THERMAL ANALYSIS

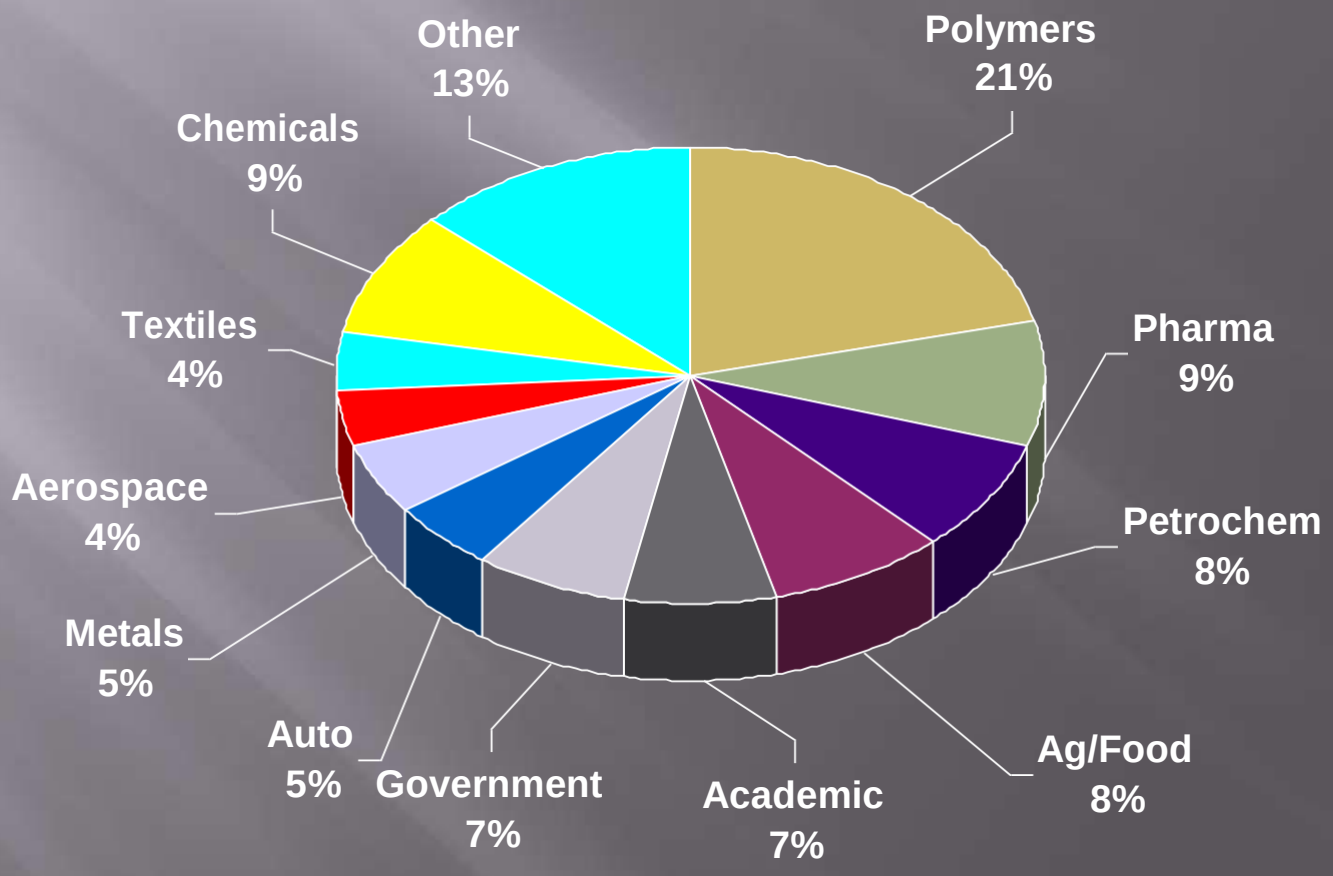
Thermal methods of Analysis

- This is based on the concept of heating a sample – followed by well-defined modified procedures, such as : gravimetric analysis, differential analysis and titrimetric analysis.
- Some property of a system is measured as a function of temperature.
- Thermal spectra or Thermograms

Conti....

- Thermo grams characterize a single or multi component system in terms of :
  - Thermodynamic properties, and
  - physicochemical reaction kinetics.

