Thermal Analysis

- Thermal analysis is a branch of materials science where the properties of materials are studied as **they change with temperature**.
- When matter is heated, it undergoes certain **physical and chemical changes**.
- **Physical changes** include phase changes such as melting, vaporization, crystallization, transitions between crystal structures, changes in microstructure in metal alloys and polymers, volume changes (expansion and contraction), and changes in mechanical behavior.
- **Chemical changes** include reactions to form new products, oxidation, corrosion, decomposition, dehydration, chemisorption, and the like.
- These physical and chemical changes take place over a wide temperature range.

- Materials are used over a wide range of temperatures, from Arctic cold to tropical heat, in corrosive environments, variable humidity, and under load (stress).
- It is necessary to **characterize** materials and their behavior over a range of temperatures to determine what materials are suitable for specific uses and to determine what temperature range materials or chemicals can withstand without changing.
- This sort of information is used to **predict safe operating conditions** for products, such as **which type of tire material is best for vehicles in extremely cold or extremely hot climates**, the average expected lifetime of materials such as paints and polymers exposed to temperature changes.

Types of thermal analysis

- **TGA** (Thermo gravimetric analysis)
- **DTA** (Differential Thermal Analysis)
- **DSC** (Differential Scanning Calorimetry)
- **TT** (Thermometric Titration)
- **DMA** (Dynamic Mechanical Analysis)
- **TMA** (Thermo Mechanical Analysis)

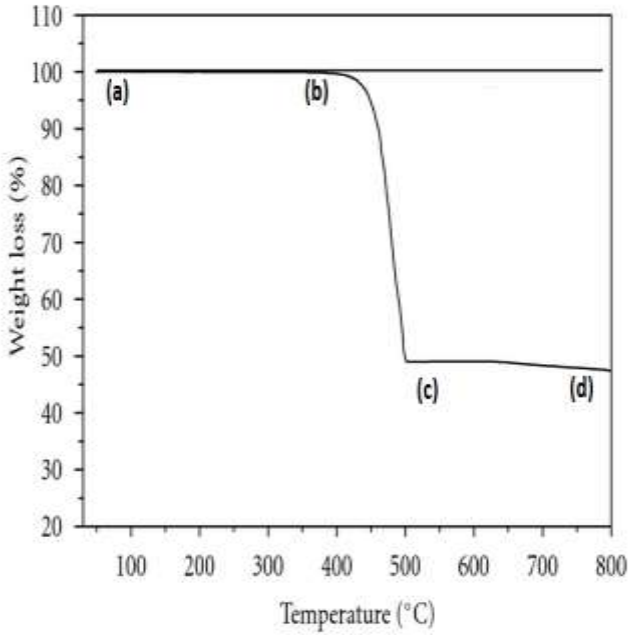
Thermo Gravimetric analysis (TGA)

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**.

Example: TGA Curve for AgNO3

- The horizontal portion of the curve indicates that, there is no change in weight (AB & CD) and the portion **BC indicates that there is weight change**.
- The weight of the substance (AgNO3) remains constant upto a temperature of 473°C indicating that **AgNO3 is thermally stable** upto a temperature of 473°C.



The diagram indicates the TGA curve for $AgNO_3$.

