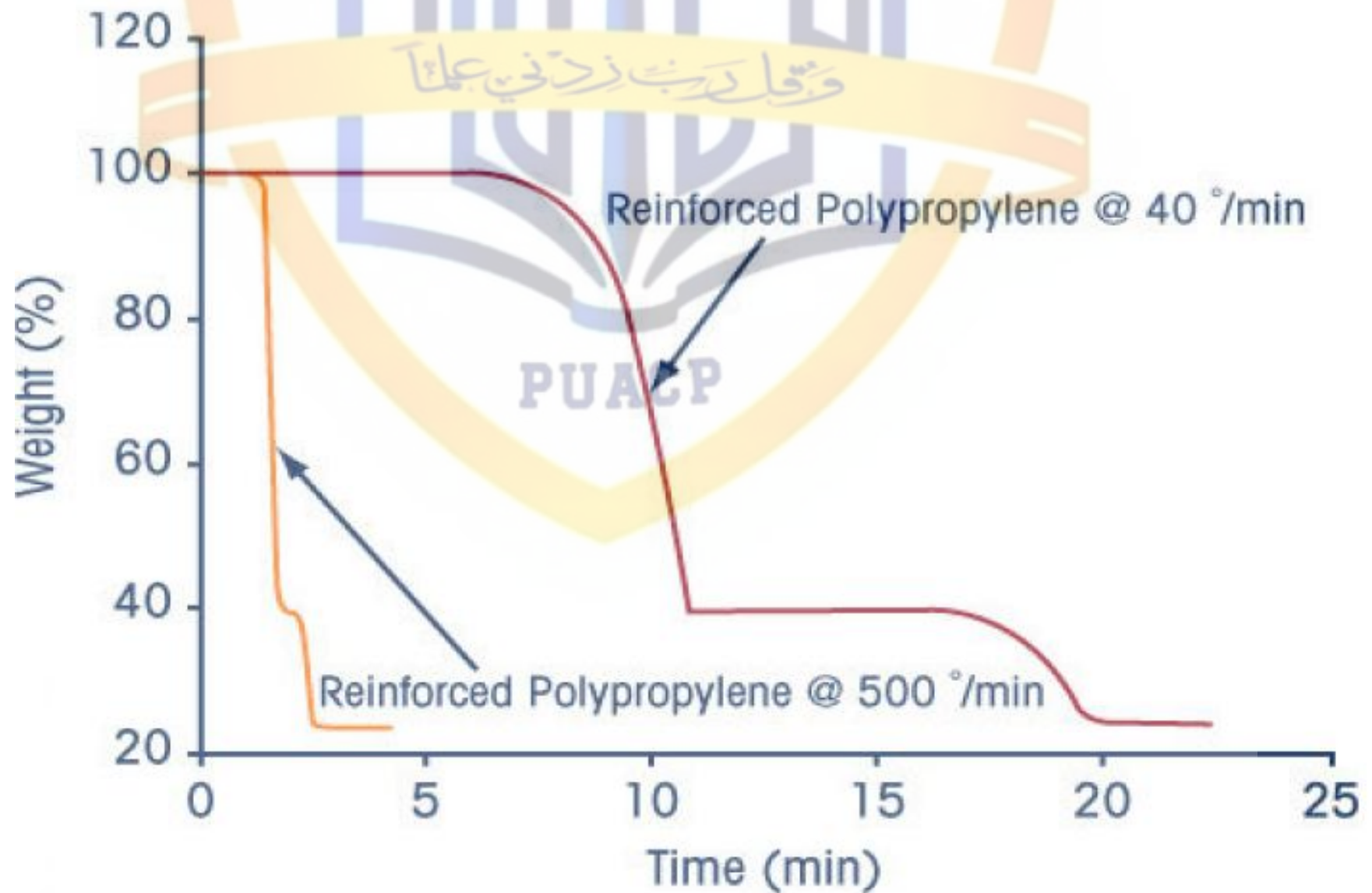
Rate effect on the curves simply reflect that thermal events are kinetic

# Time to complete degradation

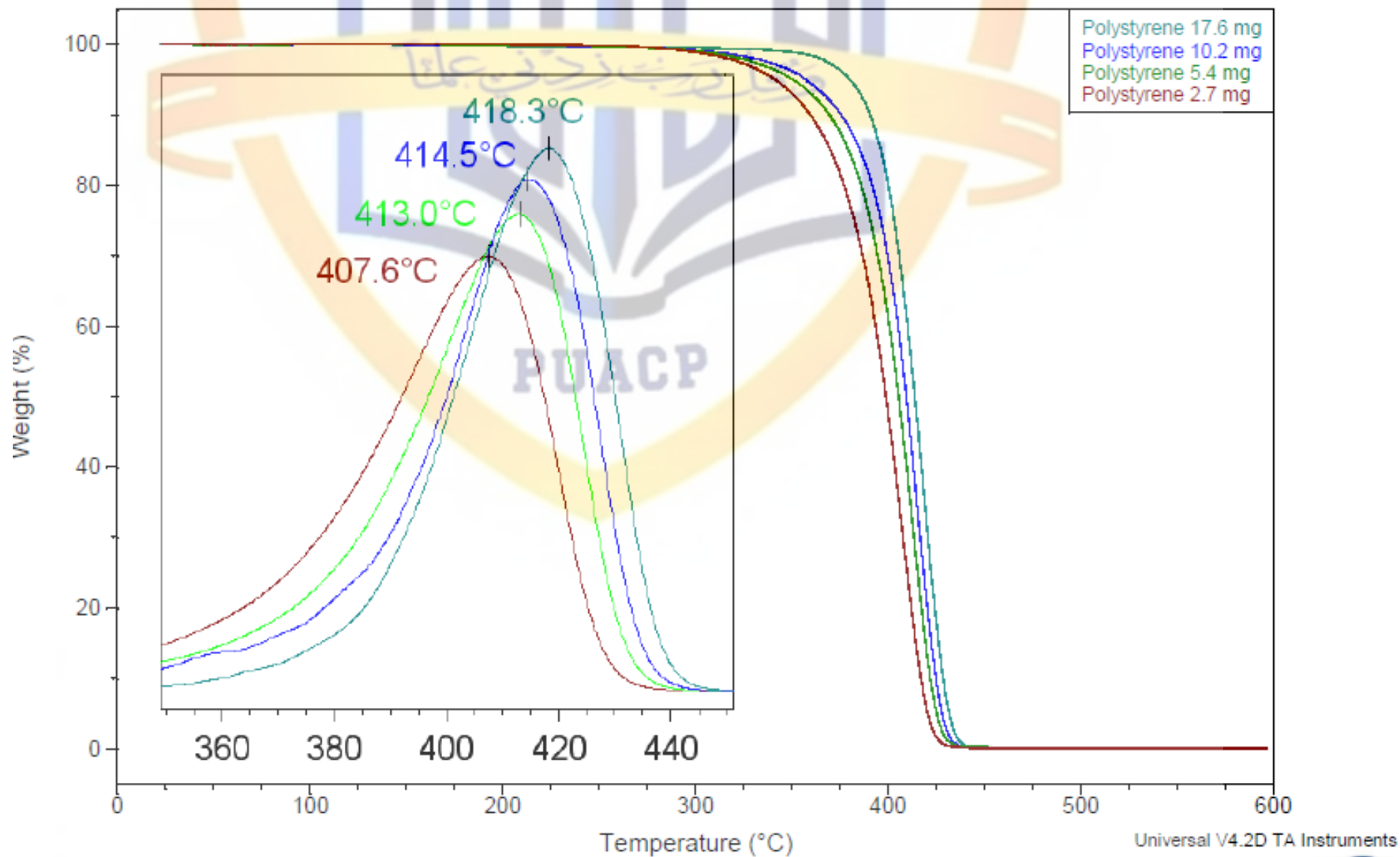




# Influence of heating rate on resolution

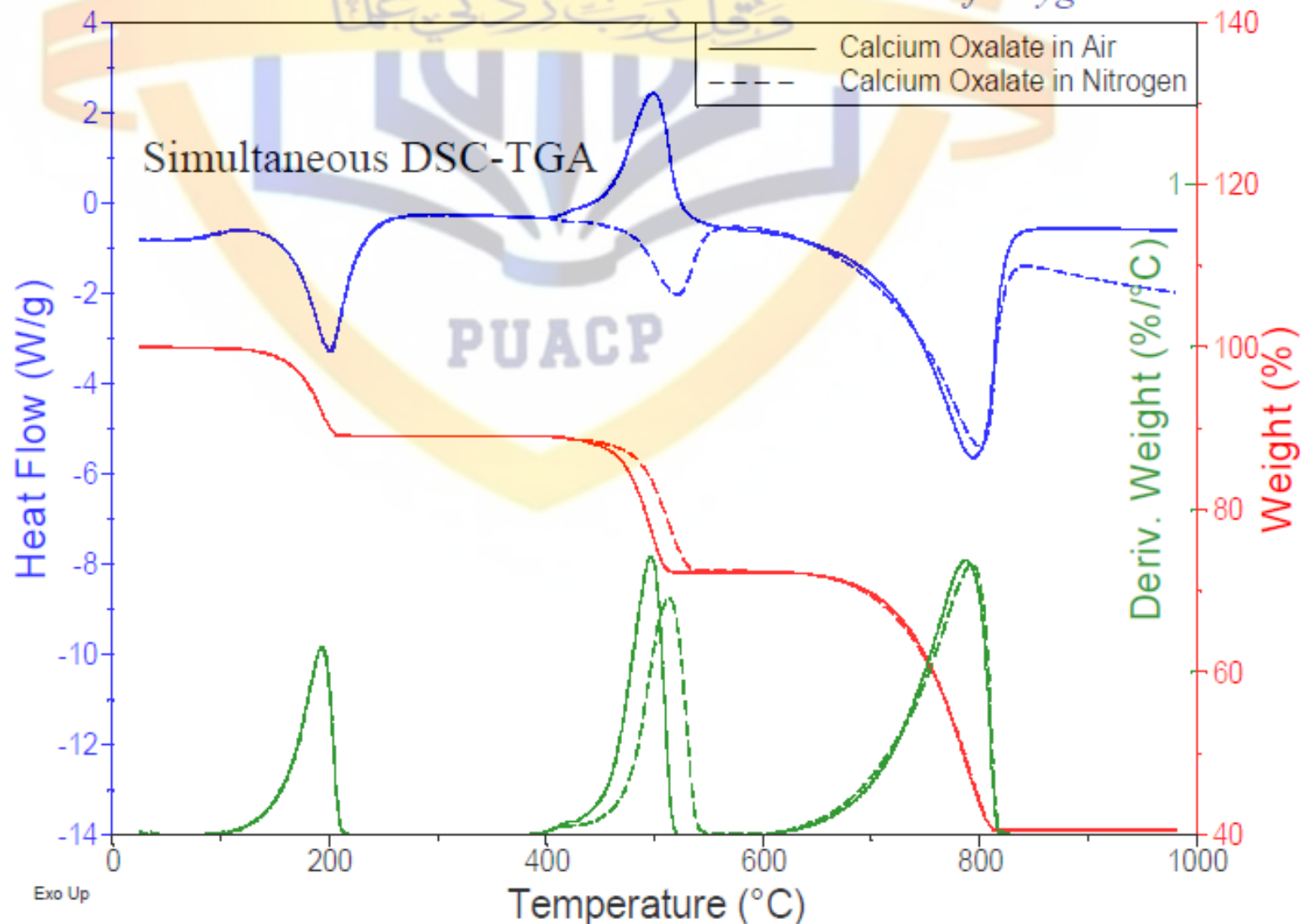


# Effect of Sample Weight



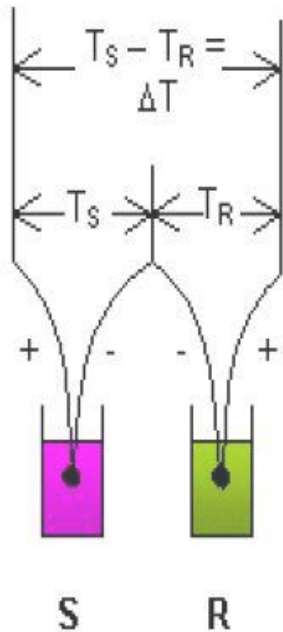
# Effect of Purge Gas

*Calcium Oxalate Decomposition as a Function of Atmosphere  
Carbon Monoxide Oxidizes in the Presence of Oxygen*



# Differential Thermal analysis (DTA)

The material under study (S) and an inert reference (R ) are made to undergo identical thermal cycles.