Thermal Analysis is widely used …



Different Techniques

- Thermometric Titration (TT)
- Thermal Mechanical Analysis (TMA)
- Dynamic Mechanical Analysis (DMA)
- Differential Scanning Calorimetriy (DSC)
- Thermal Gravimetric Analysis (TGA)
- Differential Thermal Analysis (DTA)
- Temperature Programmed Desorption (TPD)

Principle

- Sample is heated at a constant heating rate
- Sample's Property Measured
  - Wt — TGA
  - Size — TMA
  - Heat Flow — DSC
  - Temp. — DTA
  - Heat of mixing — TT
  - Tem. at which gas is desorbed at the surface. — TPD

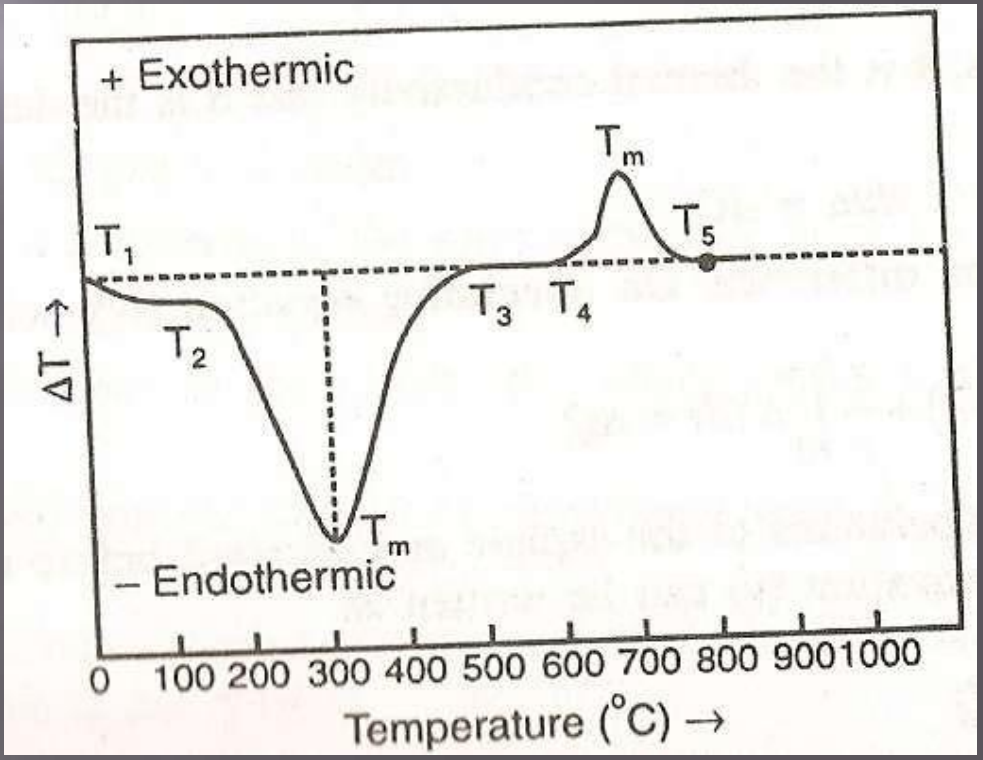
What is DTA ?

- Involves the technique of recording the difference in temperature between the Test and Reference material time being constant for both.
- Hence the Differential Thermogram consists record of difference in Temperatures.

Thermogram

A differential thermogram consists of a record of the difference in sample and reference themperature(ΔT) plotted as a function of time t, sample temperature(T_s), reference temperature(T_r) or furnace temperature(T_f).

In most of the cases, physical changes give rise to endothermic curves, whereas chemical reactions give rise to exothermic peaks.



Factors affecting DTA curve

A] Environmental factors
B] Instrumental factors
- i] Sample holder
- ii] Differential temperature sensing device
- iii] Furnace characteristics
- iv] Temperature- programmer controller
- v] Thermal Regime
- vi] Recorder