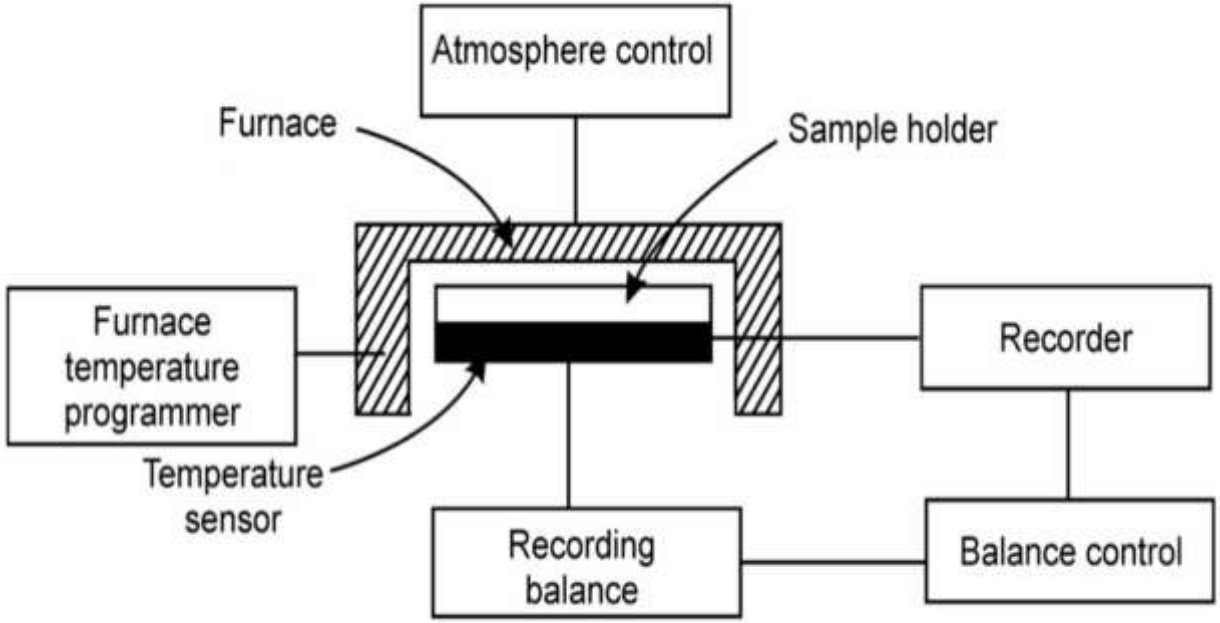
$$AgNO_3 \rightarrow Ag + NO_2 + O_2$$

- At this temperature it starts losing its weight and this indicates that the **decomposition starts at this temperature.** It decomposes to NO2, O2 and Ag. The loss in weight continues upto 608°C leaving metallic silver as the stable residue. Beyond this temperature the weight of the sample remains constant (CD).

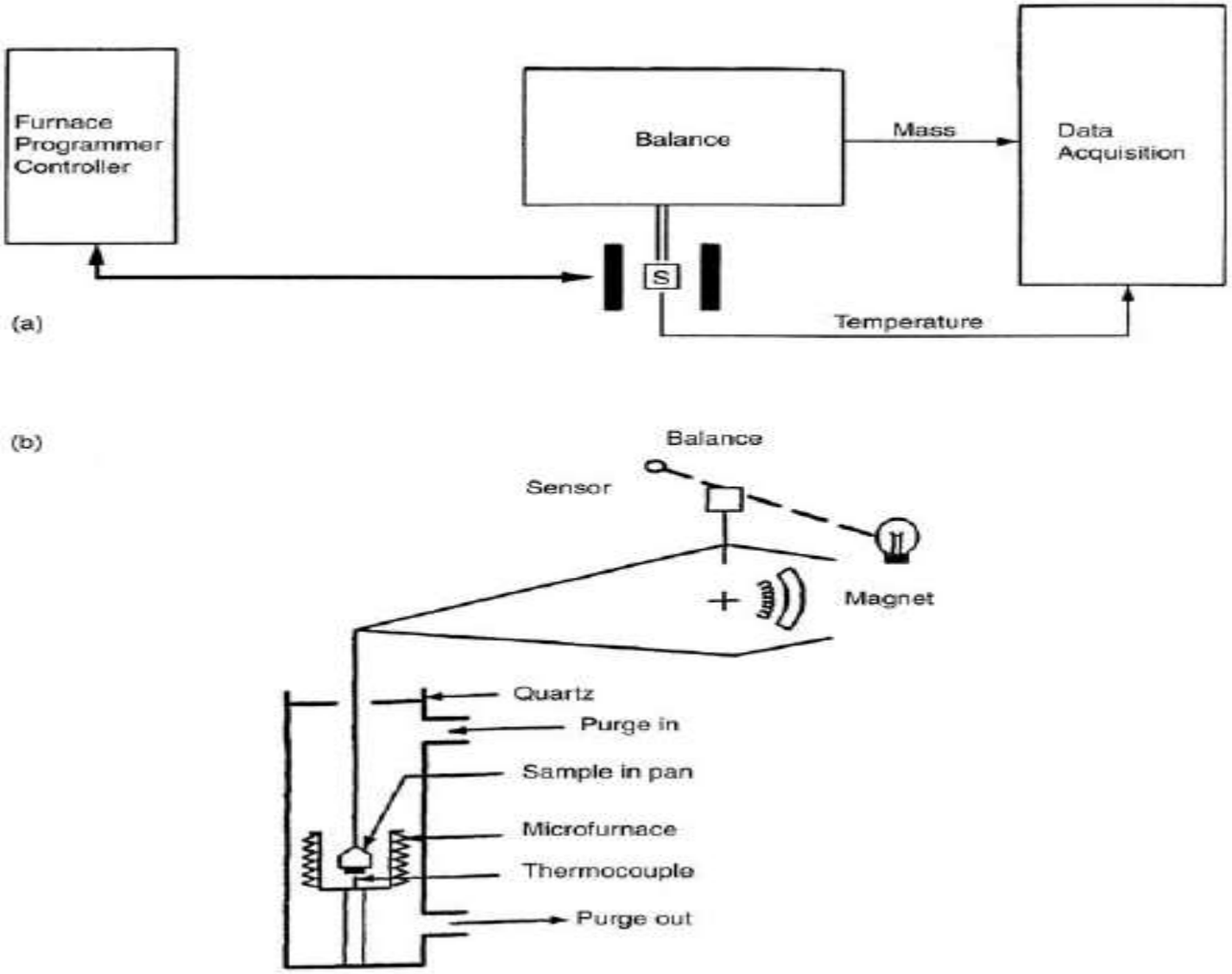
Instrumentation

- 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.