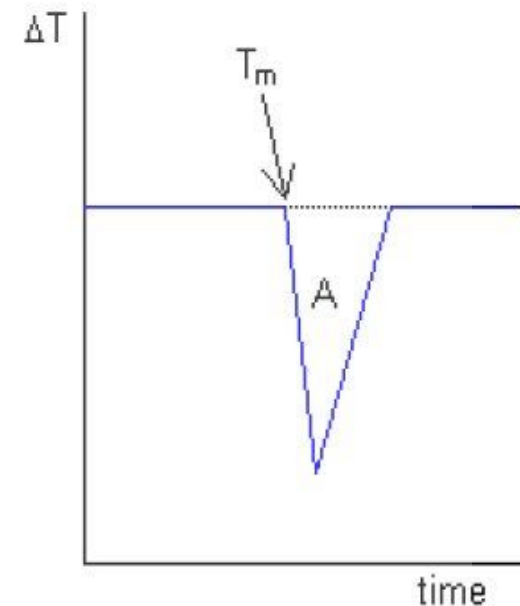
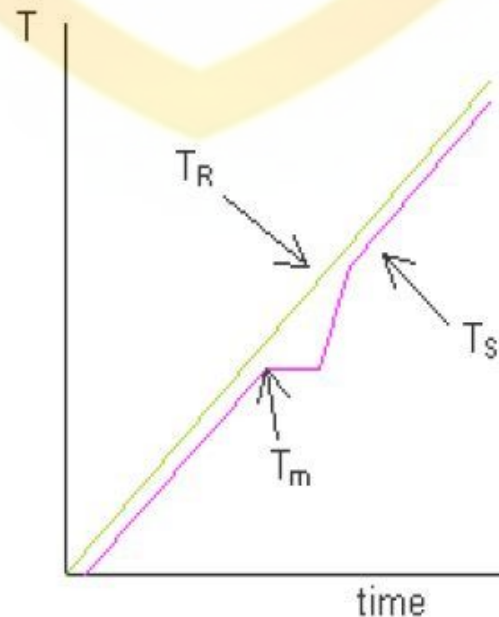
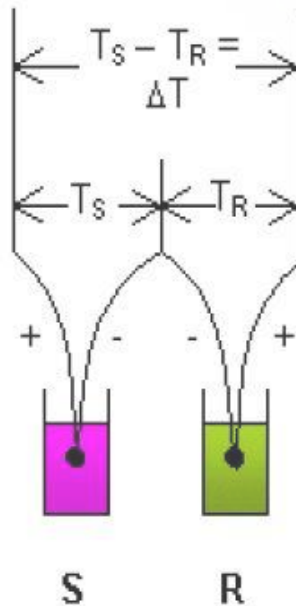


- Thermocouples measuring respective temperatures of S (sample) and R (reference material) exposed to the same heating/cooling schedule via symmetric arrangement in the same furnace
- The difference in the temperature profiles of S and R as the cycle progresses also recorded



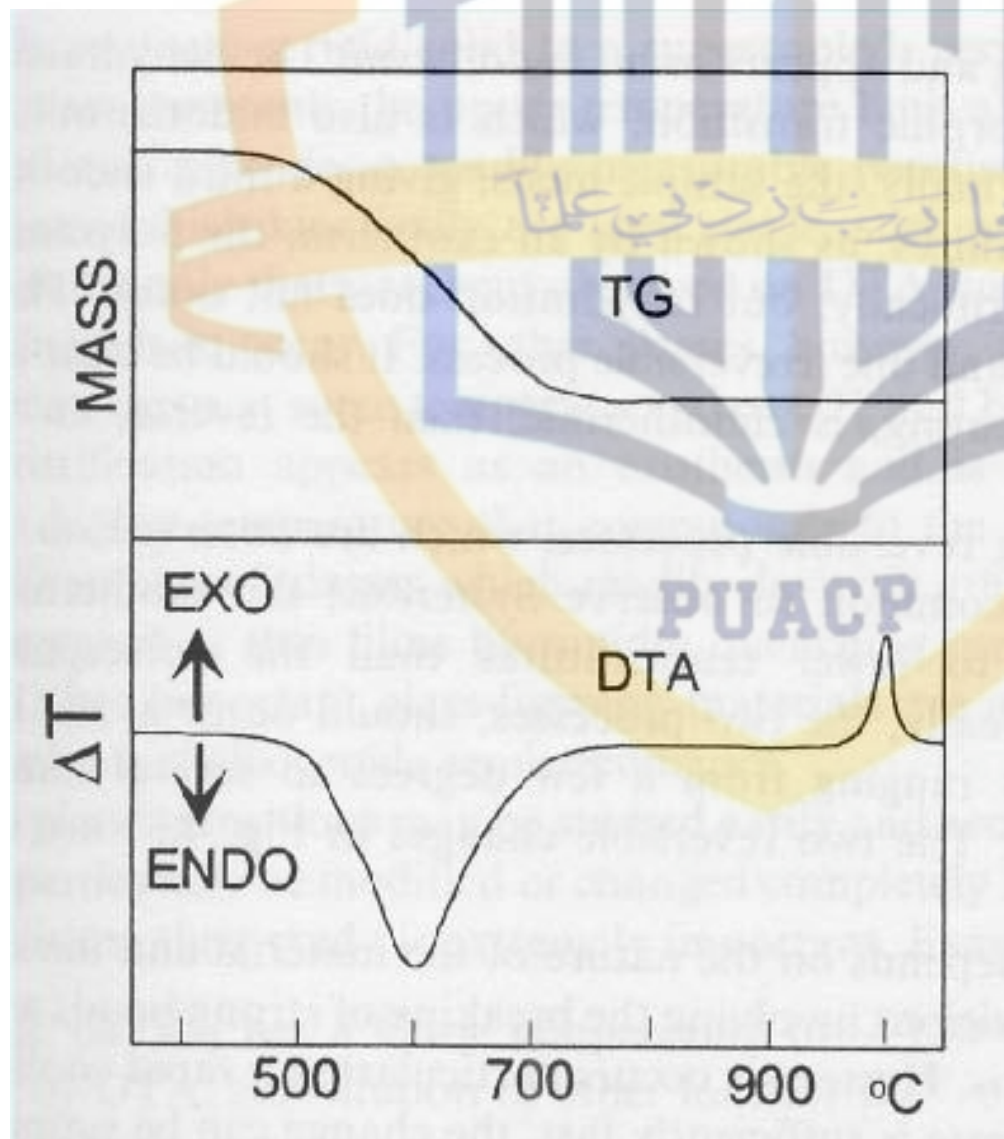
# Differential Thermal analysis (DTA)...contd

- When sample experiences energy change associated with a physical/chemical phenomena, the difference in the temperature profiles of S and R identifies the transition
- If, for instance, the sample melts, its temperature will lag behind  $T_R$  as it absorbs the heat energy necessary for melting
  - $\Delta T$  against time, or more often, sample temperature. The curve shows an endothermic (heat-absorbing) peak.





# DTA Combined with TGA



\* The area under a DTA peak is the enthalpy change

Lowering heating rate;  
Reducing sample weight

↓  
sharper peaks with improved  
resolution

While TG only measures changes caused by mass loss, DTA also register changes in material where no mass loss occur, e.g. *crystal structure changes, melting, glass transistion, etc.*

# DTA: Phenomena causing changes in heat/temperature

## Physical

Adsorption (exothermic)

Desorption (endothermic)

A change in crystal structure  
(endo – or exothermic)

Crystallization (exothermic)

Melting (endothermic)

Vaporization (endothermic)

Sublimation (endothermic)

## Chemical

Oxidation (exothermic)

Reduction (endothermic)

Break down reactions  
(endo – or exothermic)

Chemisorption (exothermic)

Solid state reactions  
(endo – or exothermic)

Crystallization	exothermic
Melting	endothermic



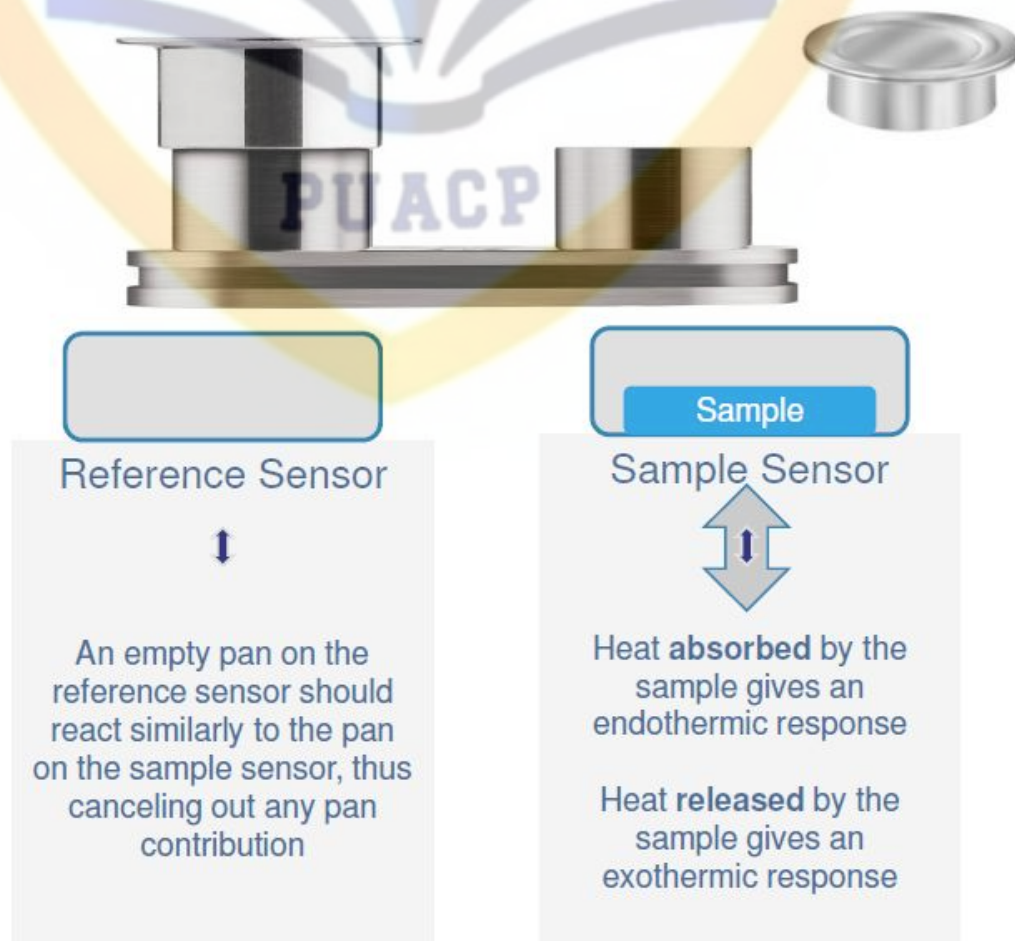
Peak orientation  $\uparrow\downarrow$  in DTA thermogram  
depends on Instrument manufacturer

DTA experiments tell us that something is happening at a specific temperature. They usually do not tell us, what is happening. Combination with other methods like X-ray diffraction, spectroscopy, microscopic investigation and composition analysis (e.g. Electron probe microanalysis) are required to interpret the results

# Differential Scanning Calorimetry (DSC)

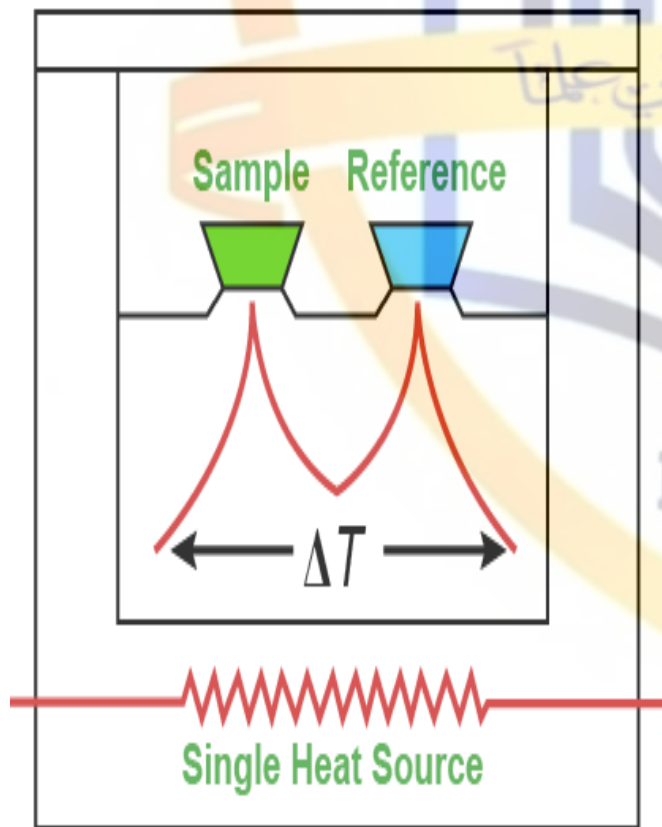
## What does a DSC measure?