C] Sample factors
- 1] Physical
- 2] Chemical

DTA

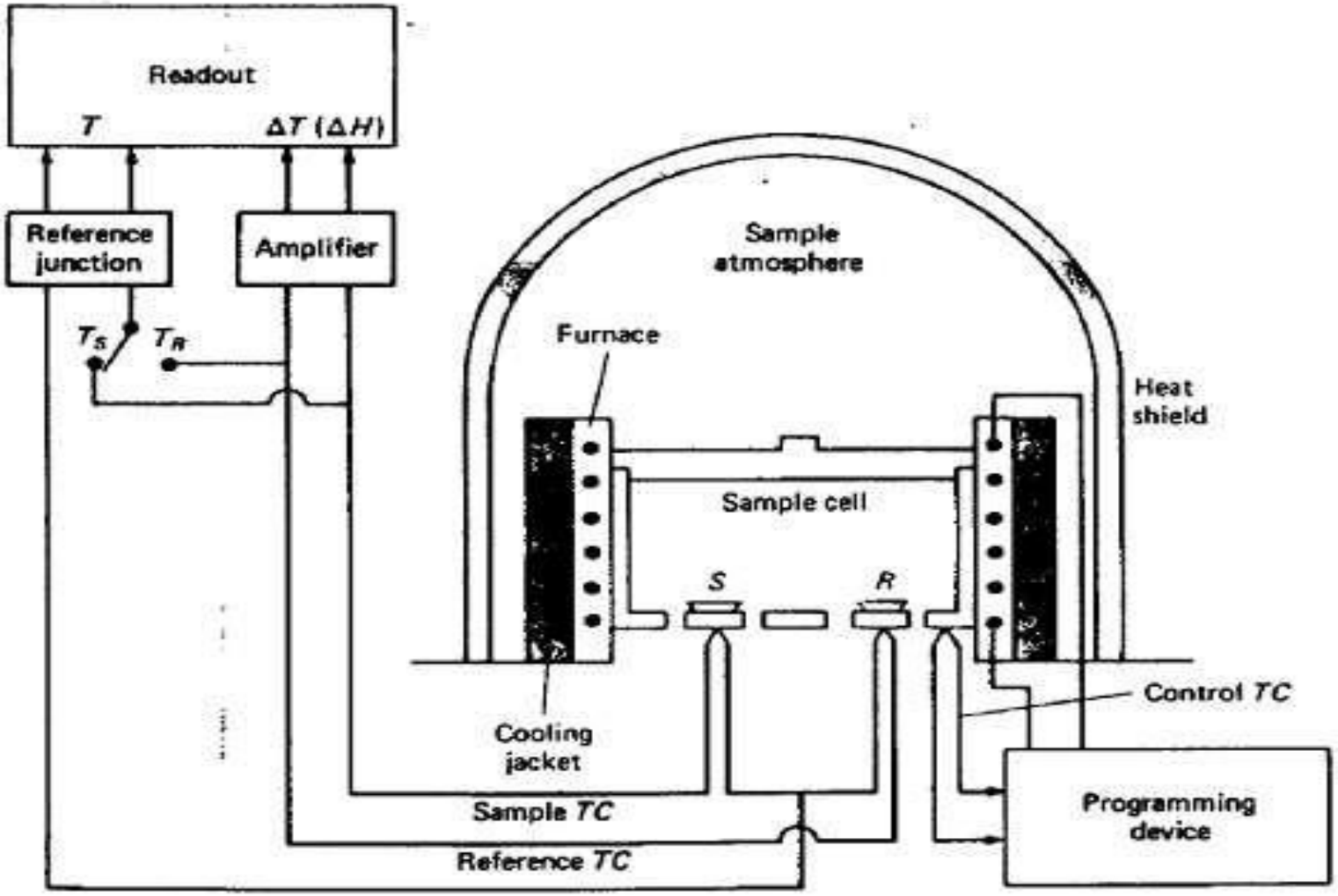


FIGURE Schematic diagram of the Fisher Series 300 differential thermal analyzer system. (Courtesy of Fisher Scientific Co., Pittsburgh, Pennsylvania.)

Instrumentation

- A differential thermal analyzer is composed of five basic components, namely :

1} Furnace

2} Sample holder

3} temperature controller and recorder

4} thermocouple

5} Cooling device

1} Furnace

- Tubular furnace is most commonly used because it possess the desired characteristic for good temperature regulation and programming.
- Dimension of the furnace is depends upon the length of the uniform temperature zone desired.
- The choice of resistance material is depends on the maximum temperature of the operation and gaseous environment.
- Grooved muffled cores preferred.

2} Sample holder

- Should having low cost, ease of fabrication and inertness towards the sample.
- Metallic material: nickel, stainless steel, platinum
- Non-metallic material: glass, vitreous silica or sintered alumina.
- Most commonly the shape of holder is cylindrical.
- The nature of physical constant between the sample, thermocouple junction and the specimen holder affect the DTA signals. So to maintain it, a sample holder with dimples in which

3} Temperature controller and recorder

A] *Temperature Controller*

- In order to control temperature, the three basic elements are required.
- These are sensor, control element and heater.
- The control element governs the rate of heat-input required to match the heat loss from the system.
- The location of sensor with respect to the heater and mode of heat transfer measure the time elapsed between sensing and variation in heat input.