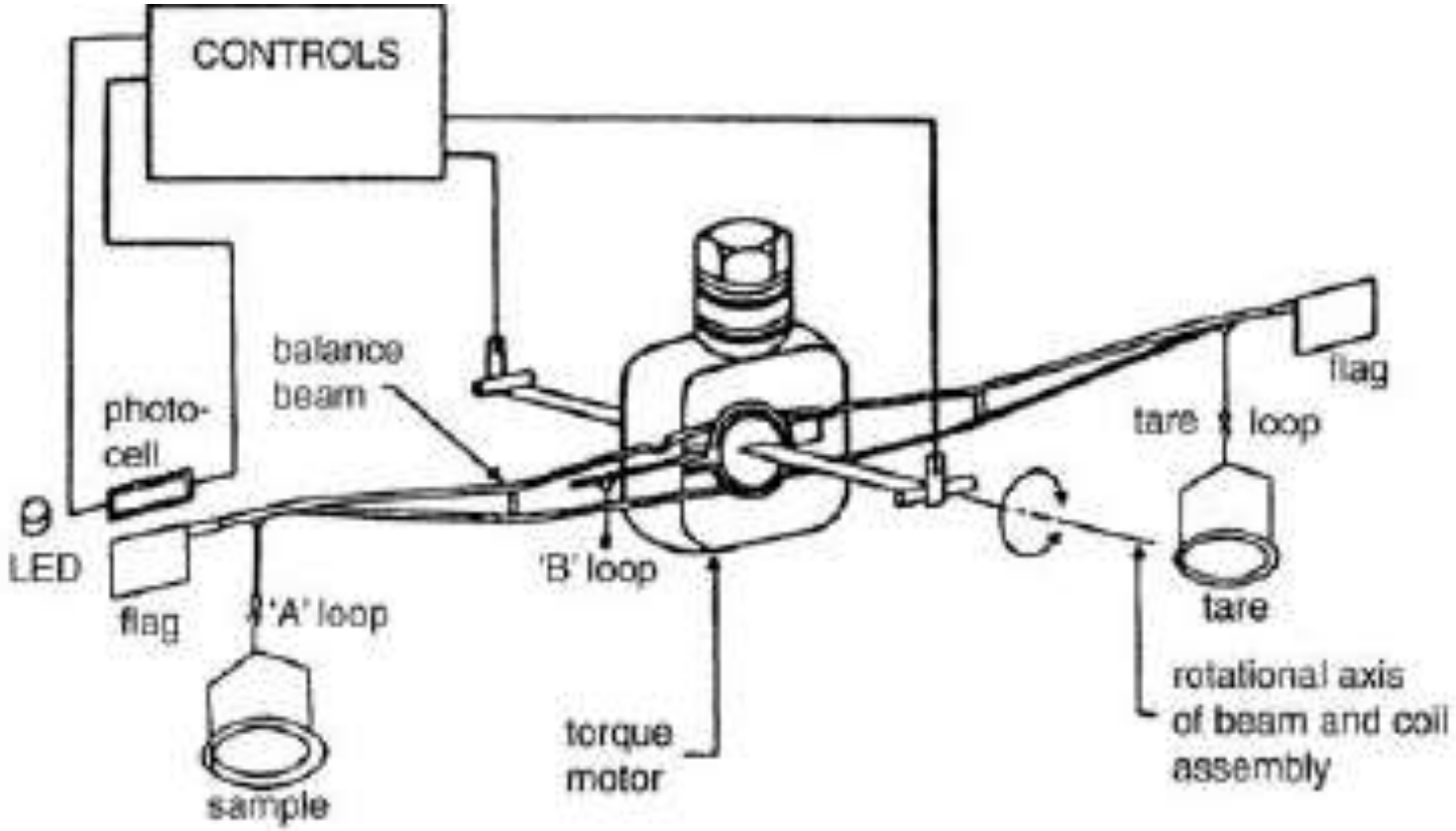
Instrumentation / Block diagram of TGA



- TGA balances are available for sample masses from 1 to 1000 mg, with the usual sample weighing between 5 and 20 mg.
- There are specialized high-capacity TGA systems available that can accommodate samples of up to 100 g.
- The balance itself must be thermally isolated from the furnace, although the sample holder and sample must be in the furnace.
- There are **two possible configurations** of the balance and furnace, a **horizontal furnace or a vertical furnace**. Both types of configuration suffer from drift as the temperature increases.
- Vertical configurations suffer from **buoyancy effects** due to the change in gas density with temperature.
- The horizontal configuration was designed to minimize buoyancy effects, but horizontal configurations experience **changes in the length of the quartz rod** connecting the sample to the balance as the temperature changes.



(a) Block diagram of a TGA system. S represents the sample pan hanging from the balance arm in position in the furnace (represented by the solid bars on each side). (b) Schematic of a commercial TGA, showing the purge gas inlet and outlet and the thermocouple position beneath the sample pan.



(a) Electrobalance for a TGA. As the sample weight changes, the balance arm tips, resulting in a change in the amount of light reaching the photocell. This generates a current to restore the arm position; the current is proportional to the change in weight of the sample.

- Buoyancy effects and changes in the quartz rod result in error in determining the mass of the sample.
- Buoyancy effect is an upward force exerted by a fluid that opposes the weight of an immersed object.
- **The furnace** surrounds the sample and sample holder. It must be capable of being programmed for a linear heating rate.
- **Modern instruments** can be heated and cooled rapidly. These instruments that heat at rates of up to 1000^0C/min are available.
- **Commercial instruments** can heat at rates up to 200^0C/min from room temperature to about 1200^0C; cooling by forced air can be done at 50^0C/min.
- There are furnaces available with upper temperatures of 1500^0C, 1700^0C, or 2400^0C; these higher temperature instruments are useful for studying refractory materials and engineering materials.