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

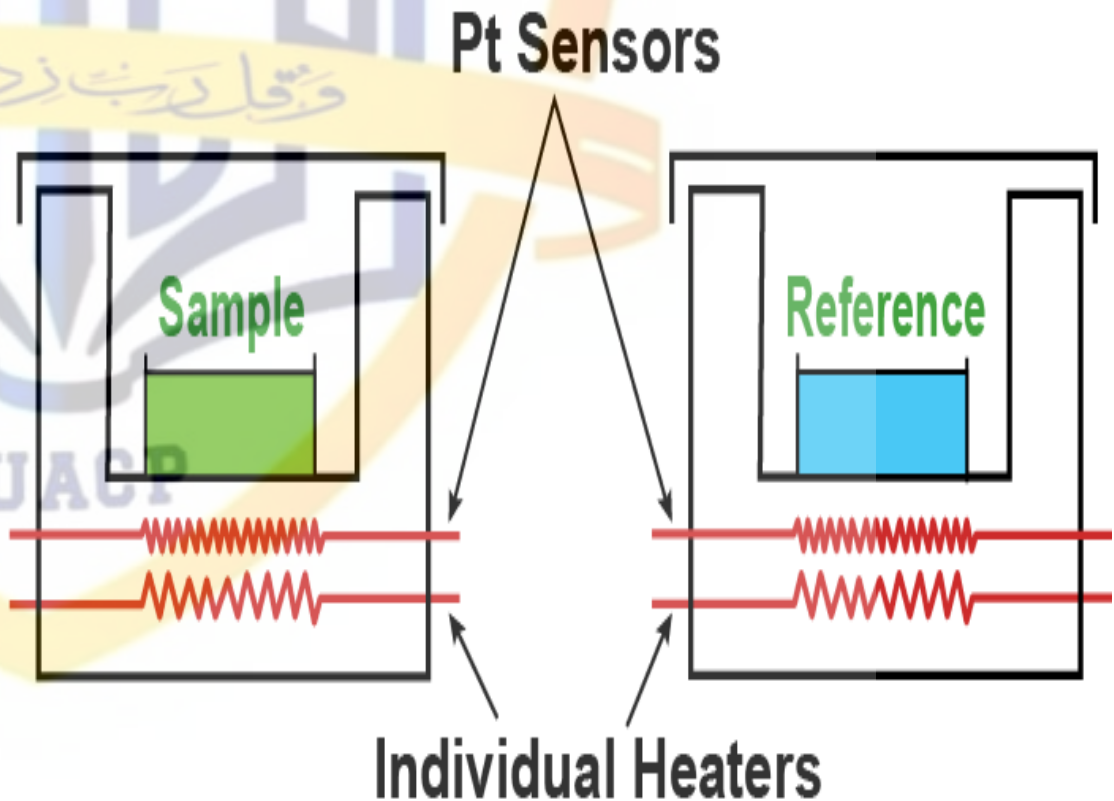




# Types of DSC



**Heat Flux DSC:**  
Quantitative DTA



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

# DSC Heat Flow

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

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

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

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

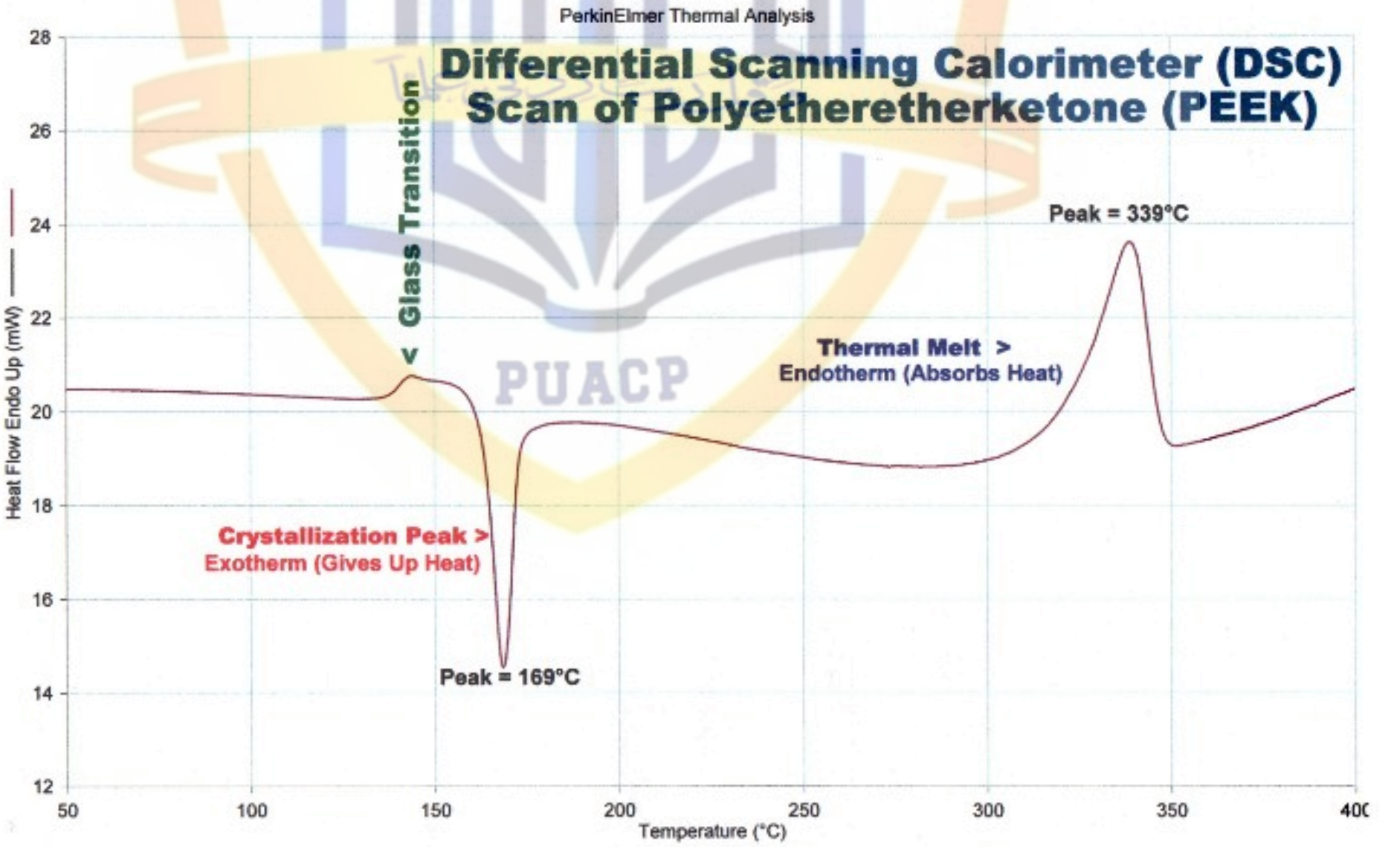
Heat flows into the sample as a result of either Heat flows out of the sample as a result of either

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

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



# DSC Data

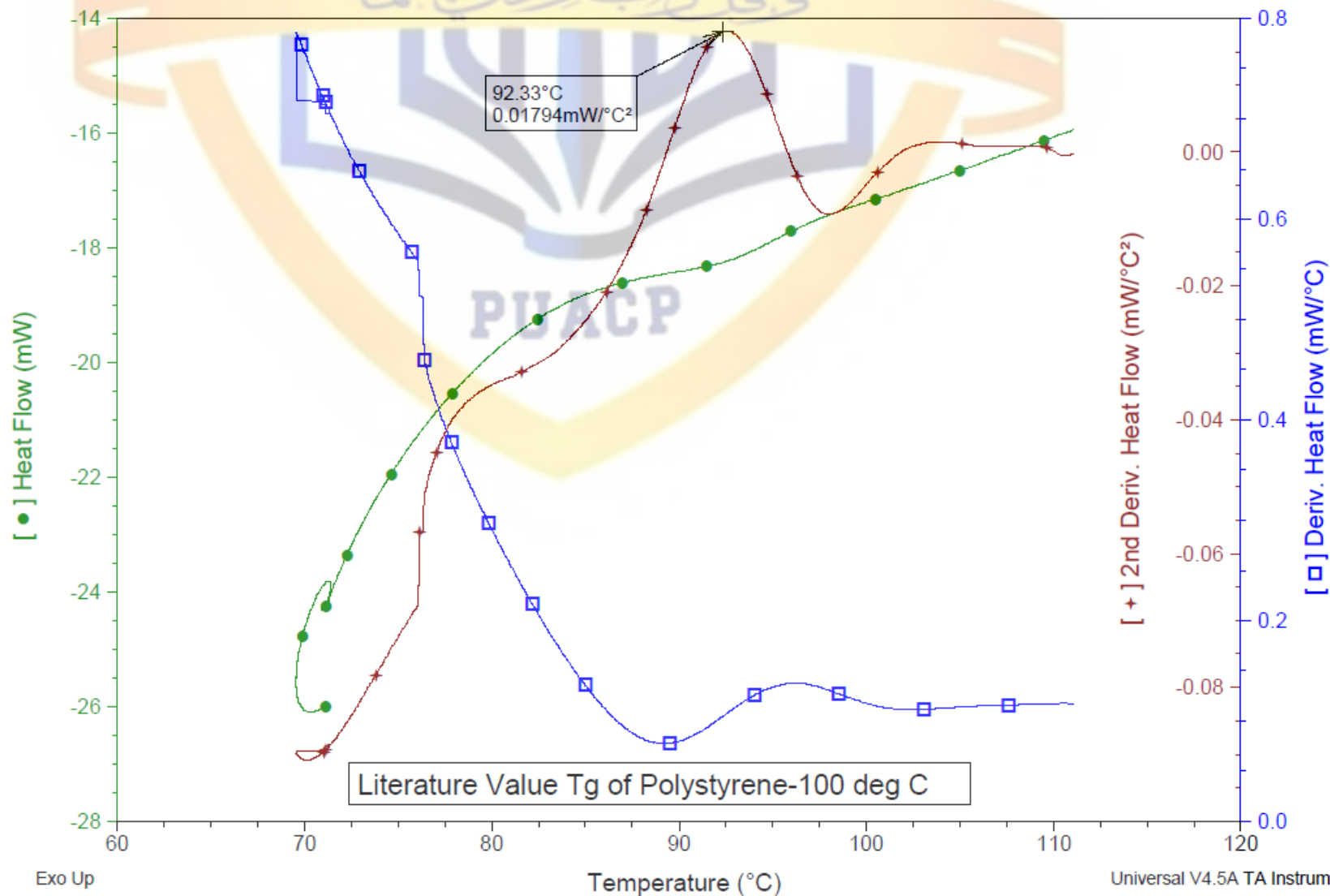


# DSC of Polystyrene

Sample: Polystyrene\_21Aug17  
Size: 16.7950 mg  
Method: Temperature  
Comment: Polystyrene\_21Aug17

DSC-TGA

File: D:\...\Polystyrene\_21Aug17.001  
Operator: TA  
Run Date: 21-Aug-2017 14:30  
Instrument: SDT Q600 V20.9 Build 20