Conti…

B] *Temperature programming*

- It transmits a certain time-based instruction to the control unit.
- By this device one can achieve linearity in the rate of heating or cooling it is driven in a non-linear fashion using a special cam-drive.
- Heating rates of 10-20 o C / mints are employed.

C] *Recorder*

- The signals obtained from the sensors can be recorded in which the signal trace is produced on paper or film, by ink, heating stylus, electric writing or optical beam.

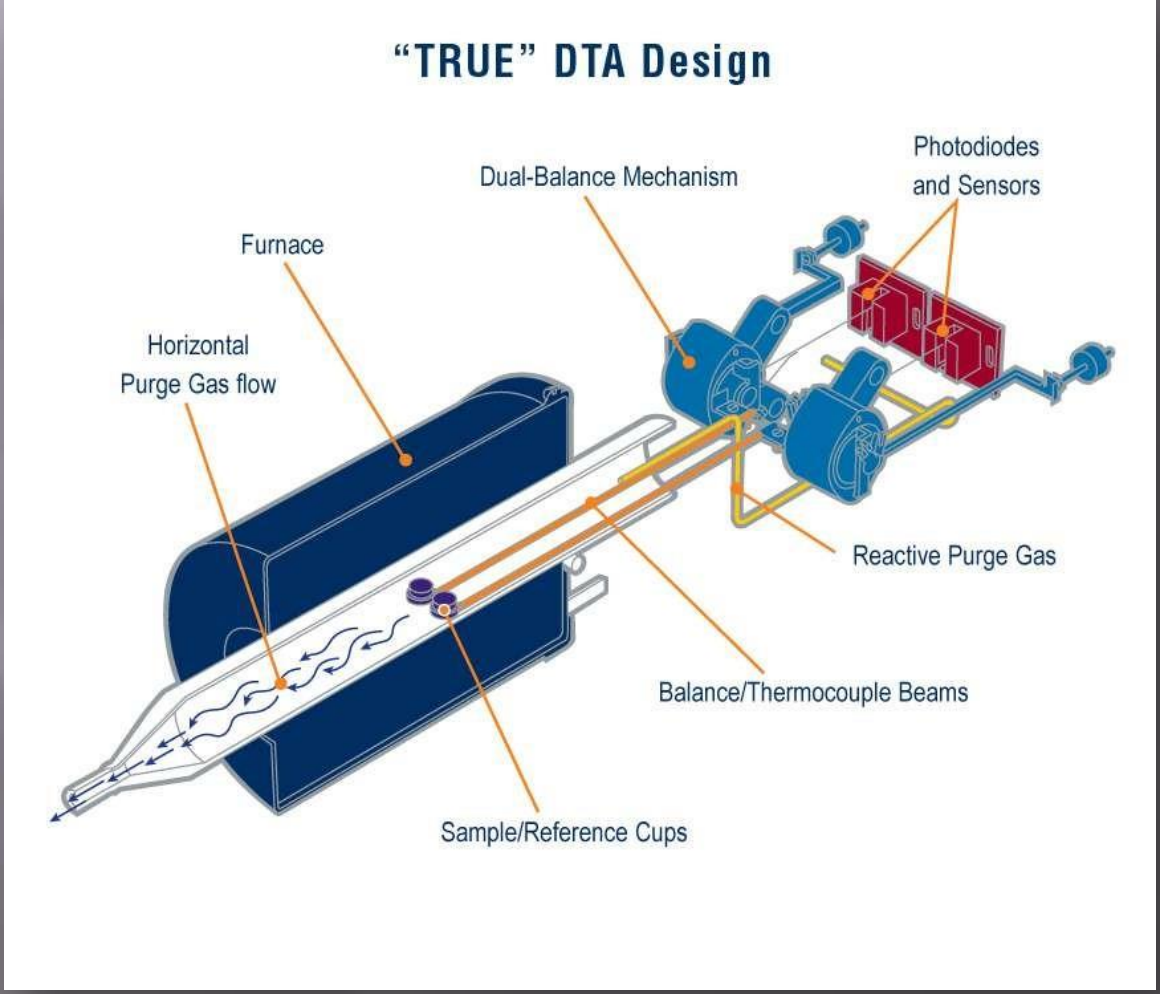
4} Thermocouple

- Thermocouples are the temperature sensors.
- It is made up from chromel p and alumel wires are used to measure and control temperature up to 1100 ^{0}C in air.
- For above 1100 ^{0}C one should use thermocouple made from pure platinum & platinum-rhodium alloy wires.

