CH 2252 Instrumental Methods of Analysis

Unit – III

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Differential Thermal Analysis

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Differential Thermal Analysis (DTA)

- Differential Thermal Analysis is a technique in which the difference in temperature ΔT between the sample and an inert reference material is measured as a function of temperature

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

- If the sample undergoes a physical change or a chemical reaction, its temperature will change while the temperature of the reference material remains the same. That is because physical changes in a material such as phase changes and chemical reactions usually involve changes in enthalpy

- Enthalpy change processes (Physical / Chemical): Exothermic / endothermic reactions, decompositions, transitions between crystal structures, adsorption, freezing, crystallization, glass transitions

DTA plot

- It is not necessary that the sample's weight change in order to produce a DTA response. However, if a weight change does take place, as occurs on loss of water, the enthalpy of the sample invariably changes, and a DTA response will be observed

- So DTA is capable of measuring the same changes measured by TGA, plus many additional changes that TGA cannot measure because no mass change occurs

- A DTA plot or thermal curve has ΔT on the y-axis and T (or time) on the x-axis. The x-axis temperature can be the temperature of the heating block, the temperature of the sample or the temperature of the reference, or it can be time.

- By convention, exothermic changes are plotted as positive, and the peaks point up, while endothermic changes are plotted as negative, and the peaks point down.

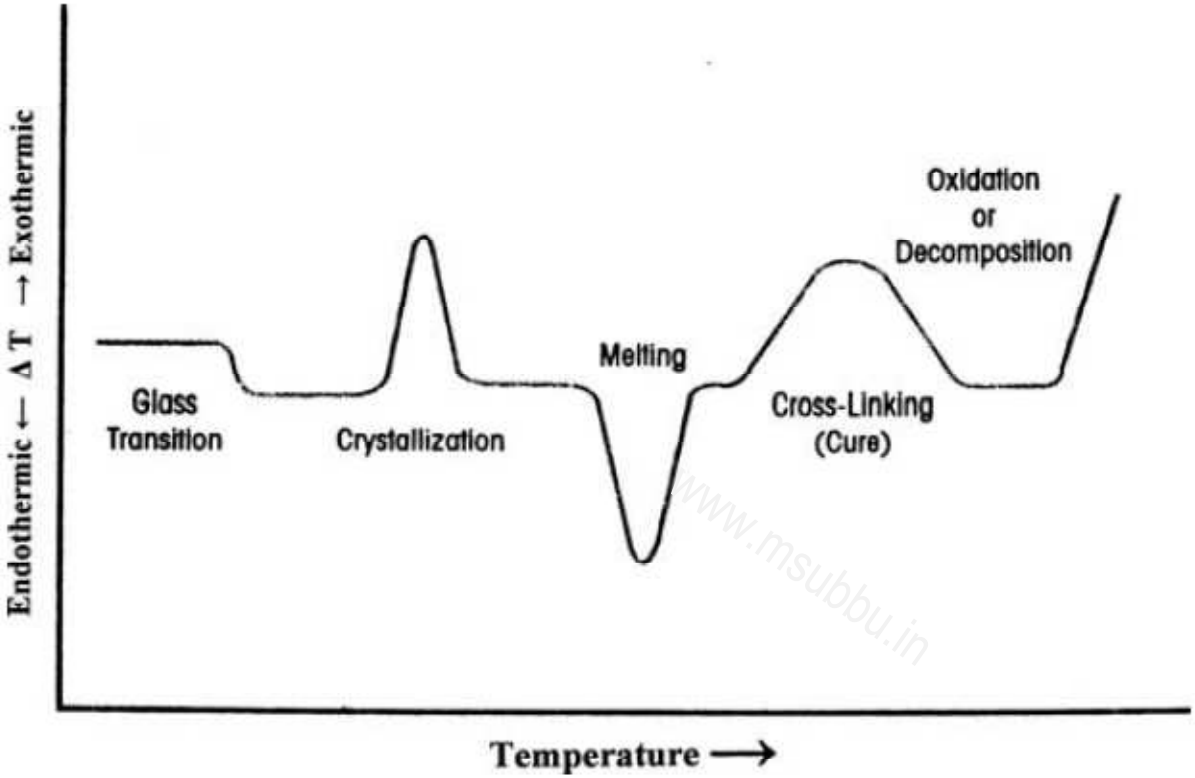
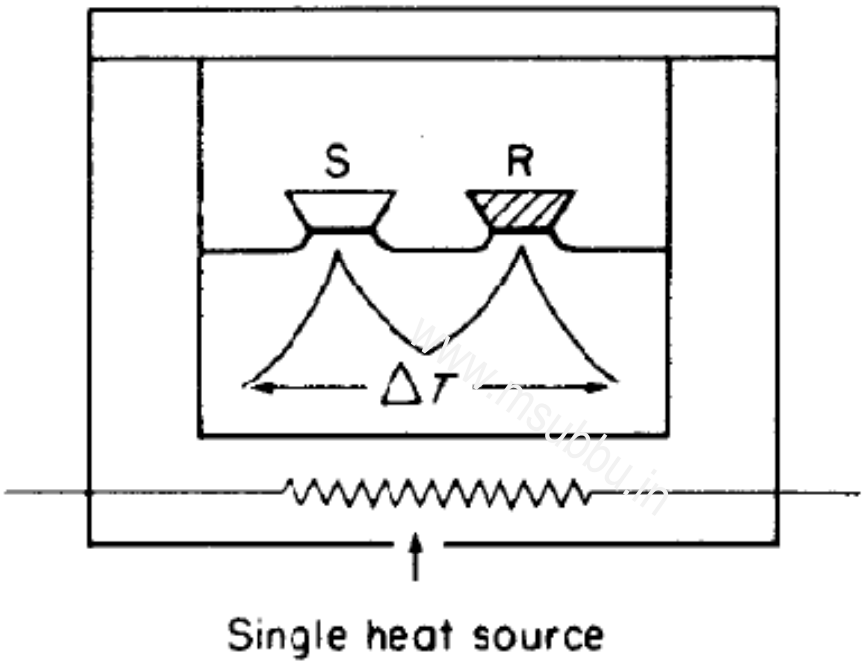