# DSC of PMMA

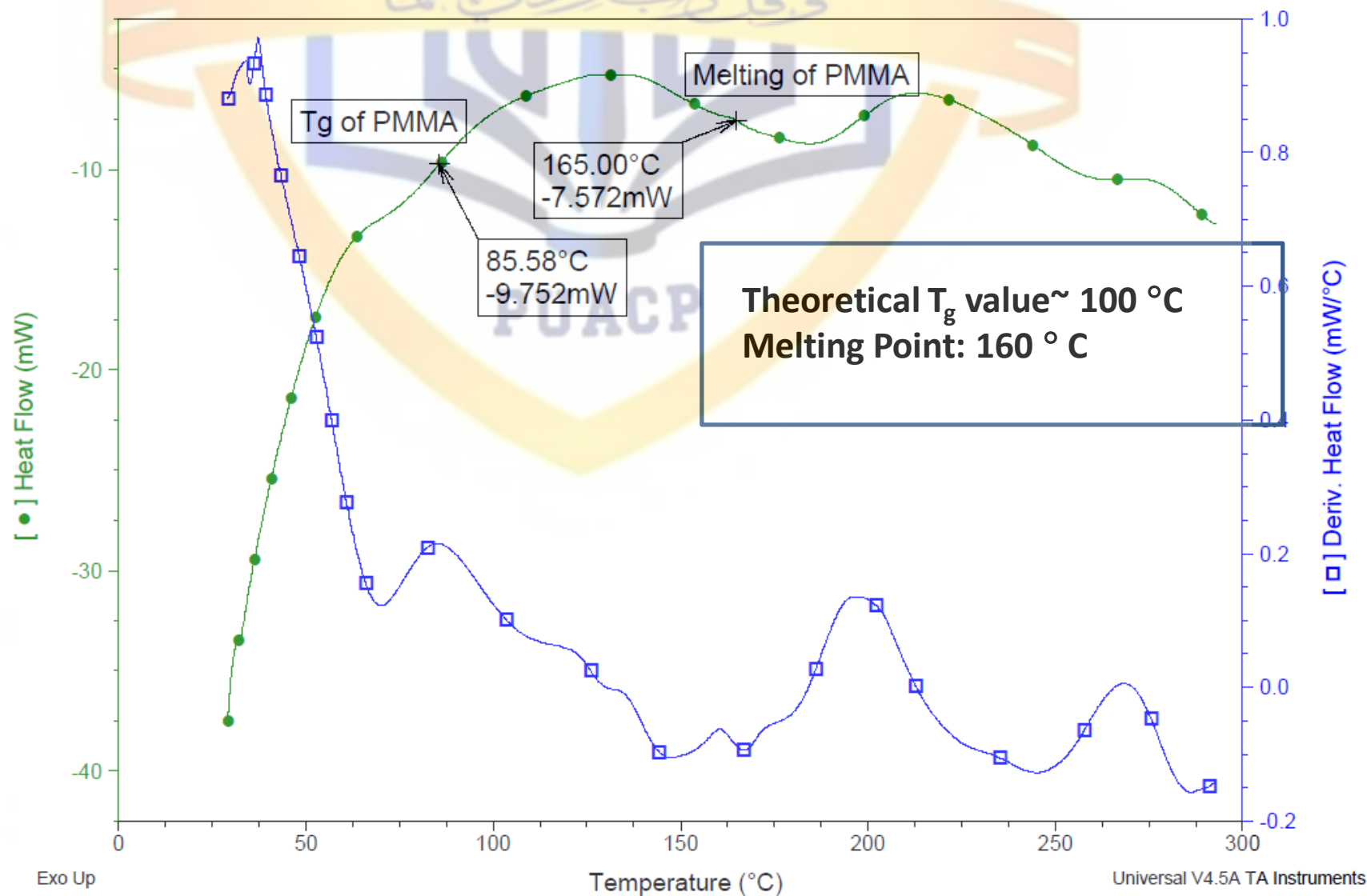
Sample: PMMA-Std-Heat flow-27Jul17  
Size: 11.8600 mg  
Method: DSC Heatflow  
Comment: PMMA-Std-Heat flow-27Jul17

DSC-TGA

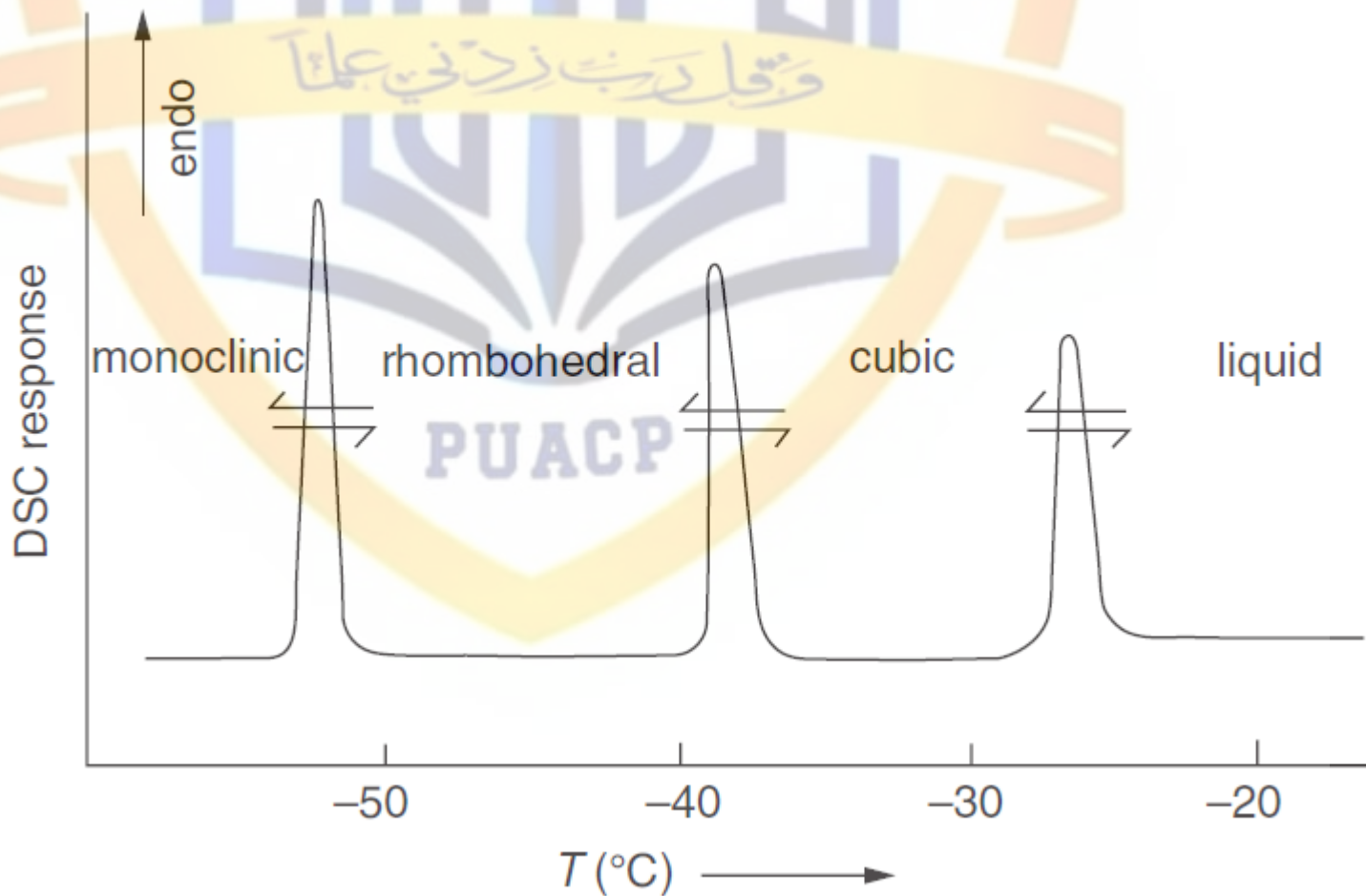
File: D:\...PMMA-Std-Heat flow-27Jul17.001

Run Date: 27-Jul-2017 12:41

Instrument: SDT Q600 V20.9 Build 20



# DSC of Carbon Tetrachloride

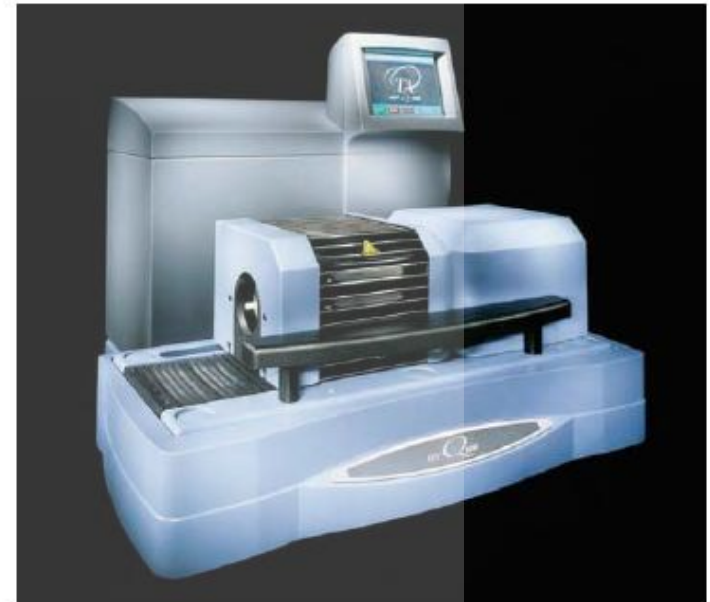


The DSC curve of carbon tetrachloride exhibits three solid-state phase transformations before melting

# DSC-TGA (SDT): The Technique

Simultaneous DSC-TGA measures both heat flow and weight changes in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complimentary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g., melting and crystallization) and those which involve a weight loss (e.g., degradation).

**Q600 SDT Simultaneous DSC-TGA:**  
Measures heat flow and weight changes simultaneously





# DSC-TGA (SDT): Specifications

## TA instruments SDT Q600

**Max. temperature:** 1500 °C

**Heating rates:** 100 °C/min to 1000 °C

25 °C/min to 1500 °C

**Sample cups:** Platinum 110 µl

Alumina (Al<sub>2</sub>O<sub>3</sub>) 90 µl

**Weight sensitivity:** 0.1 µg

**ΔT sensivity (DTA):** 0.001 °C (200 to 1300 °C)

**Furnace Purge Gases:** Helium, nitrogen, air, argon.

**Flow rate:** 20 to 1000 ml/min (100 ml/min typical during experiments).

Regulated by a mass flow controller with gas switching capability.

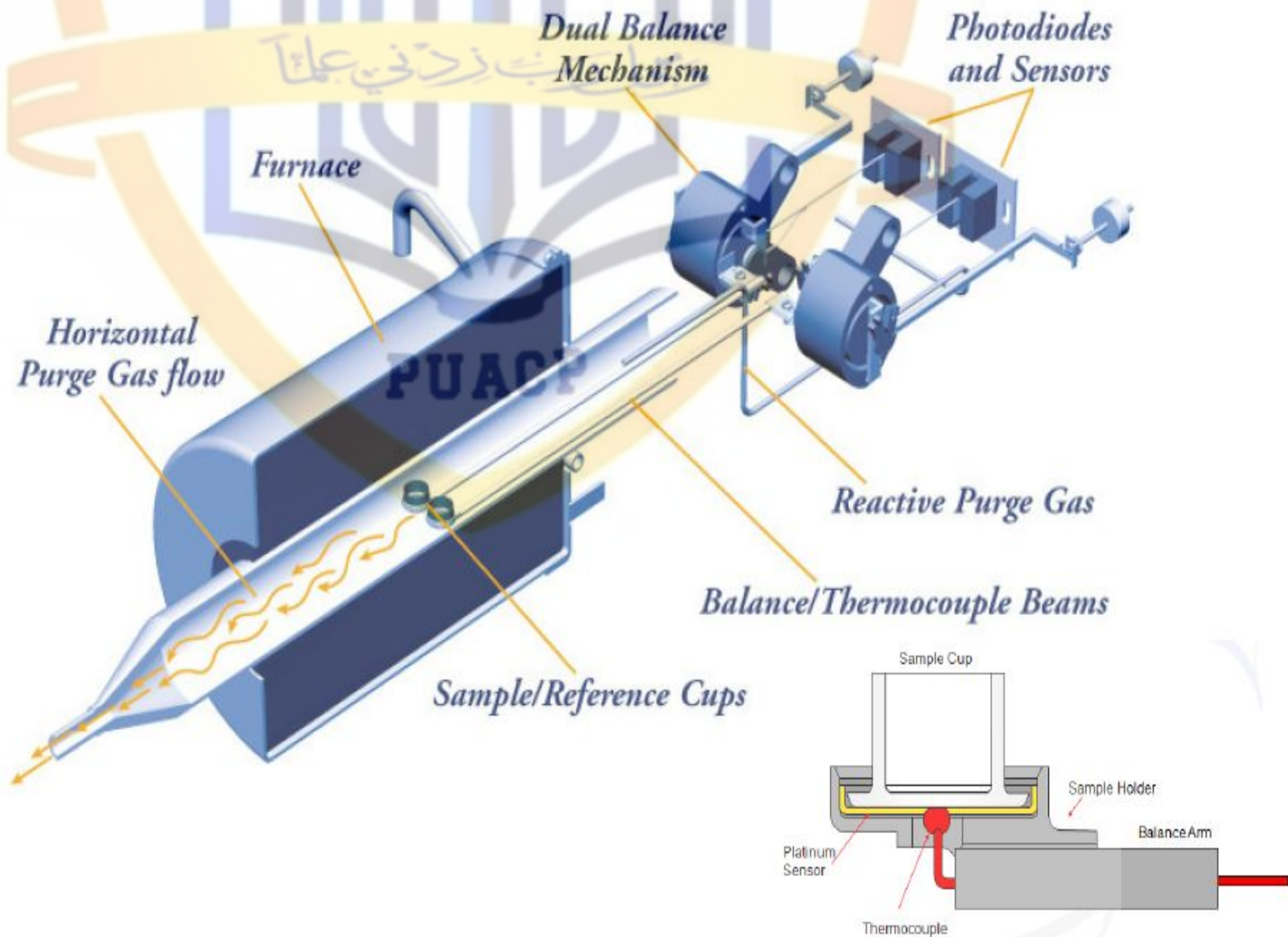
**Secondary Purge:** Oxygen, air, carbon monoxide, carbon dioxide, nitrogen, helium, argon.