5} Cooling device

- It is separate from the temperature programmer because it is independent from heating.

DTA Analyzer



Methodology

- Insert a very thin thermocouple into a disposable sample tube 2 mm in diameter and containing 0.1- 10 mg of sample,
- Another identical tube is either kept empty or filled with a reference substance, such as quartz, sand, alumina.
- The two tubes are simultaneously inserted into the sample block and subsequently heated (or cooled) at a uniform predetermined programmed rate

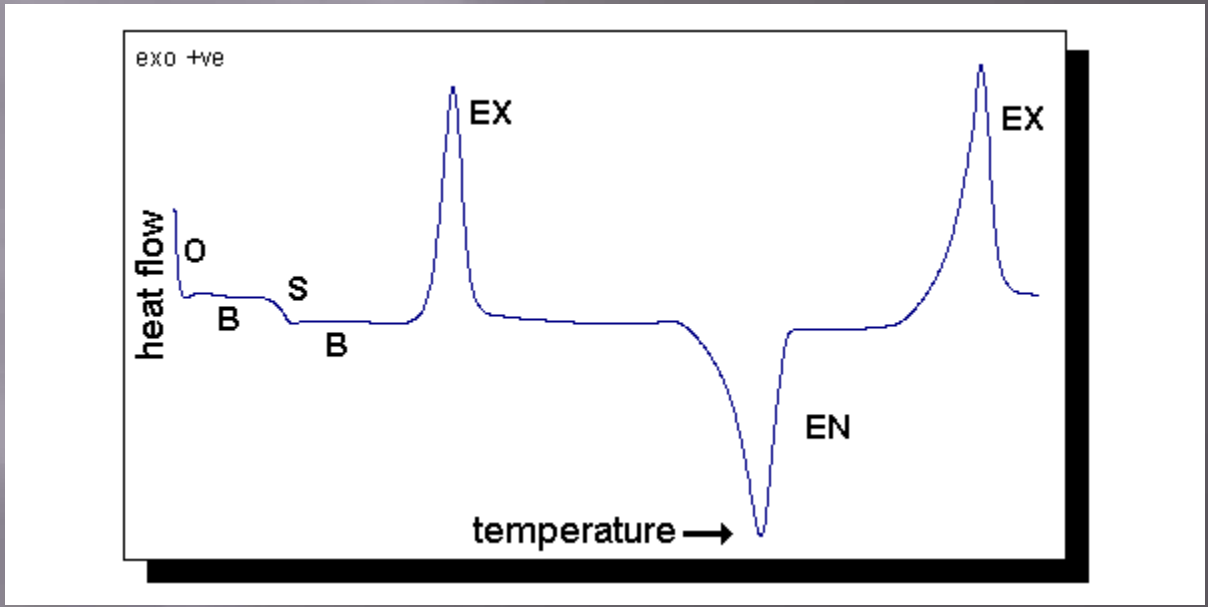
Requirements

- DTA—A few of the vital aspects are :
  - Pre-treatment of the specimen,
  - Particle size and packing of the specimen,
  - Dilution of the specimen,
  - Nature of the inert diluent,
  - Crystalline substances must be powdered, and sieved through 100-mesh sieve

Cont...

- Either to suppress an unwanted reaction (e.g., oxidation), or to explore the study of a reaction(e.g., gaseous reaction product)—the atmosphere should be controlled adequately.

DTA Curve



Advantages:

- Instruments can be used at very high temperatures.
- instruments are highly sensitive.
- flexibility in crucible volume/form.
- characteristic transition or reaction temperatures can be accurately determined.

Disadvantage:

- uncertainty of heats of fusion, transition, or reaction estimations is 20-50%.