- The furnace **must be** able to be **purged with a desired gas, to provide the correct atmosphere** for the experiment and to remove gaseous products from the sample compartment.
- **Argon or nitrogen** is used when an inert atmosphere is desired.
- **Air** is often used for oxidation and combustion studies.
- **Hydrogen gas** may be used to provide a reducing atmosphere, with the appropriate precautions to prevent explosions.
- Modern instruments permit the purge gas to be switched automatically, so that the sample can start heating in an inert atmosphere and be switched to air or other reactive gas at high temperatures,
- for example, the sample holder and any instrument parts inside the furnace, such as the thermocouple for measuring the temperature, must be able to withstand high temperature and be inert at these high temperatures.

- **Quartz, platinum, and various ceramics** are used for the sample holder and other parts.
- The sample is placed in a small pan or crucible made of Pt, quartz, or ceramic. Ideally, the temperature recorded is the exact temperature of the sample.
- This entails measuring the temperature of the sample while the analysis is carried out. It is particularly important to measure the temperature of the sample rather than that of the furnace. This is difficult because the temperature is measured with a **thermocouple** that is near but not in the sample.
- The thermocouple is never inserted directly into the sample because of **possible sample contamination** (or contamination of the thermocouple resulting in errors in temperature).
- The temperature actually recorded may be **slightly different** from the sample temperature; the sample temperature generally is lower than the temperature recorded by the thermocouple. This is due to factors such as **rate of heating, gas flow, thermal conductivity of the sample, and the sample holder**.

- The problem is compounded by the fact that at temperatures below 500^0C, most of the heat transferred from the furnace to the sample takes place by **convection and conduction**, but at temperatures above 500^0C, where the furnace is red-hot, most of the **energy is transferred by radiation.**
- The switch from **conduction–convection to radiative energy transfer** makes choosing the position of the thermocouple to obtain accurate temperature measurements of the sample quite a complicated problem.

Sample Preparation

- Sample preparation has a significant effect in obtaining good data.
- It is suggested that **maximizing the surface area of the sample** in a TGA pan improves resolution and reproducibility of weight loss by the temperatures.
- The sample weight affects the accuracy of weight loss measurements.
- Typically **10-20mg** of sample is preferred in most applications.
- Whereas, if the **sample has volatiles** **50-100mg** of sample is considered adequate.
- It is to be noted that most TGA instruments have baseline drift of ±0.025mg which is ±0.25% of a 10mg sample.

TGA of calcium oxalate monohydrate ($CaC_2O_4.H_2O$)

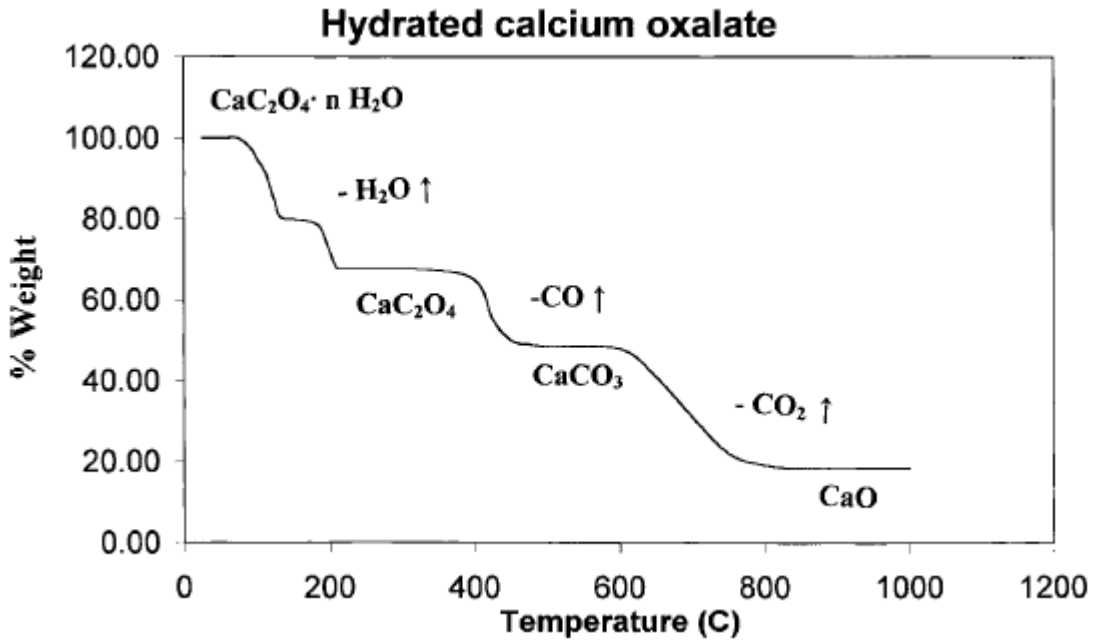
- The successive plateau corresponds to the formation of anhydrous salt, calcium carbonate and calcium oxide.

$$(a)\ CaC_2O_4.H_2O \rightarrow CaC_2O_4 + H_2O$$

$$(b)\ CaC_2O_4 \rightarrow CaCO_3 + CO$$

$$(c)\ CaCO_3 \rightarrow CaO + CO_2$$

- The thermogram indicates that the loss of water begins at 100°C and loss of CO at 450°C and CO_2 at 600°C



Factors affecting the TG curve

The factors which may affect the TG curves are classified into two main groups.