**Flow Rate:** 10 to 100 ml/min (20 ml/min is typical for experiments)

# What Simultaneous DSC-TGA can tell you?

- Oxidative/Thermal Stability of Materials
- Composition of Multi-component Systems
- Estimated Lifetime of Products
- Decomposition Kinetics of Materials
- The Effect of Reactive Atmospheres on Materials
- Moisture and Volatiles Content of Materials
- **Transition Temperatures**
- **Heats of Fusion and Reactions**
- **Melting and Boiling Points**

# DSC-TGA (SDT): Instrument Design



# SDT Q600 Calibration

## TGA weight calibration using standard weights:

- ✓ Drift in weight as a function of temperature is observed & corrected.
- ✓ Mass Loss Reference Materials

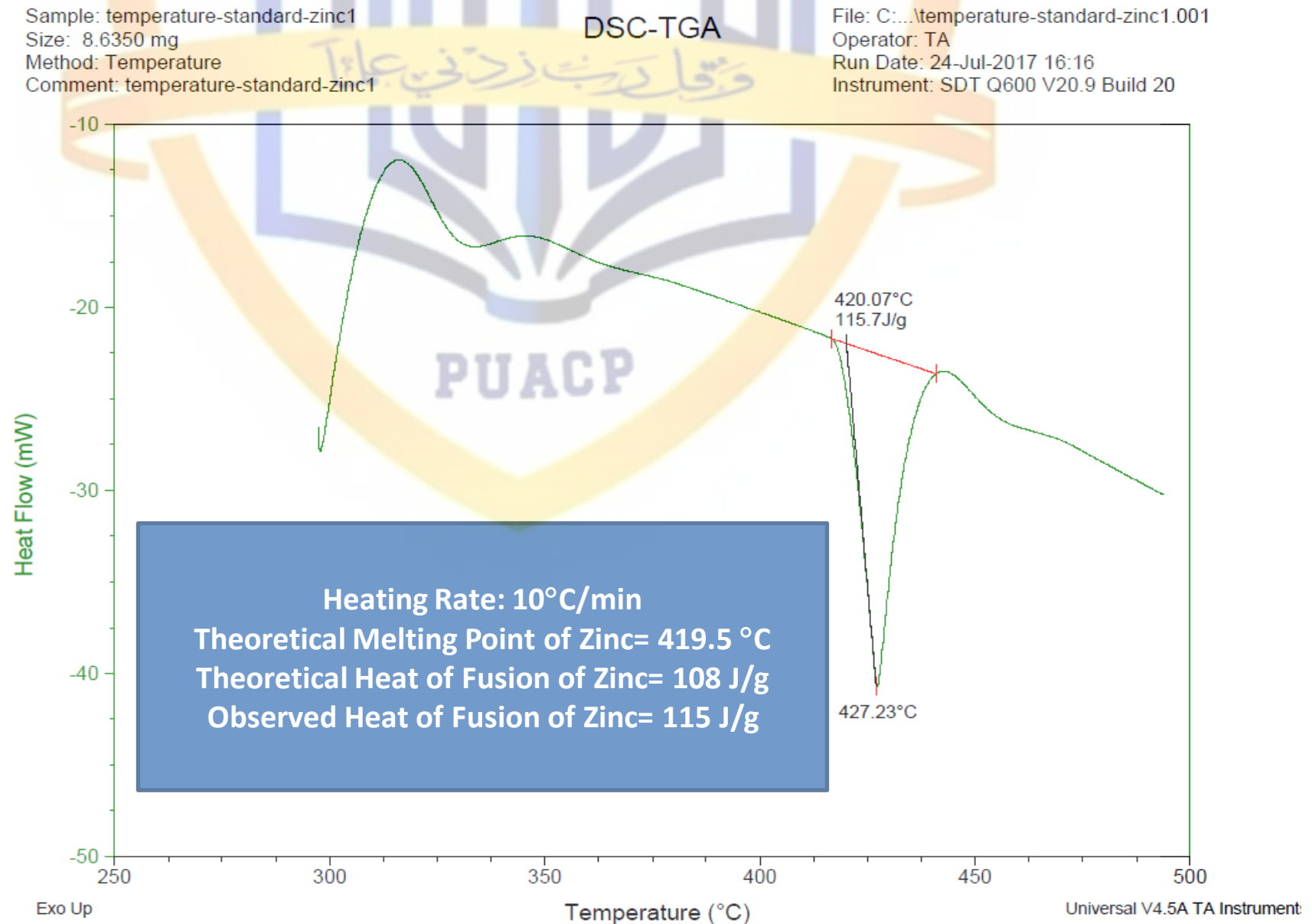
## Temperature Calibration:

- ✓ Melting endotherms of high purity metal standards like Zinc, Indium, Gold.
- ✓ Curie point measurements of Ferromagnetic Materials

## DSC Heat Flow & Cell Constant Calibration:

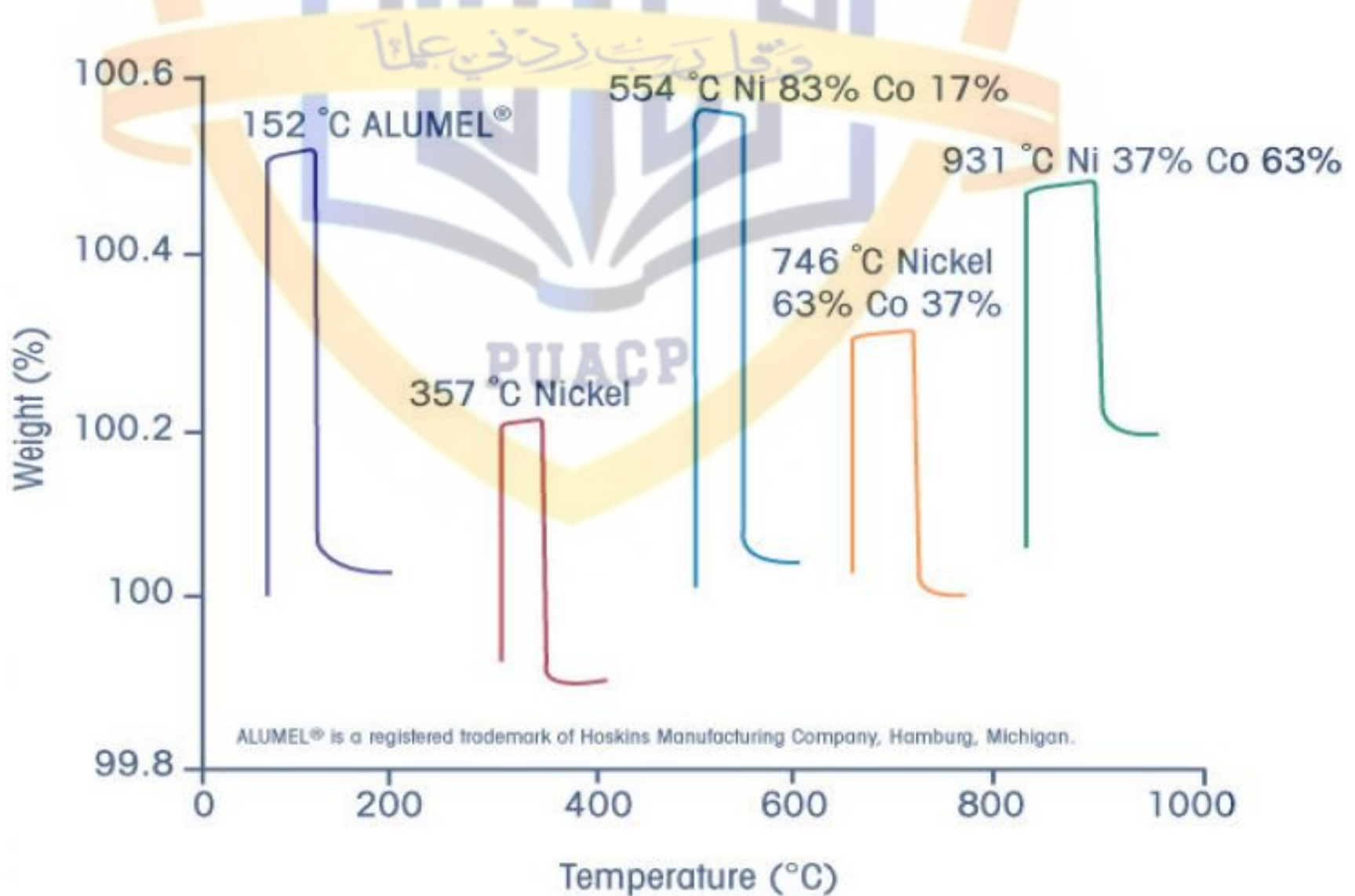
- ✓ Calibrating the heat flow response of a DSC by recording the melting endotherm of a high-purity standard material as a function of time. The peak is then integrated (over time) to yield an area measurement proportional to the enthalpy of melting of the standard material.
- ✓ Comparing the experimentally observed value of Heat of Fusion of high purity metal standard with the literature value, the cell constant is calculated.
- ✓ With corrected value of Cell Constant, the DSC empty pan baseline is measured.