Applications of DTA

- *Physical Chemistry*

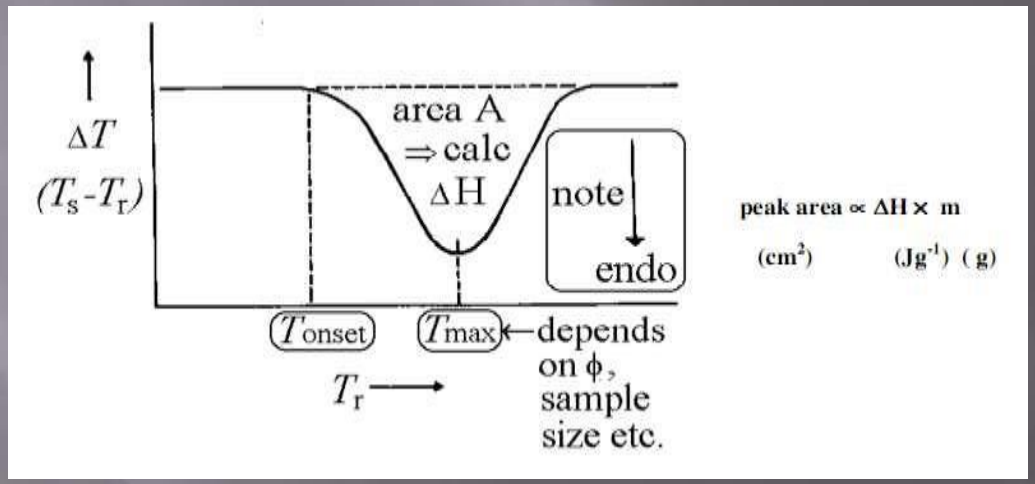
1. Heat of a Reaction
2. Specific Heat of substance like Naphthalene.
3. Thermal Diffusivity of samples

- *Analytical Chemistry*

1. Identification of Products since no two products have identical curves.
2. Determination of Melting point.

Applications of DTA

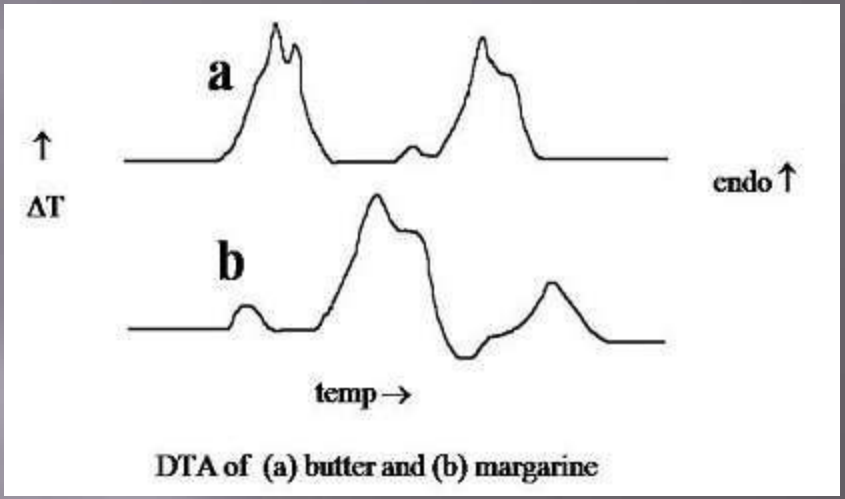
1. To construct phase diagrams and study phase transitions.
2. To find ΔH
   Peak areas depend upon sample mass, m, enthalpy change ΔH of the process, and geometric and conductivity factors such as heating rate φ and particle size (included in a constant k for a certain substance).



Usually the sample peak area is compared with a standard undergoing an enthalpy change at a similar T (since the calibration constant depends on T), under the same conditions,

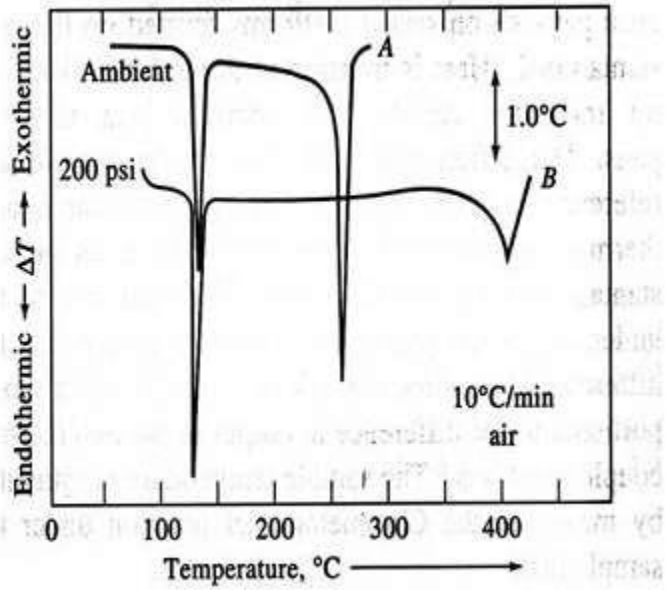
e.g. indium MPt 156.4 C; ΔH fusion = 28.5 J g-1

3. To fingerprint substa



DTA of (a) butter and (b) margarine

4. To determine M.Pt., B.Pt., decomposition temperatures of organic compounds .



DTA of benzoic acid

A ambient pressure;

B 200 lb in^{-2} pressure

what are the two peaks?