(1) Instrumental factors

(a) Furnace heating rate

(b) Furnace atmosphere

(2) Sample characteristics includes

(a) Weight of the sample

(b) Sample particle size

Instrumental factors

Furnace Heating rate: The temperature at which the compound (or sample) decompose depends upon the heating rate. When the heating rate is high, the decomposition temperature is also high. A **heating rate of 3.5°C per minute is usually recommended** for reliable and reproducible TGA.

Furnace atmosphere: The atmosphere inside the furnace surrounding the sample has a profound effect on the decomposition temperature of the sample. **A pure N2 gas** from a cylinder passed through the furnace which provides an inert atmosphere.

Sample characteristics

(a)Weight of the sample: A small weight of the sample is recommended, using a small weight eliminates the existence of temperature gradient through the sample.

(b) Particle size of the sample: The particle size of the sample should be **small and uniform**. The use of large particle or crystal may result in apparent, very rapid weight loss during heating.

Applications of TGA

- From TGA, we can determine the **purity and thermal stability** of both primary and secondary standard.
- Determination of the **composition of** complex mixture and decomposition of complex.
- For studying the **sublimation behaviour** of various substances.
- TGA is used to study the **kinetics** of the reaction rate constant.
- **Used in the study of catalyst:** The change in the chemical states of the catalyst may be studied by TGA techniques. (Zn-ZnCrO4) Zinc-Zinc chromate is used as the catalyst in the synthesis of methanol.

- Evaporation of free (unbound) water **begins at room temperature** due to dry gas flowing over the sample.
- Dehydration/Desolvation of bound water always begins at temperatures **above room temperature** and typically at 125°C.
- **Eg:** Determination of the **bound and unbound water** in the suspension of Milk of Magnesia (MoM), used as a laxative.
- Decomposition can have multiple stages (weight losses) but the presence of multiple weight loss steps can also indicate the **presence of multiple components** in the sample.

- In an overview of thermal analysis testing it is always preferable to do a TGA experiment on unknown samples **before doing a DSC experiment** (especially for pharmaceuticals) because Decomposition of pharmaceuticals renders products which are insoluble and generally sticky on the inside of a DSC cell. These products will **lower the life use** of a DSC cell.
- Therefore, knowing of the decomposition temperatures of all drugs, heat in a DSC evaluation should maintain 50°C below to those decomposition temperatures.

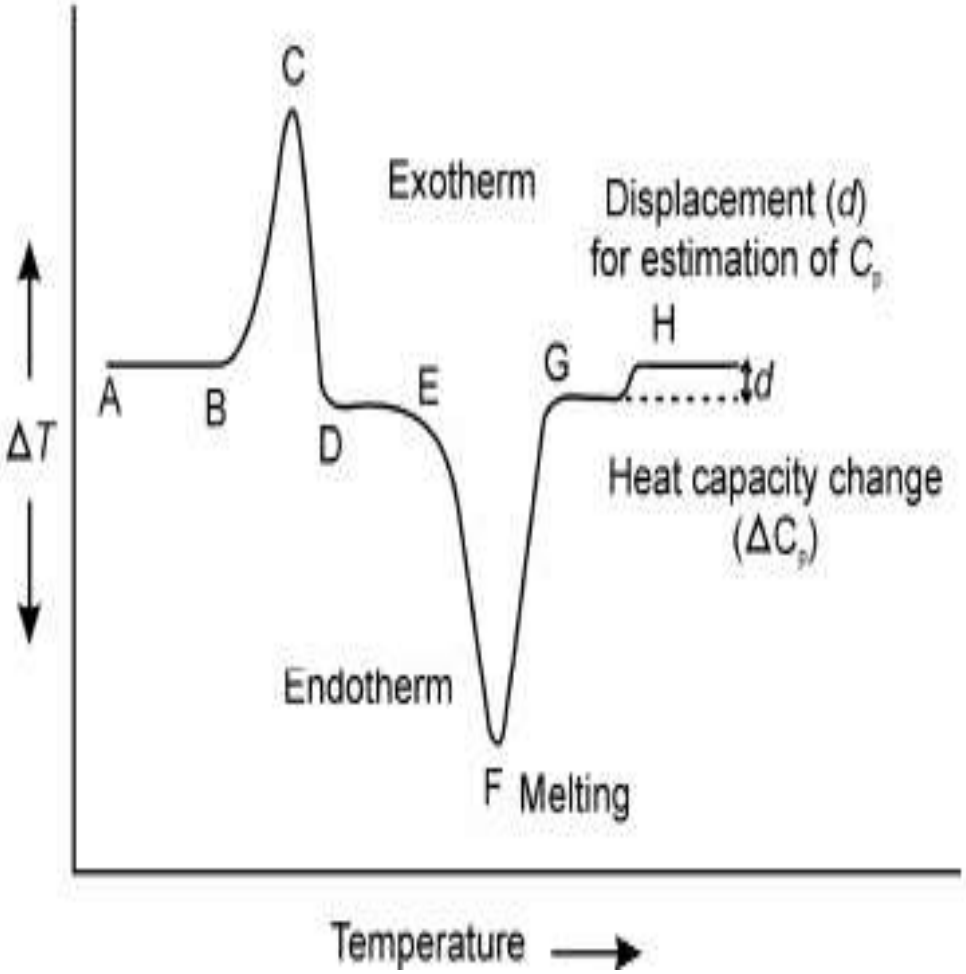
Differential Thermal Analysis (DTA)