# Temperature Calibration using melting endotherm of high purity Zinc standard

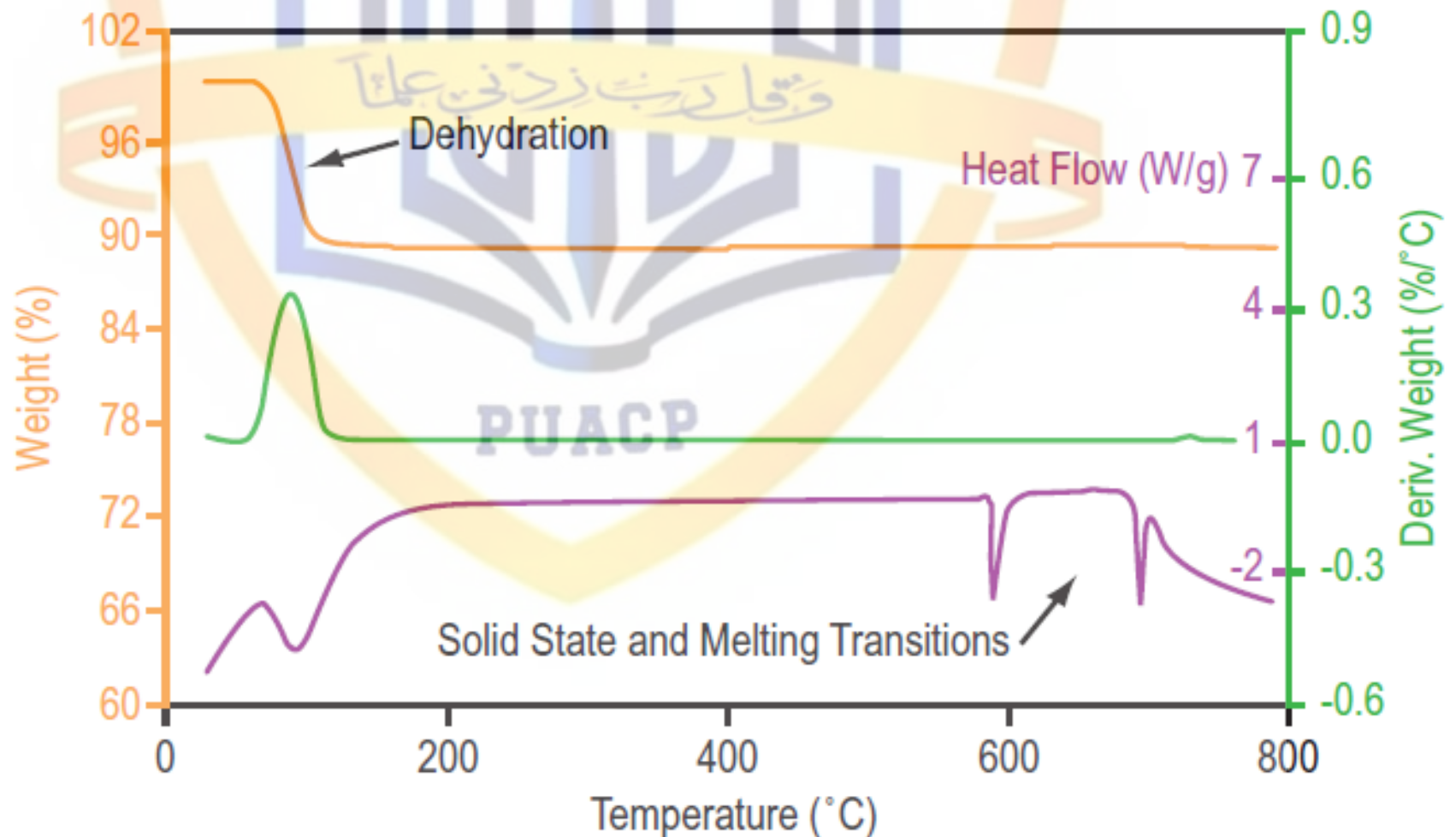




# Curie Point Standards for Temperature Calibration

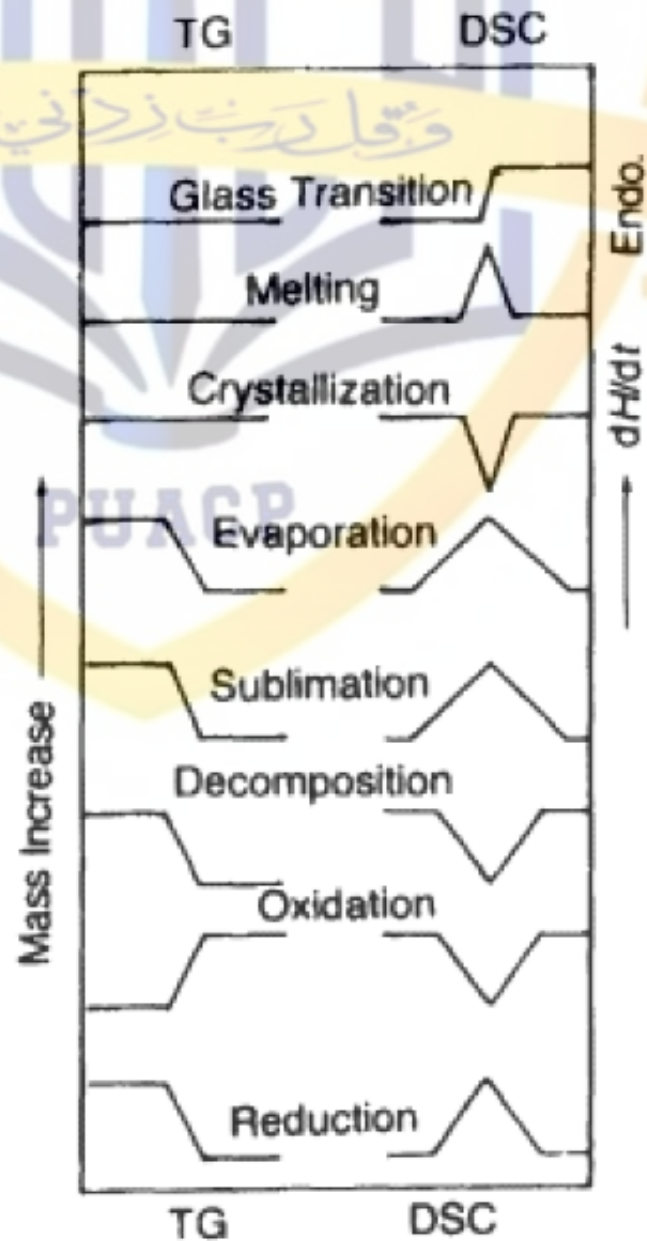


# DSC with TGA



Combine the thermo/kinetic data of DSC with the stoichiometric data from TGA (Sodium Tungstate)

# Comparison of TG-DSC for variety of physicochemical processes



# What is Heat Capacity?

- Heat capacity is the amount of heat required to raise or lower the temperature of a material
- $C_p$  is the absolute value of heat flow divided by heating rate (times a calibration factor)
- Most DSC's do not measure absolute heat flow or heat capacity
- Baseline subtraction is required on most DSC's when measuring  $C_p$

# Why is it Important?

- Thermodynamic property of material (heat flow isn't)
- Heat capacity is a measure of molecular motion. Heat capacity increases as molecular motion increases
- Provides useful information about physical properties of the material as a function of temperature

# Measuring Heat Capacity

- In a DSC experiment, heat capacity is measured as the absolute value of the heat flow, divided by the heating rate, and multiplied by a calibration constant.

$$dH/dt = C_p dT/dt$$

Sample  
Heat  
Capacity

$$C_p = \left[ \frac{dH/dt}{dT/dt} \right] \times K$$

Heat Flow

Heating  
Rate

Calibration  
constant

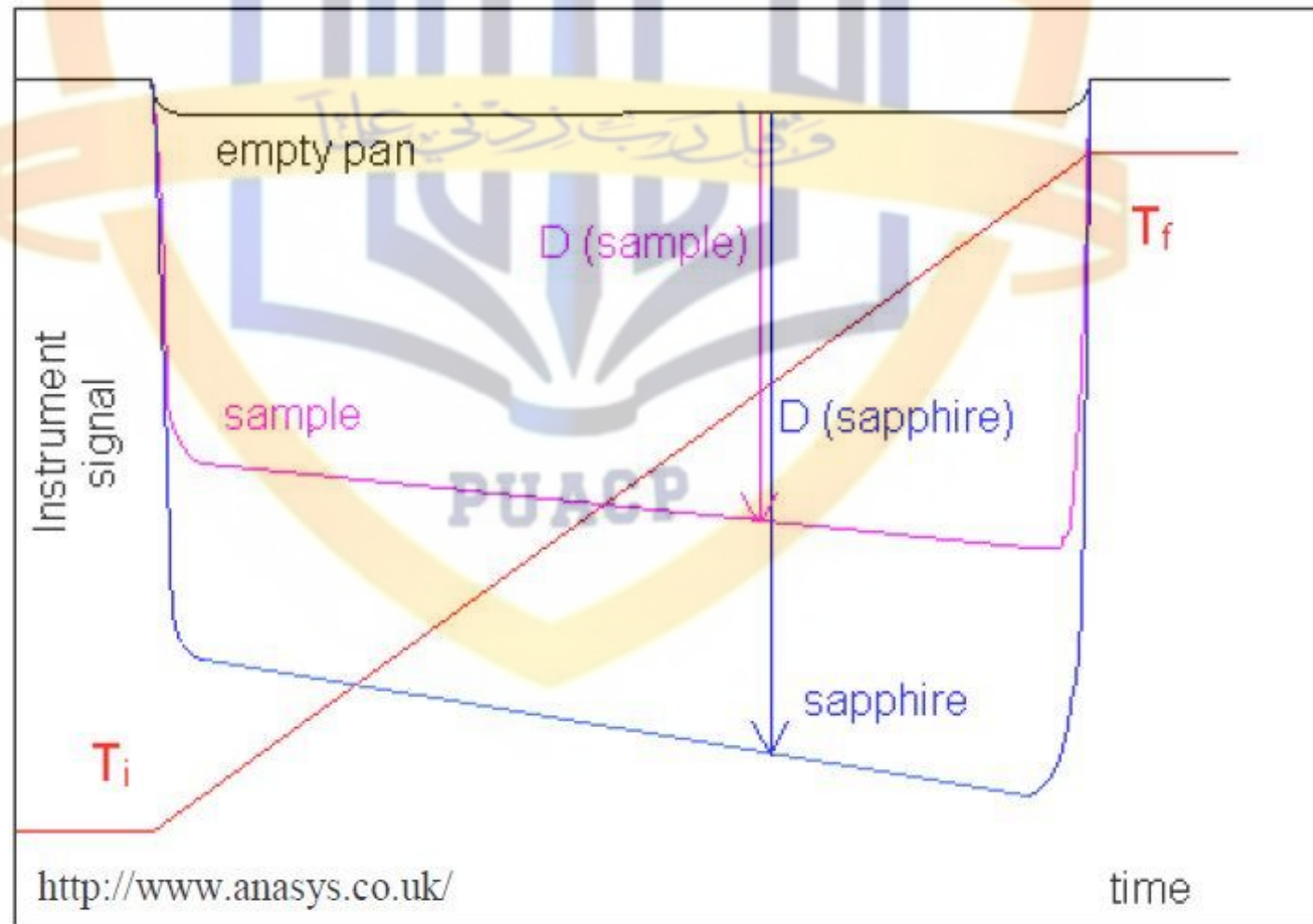
$$C_p \left( \frac{J}{g \cdot ^\circ C} \right) = \frac{\text{Heat flow} \left( \frac{mJ}{sec} \right)}{\text{Heat Rate} \left( \frac{^\circ C}{min} \right) \times wt (mg)} \times 60 \left( \frac{sec}{min} \right)$$



# Measuring Heat Capacity

- ASTM Method E1269
  - Requires 3 runs
    - Run Empty pans for baseline
    - Run calibrate (typically sapphire)
    - Run sample
- Typical Method
  - Iso for 10 min
  - Heat @  $10^{\circ}$  C/min
  - Iso for 10 min