5. To characterize inorganic materials

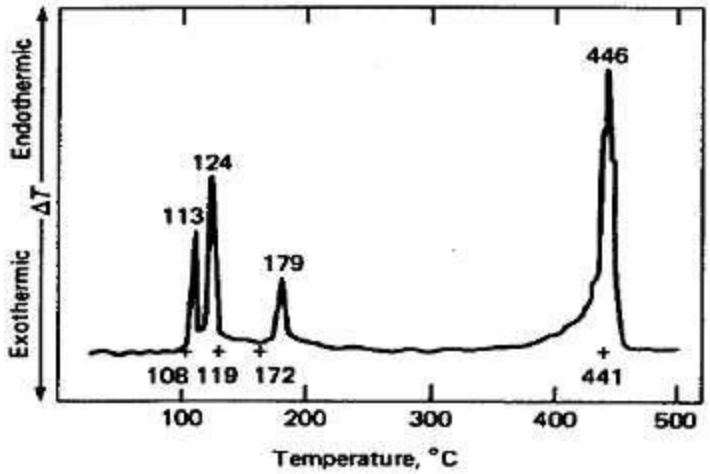


FIGURE Differential thermogram for sulfur. [Reprinted with permission from J. Chiu, *Anal. Chem.*, 35, 933 (1963).

The peak at 113°C corresponds to a solid-phase change from the rhombic to the monoclinic form, while the peak at 124°C corresponds to the melting point of the element.

Liquid sulphur is known to exist in at least three forms, and the peak at 179°C apparently involves a transition among these.

The peak at 446°C corresponds to the boiling point of sulphur.