- **Le-Chateliar** studied clays & minerals by an examination of temperature –time curves.
- Later **Robert Austen** improved technique by introducing thermocouples.

Definition: DTA is a technique in which the temperature between sample & thermally inert reference substance is continuously recorded as a function of temperature /time.

DTA Principle

- Differential thermal analysis is a technique in which the temperature of the substance under investigation is compared with the temperature of a thermally inert material.



This differential temperature is then plotted against time, or against temperature (**DTA curve, or thermogram**).

The area under a DTA peak is the **enthalpy change** and is not affected by the heat capacity of the sample.

- Both sample and reference material must be heated under **carefully controlled conditions.**

- If **zero temperature** difference b/w sample & reference material – sample does not undergo any chemical or physical change.

- If any reaction (physical or chemical change) takes place **temperature difference (ΔT)** will occur b/w sample & reference material .

- Some changes result in heat being absorbed by the sample. These types of changes are called **endothermic**.
- Examples of endothermic changes include **phase changes such as** melting (fusion), vaporization, sublimation, and some transitions between two different crystal structures for a material. **Chemical reactions** can be endothermic, including dehydration, decomposition, oxidation–reduction, and solid–state reactions.
- Other changes result in heat being given off by the sample. Such changes are termed **exothermic.**
- Exothermic changes include **phase changes** such as freezing (crystallization), some transitions between different crystal structures and **chemical reactions;** decomposition, oxidation–reduction, and chemisorption can be exothermic.

- There are also **physical changes** that are not simple phase changes that still cause the sample temperature to change.
- Examples of such physical changes include adsorption and desorption of gases from surfaces and glass transitions in amorphous glasses and some polymers.
- The **glass transition** is a change in an amorphous material from a brittle, vitreous state to a plastic or rubber like state. Glass transitions are second order phase transitions.
- The reverse transition, achieved by supercooling.
- A viscous liquid into the glass state, is called vitrification.

Instrumentation

➢Sample holder

- ✓ Sample & reference crucibles are generally metallic (Al, Pt) or ceramic (silica) and may or may not have a lid. Many metal pans with lids have the lid crimped on using a special tool.
- ✓ Best results are obtained when the area of contact between the sample and the pan or crucible is maximized.
- ✓ Samples are generally in the 1–10 mg range for analytical applications.
- ✓ The dimensions of the two crucibles and of the cell wells are as nearly identical as possible; furthermore, the weights of the sample and the reference should be virtually equal.