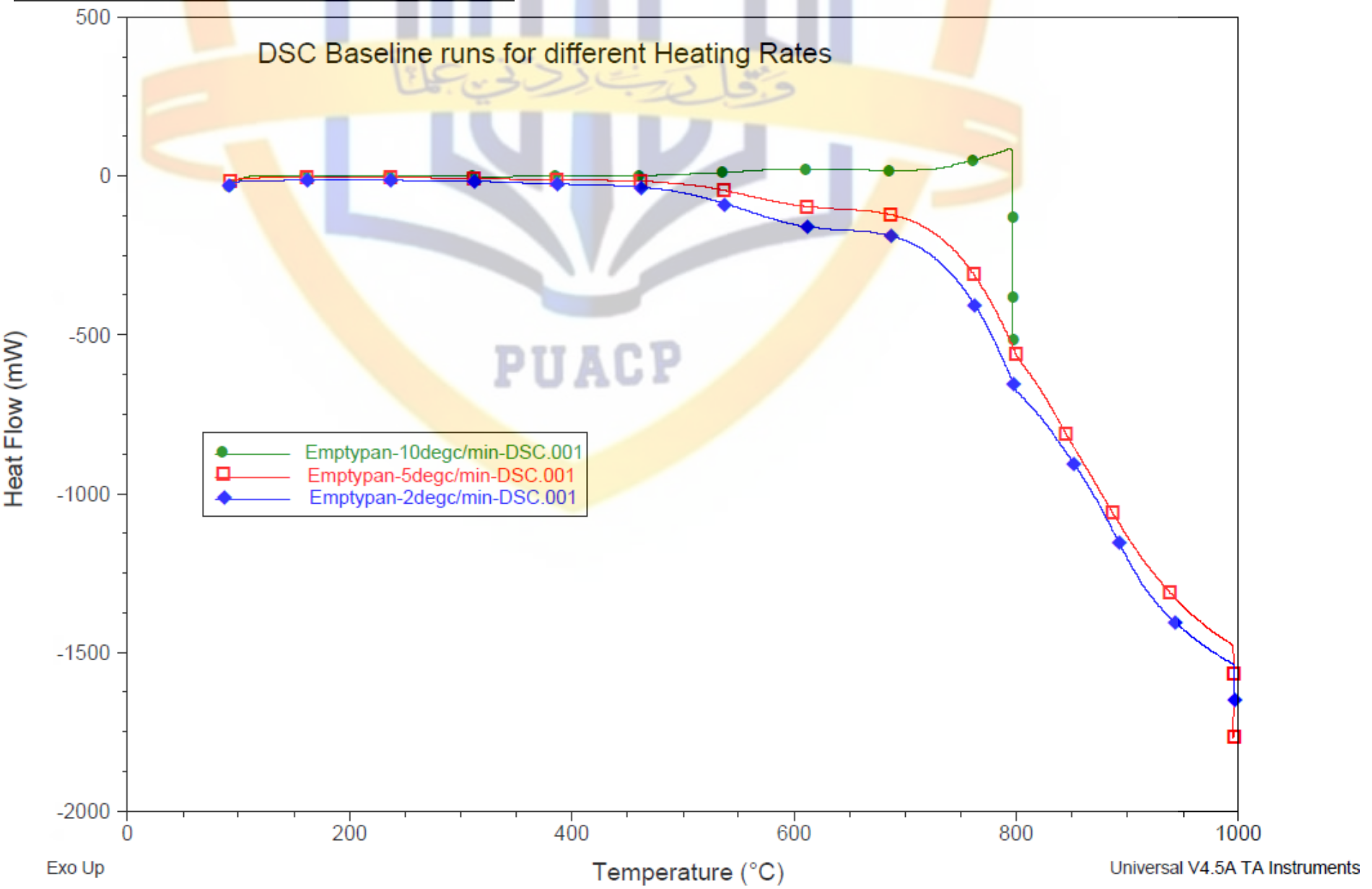
# Heat Capacity measurements using DSC



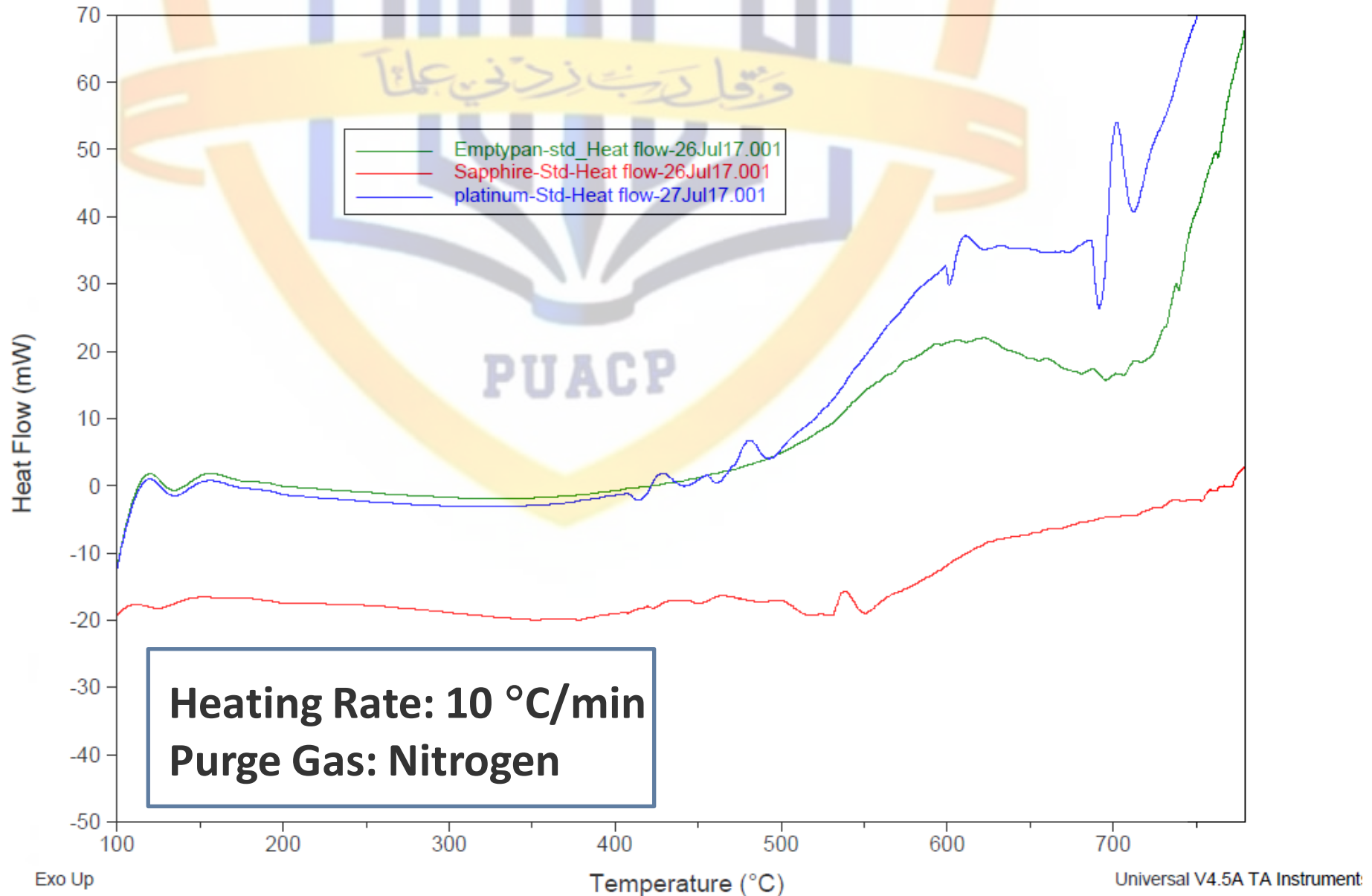
$$\frac{D(\text{sample})}{D(\text{sapphire})} = \frac{C_p(\text{sample}) \times \text{mass of sample}}{C_p(\text{sapphire}) \times \text{mass of sapphire}}$$

**ASTM E1269**

# Empty pan baseline measurements at different heating rates using SDT Q600



# Heat Flow measurements: Baseline, Sapphire (Standard) & Platinum (Sample) using SDT Q600



# Limitations in measurement of Heat Capacity using SDT Q600

DSC comprises of two identical calorimeters in a common enclosure that are assumed to be identical.

The heat flow rate of an empty perfectly symmetrical twin calorimeter should be zero. However, It almost never is because the DSC is rarely symmetrical as assumed.

The asymmetry is the inevitable result of manufacturing tolerances and is unavoidable.

The resistance between sample sensor and the furnace equals the resistance between reference sensor and the furnace

Measured temperature equals sample temperature.

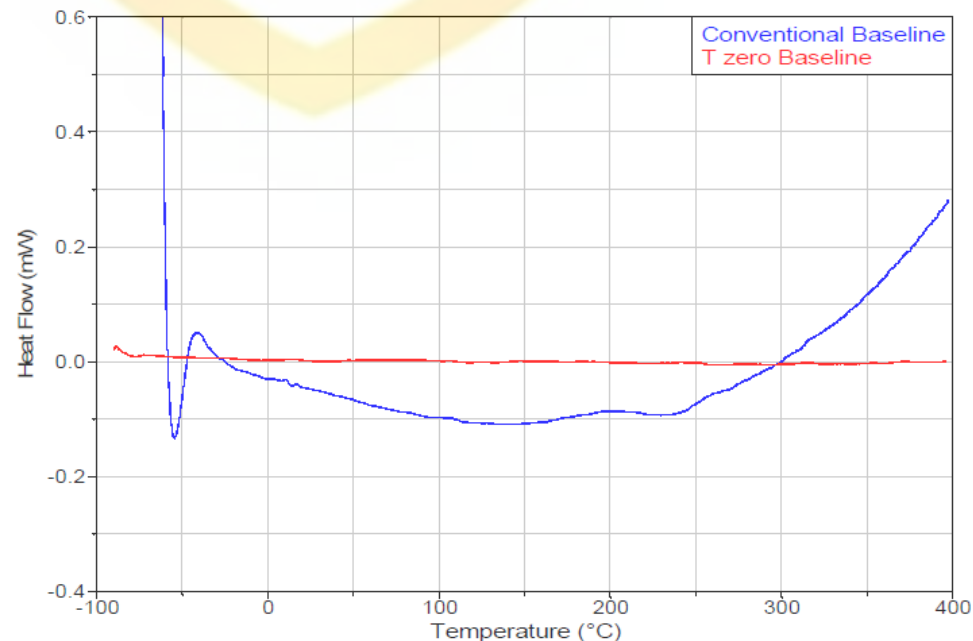
No heat exchange with the surroundings



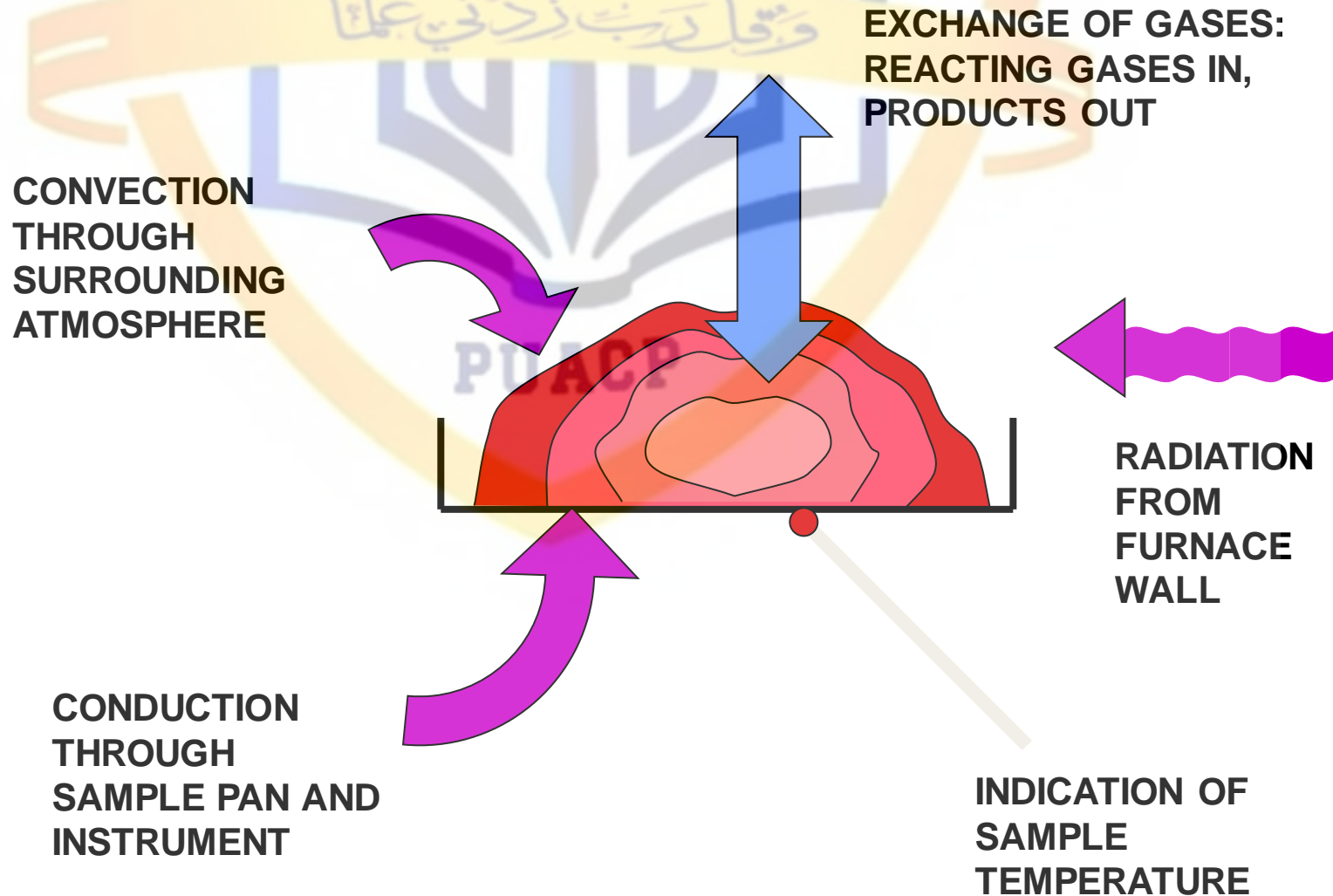
Whenever the heating rate of the sample and reference calorimeters is not identical, the measured heat flow is not the actual sample heat flow rate. Resolution and sensitivity suffers due to these issues.

The sample and reference calorimeter heat capacities do not match thereby giving rise to non zero empty DSC heat flow baseline.

Heat Capacity should be measured using the dedicated DSC set up of TA Instrument where they measure the capacitance and resistance of each DSC cell without assuming that they are identical.



# Physical limitations on the heating process



# Good Praxis for thermal experiments

- "Always" run a TGA experiment before beginning DSC tests on new materials
- Heat approximately 10mg sample in the TGA at 10°C/min to determine volatile content & decomposition temperature
- Use TGA data to help select DSC experimental conditions
- Fine grained powder should be used to achieve greater contact area and better equilibrium conditions.
- Chemical nature & Flow of Purge gas affect TA data
- The time at any temperature must be sufficiently long in order to permit completeness of reactions
- Larger mass and larger heating rate produce larger peak, but make detection of closely spaced thermal events more difficult.

# Good Praxis for thermal experiments....contd.

- Powder samples increase oxidation, reduce heat flow.
- Evaporation can reduce sample mass, lead to incorrect measurement of enthalpy and contamination of instrument.
- Regular Calibration is extremely important.
- Instrument must be isolated from mechanical vibrations.
- Sample with unknown decomposition products must be carefully studied so that all evolved gases can be removed safely.
- Make sure that crucible size, shape and material does not hamper your measurements.
- Identify artefacts by using baseline empty pan runs.