6. To quantitatively analyze polymer mixtures

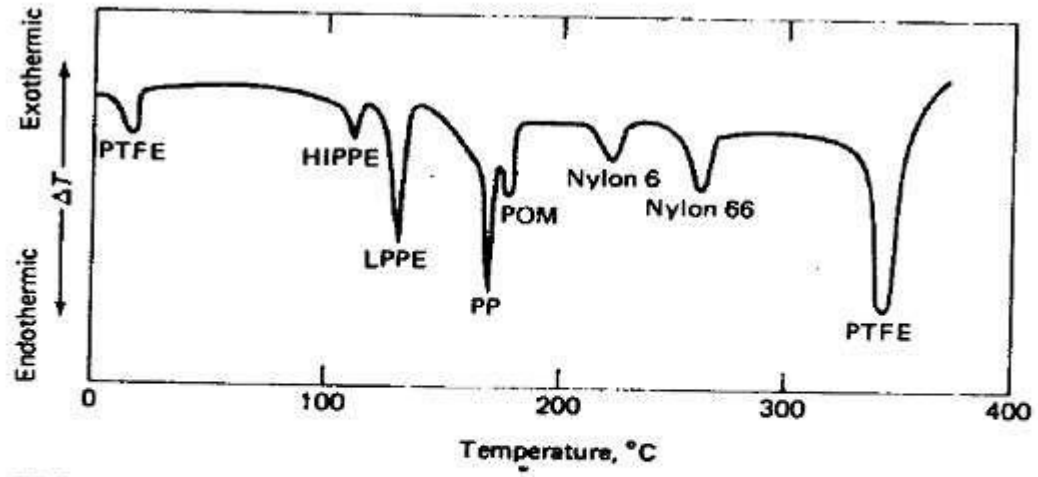
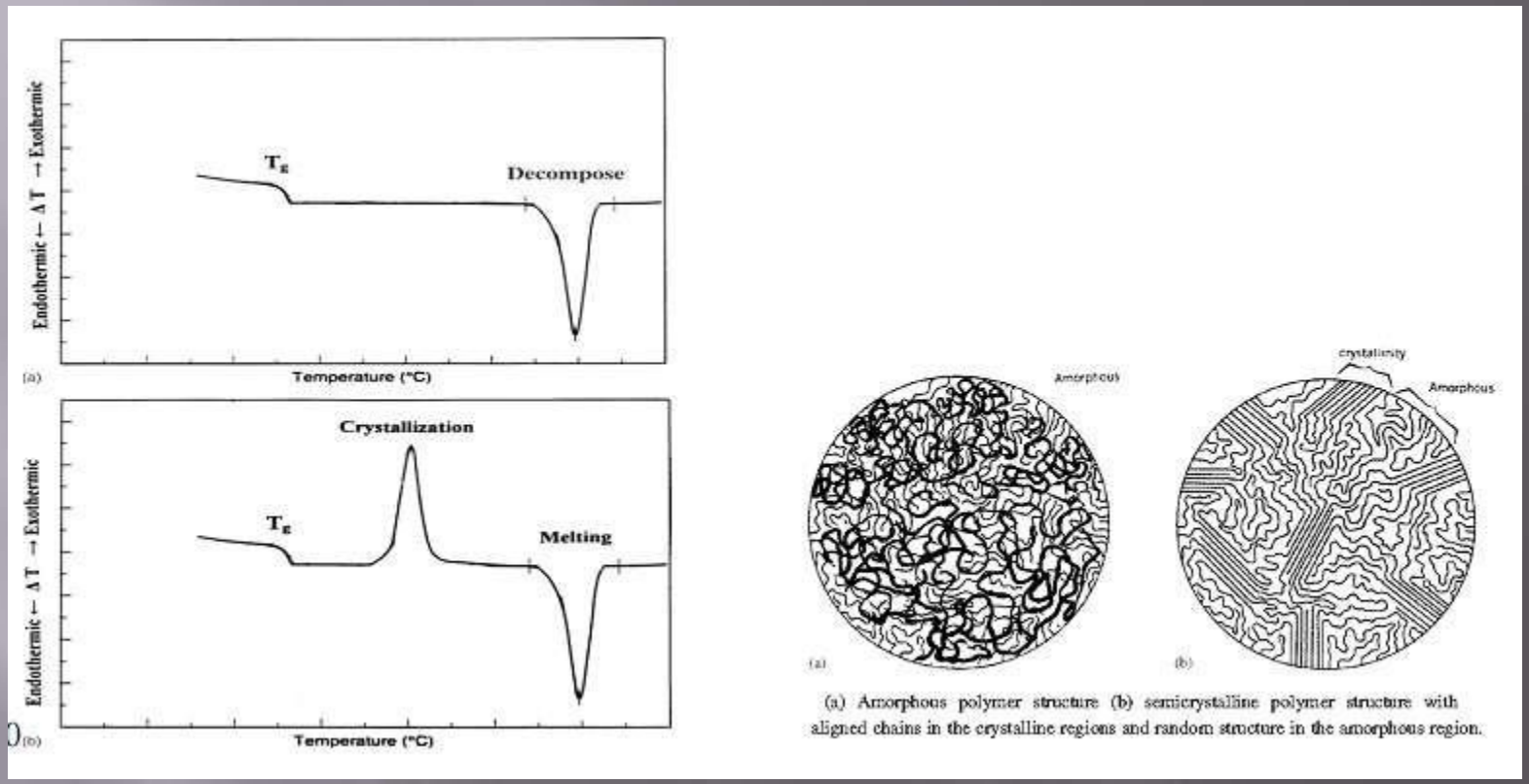


FIGURE Differential thermogram for a mixture of seven polymers. PTFE = polytetrafluoroethylene; HIPPE = high-pressure polyethylene; LPPE = low-pressure polyethylene; PP = polypropylene; POM = polyoxymethylene. [From J. Chiu, *DuPont Thermogram*, 2, (3), 9 (1965). With permission.]

This is a thermogram of a physical mixture of seven commercial polymers. Each peak corresponds to the characteristic melting point of one of the components. Poly tetrafluoroethylene (PTFE) has an additional low temperature peak, which arises from a crystalline transition. Clearly, differential thermal methods can be useful for qualitative analysis of polymer mixtures.

7. To characterize polymers



(a) Amorphous polymer structure (b) semicrystalline polymer structure with aligned chains in the crystalline regions and random structure in the amorphous region.

Schematic DTA thermal curves for the totally amorphous polymer structure and the semi crystalline polymer structure. Both show Tg ; only the semi-crystalline polymer has a crystallization exotherm.

Cont...

- Quantitative analysis of Compounds
- Determination of Structural and Chemical changes occurring during heat treatments.
- Quality Control of Cement, glass, textiles, soils, explosives and resins.