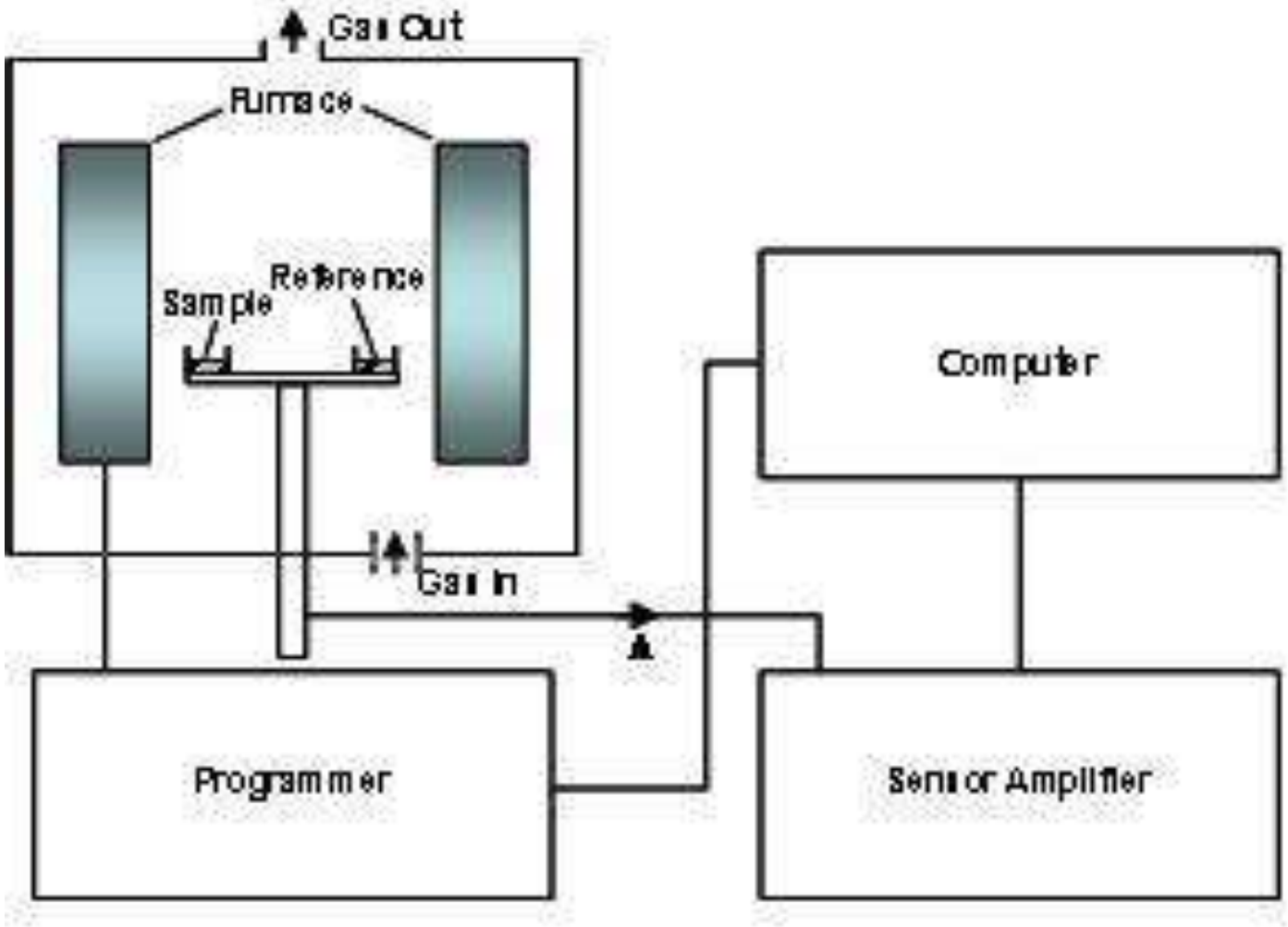
➢Furnace

- ✓ The sample and reference should be matched thermally and arranged symmetrically with the furnace so that they are both heated or cooled in an identical manner.
- ✓ The metal block surrounding the wells acts as a heat sink.
- ✓ The temperature of the heat sink is slowly increased using an internal heater.
- ✓ The sink in turn simultaneously heats the sample and reference material.

➢Sensors & Recording system

- ✓ A pair of matched thermocouples is used.
- ✓ One pair is in contact with the sample or the sample container, the other pair is in contact with the reference.
- ✓ The output of the differential thermocouple, Ts - Tr or ΔT, is amplified and sent to the data acquisition system.
- ✓ This allows the difference in temperature between the sample and the reference to be recorded as a function of either the sample temperature, the reference temperature or time.