## Literature Sources

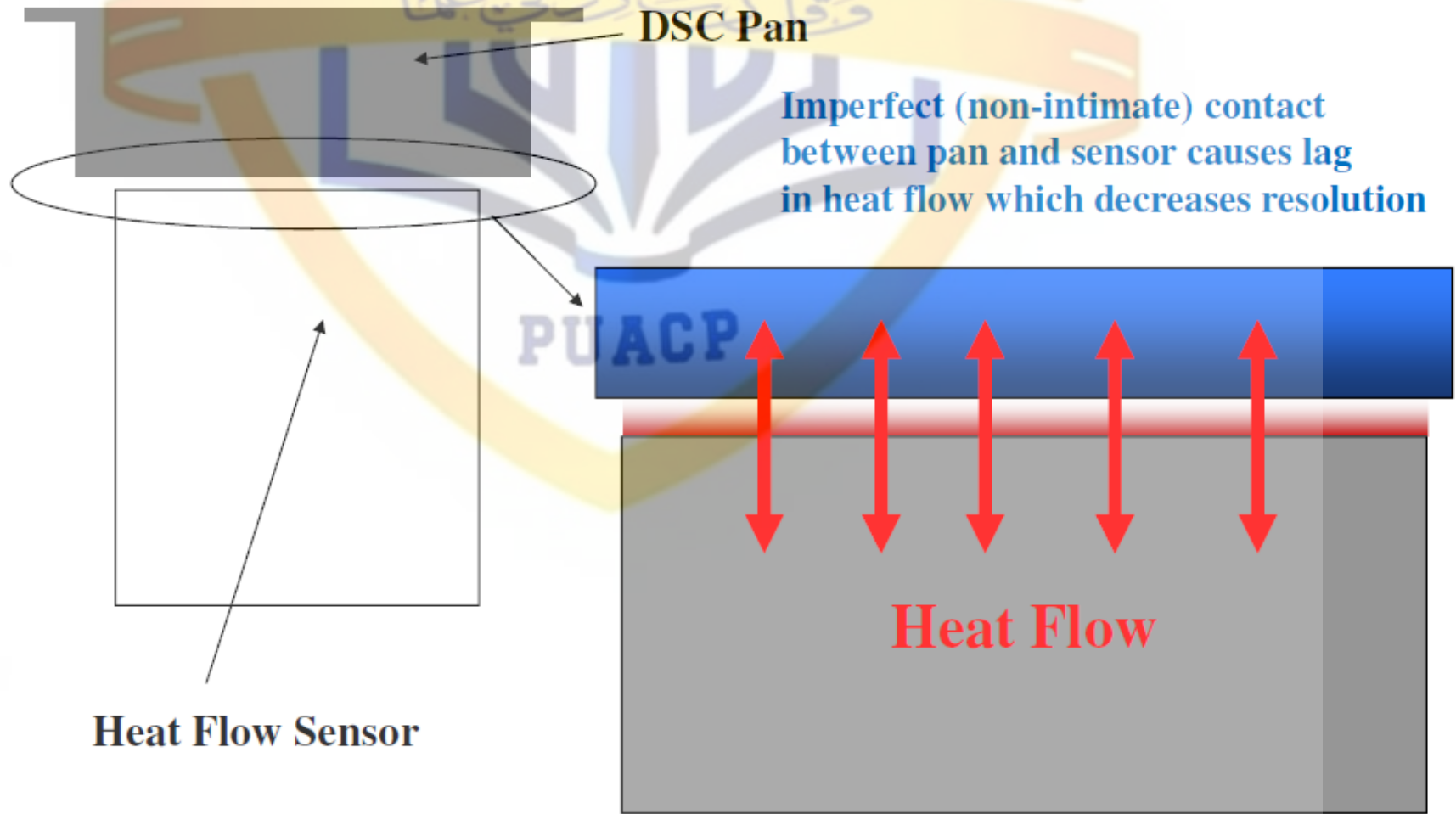
- 1) M.E.Brown , Introduction to thermal analysis : Techniques and application , second edition, Springer, 2007
- 2) Paul Gabbot, Principles and Applications of Thermal Analysis, Blackwell Publishing
- 3) Peter J. Haines, Thermal methods of Analysis, Principles, Applications & Problems, Chapman and Hall
- 4) Wesley Wendlandt, Thermal Analysis, Wiley
- 5) Mackenzie, Differential Thermal Analysis, Academic Press
- 6) TA Instruments, TGA & DSC Manuals
- 7) Perkin Elmer, TGA manuals
- 8) Mettler Toledo Thermal Analysis Manuals
- 9) MATERIALS CHARACTERIZATION Introduction to Microscopic and Spectroscopic Methods by Yang Leng
- 10) Handbook of Thermal Analysis & Calorimetry: M. E. Brown & P. K. Gallagher



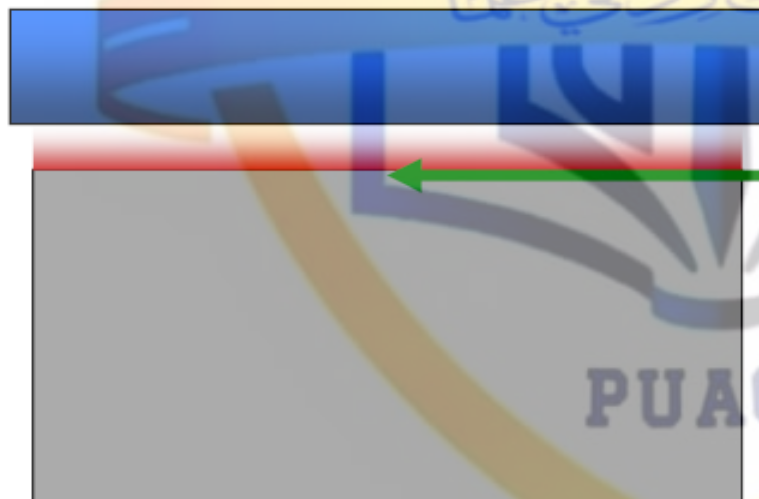


**Thank you for your attention!!**

# What is Pan Contact Resistance?

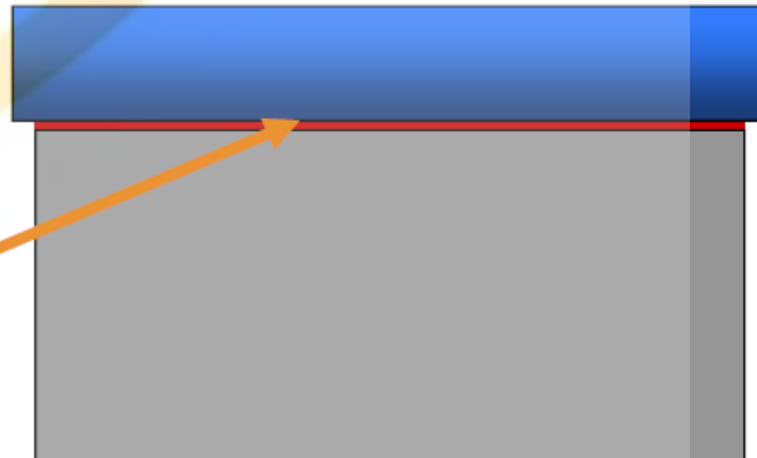


## Result of Pan Contact Resistance Factor

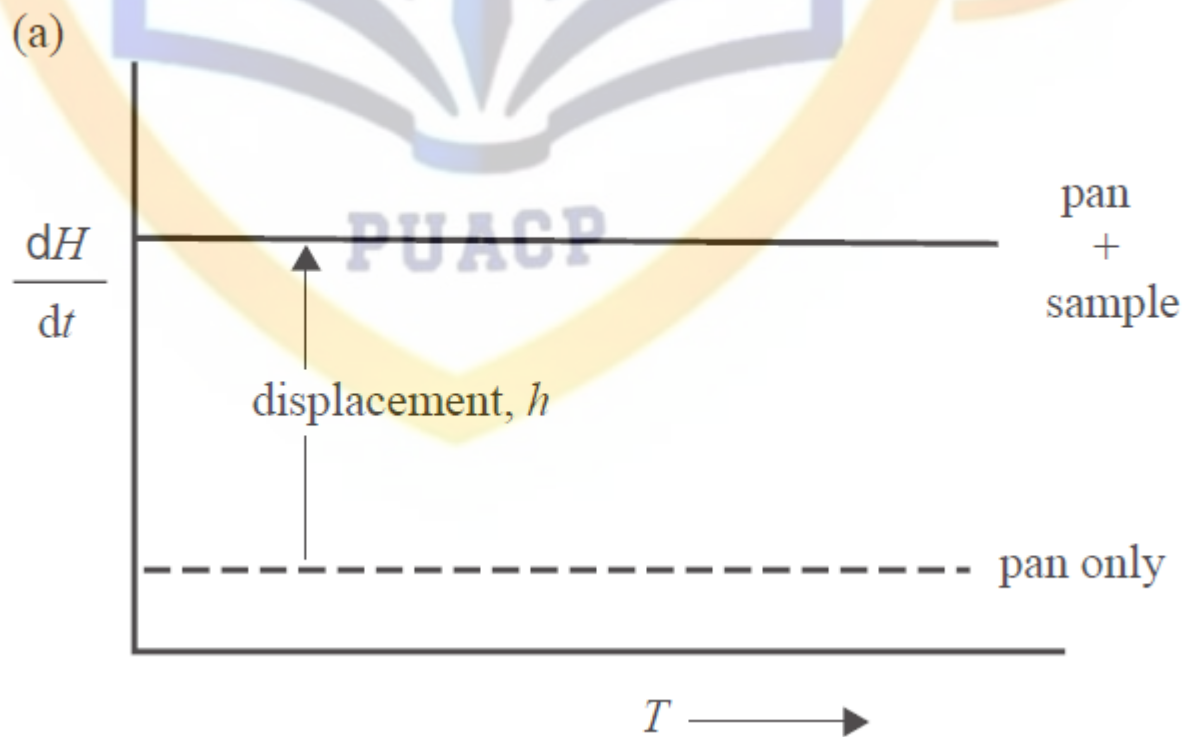


Without pan contact resistance factor, temperature is measured at the sensor

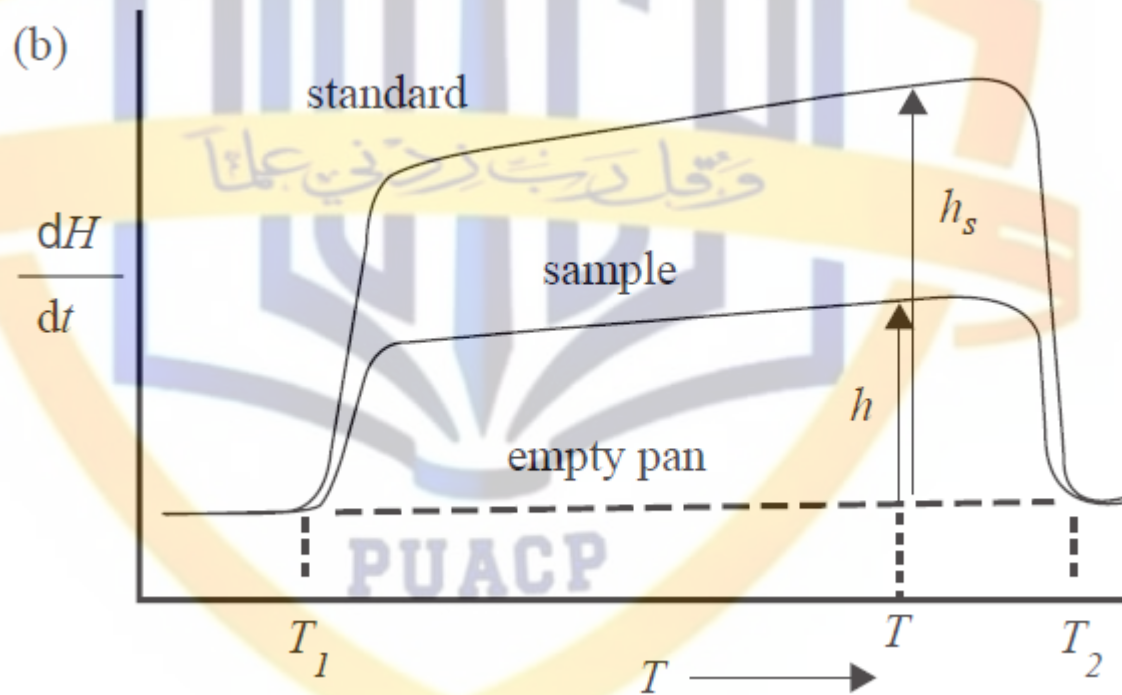
With pan contact resistance factor, temperature is measured at the bottom of the pan, in intimate contact with the sample



$$C_P \equiv \left( \frac{\partial H}{\partial T} \right)_P$$



$$h = B\beta C_p$$



$$C_P = C_{Ps} \left( \frac{h M_s}{h_s M} \right)$$

$M_s$  and  $M$  are the mass of standard and sample