DTA Instrument

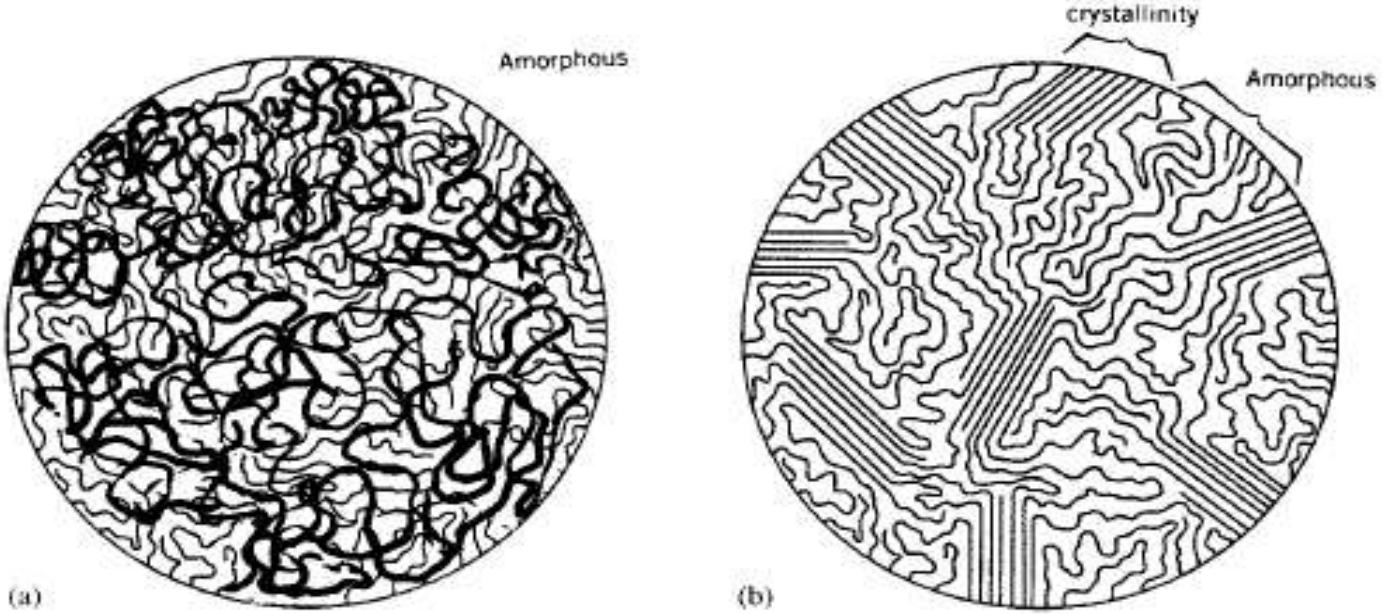


- Operating temperatures for DTA instruments are generally room temperature to about 1600^0C, although one manufacturer makes a DTA capable of operating from -150_0C to 2400^0C.
- To reach the very low subambient temperatures, a liquid nitrogen cooling accessory is needed.
- Some low temperatures (but not -150^0C) may be reached with electrical cooling devices or with forced air-cooling.
- When a physical change takes place in the sample, heat is absorbed or generated.
- For example, when a metal carbonate decomposes, CO2 is evolved. This is an endothermic reaction; heat is absorbed and the sample temperature decreases. The sample is now at a lower temperature than the reference. The temperature difference between the sample and reference generates a net signal, which is recorded.

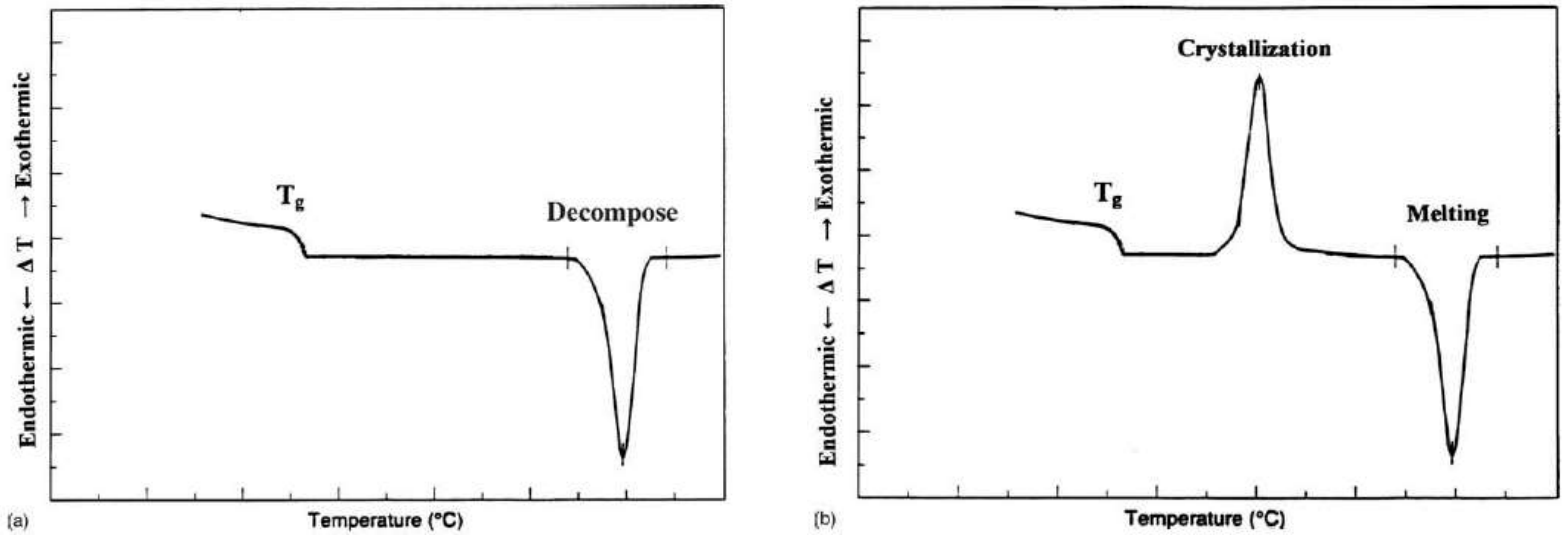
Applications of DTA

DTA is based on changes of heat flow into the sample

- Using DTA, we can detect the **decomposition or volatilization of the sample**, just as we can with TGA.
- In addition, however, **physical changes that do not involve weight changes can be detected** by DTA. Such changes include crystallization, melting, changes in solid crystal phases, and homogeneous reactions in the solid state. In each of these changes there is a **flow of heat** between the sample and its surroundings caused by **endothermic or exothermic transitions** or by changes in the heat capacity.
- The main use of DTA is to detect thermal processes and characterize them as **exothermic or endothermic, reversible or irreversible**, but only **qualitatively**.



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



Both show T_g; only the semicrystalline polymer has a crystallization exotherm.

- DTA thermal curves can be used to determine the **order of a reaction (kinetics),** and can provide the information required to construct phase diagrams for materials.
- Qualitative identification of materials is done by comparing the DTA of the sample to DTA thermal curves of known materials. **DTA thermal curves serve as fingerprints for materials.**
- DTA can be used for **characterization** of engineering materials, for the determination of the structural and chemical changes occurring during sintering, fusing, and heat treatments of alloys to change microstructure, identification of different types of synthetic rubbers, and determination of structural changes in polymers.
- DTA is widely used in the pharmaceuticals and food industries.
- DTA may be used in **cement chemistry, mineralogical research and in environmental studies.**
- DTA curves may also be used to date bone remains or to study archaeological materials.