Figure 16.15 Hypothetical DTA thermal curve for a semicrystalline polymer with the ability to cross-link. The plot shows the baseline shift that occurs at the glass transition temperature, T_g, exothermic peaks for crystallization and cross-linking (or curing), an exothermic peak (offscale) for oxidative decomposition, and an endothermic peak for melting of the polymer. A similar thermal plot would be obtained by DSC analysis. (Courtesy of TA Instruments, New Castle, DE, www.tainst.com.)

Robinson, Undergraduate Instrumental Analysis, 6th Edition, Marcel Dekker, New York



T_r

Schematic of DTA

Instrumentation of DTA

- 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. Samples are generally in the 1–10 mg range. Sample crucibles are generally metallic (Al, Pt) or ceramic (silica) and may or may not have a lid.

- 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.

- A pair of matched thermocouples is used. The output of the differential thermocouple, Ts - Tr or ΔT, is amplified and sent to the data acquisition system. If there is no difference in temperature, no signal is generated, even though the actual temperatures of the sample and reference are both increasing.

- Operating temperatures for DTA instruments are generally room temperature to about 1600^{o}C

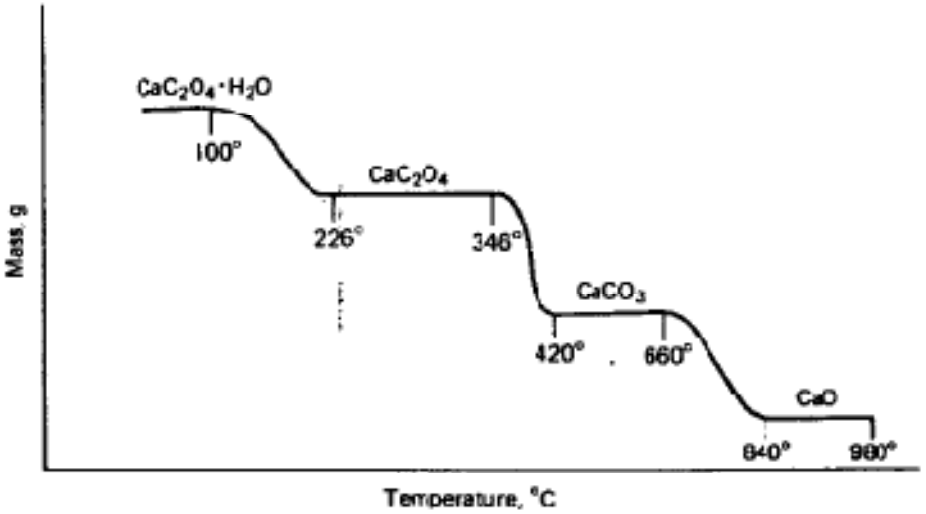


FIGURE 23-2 A thermogram for decomposition of $CaC_2O_4 \cdot H_2O$.

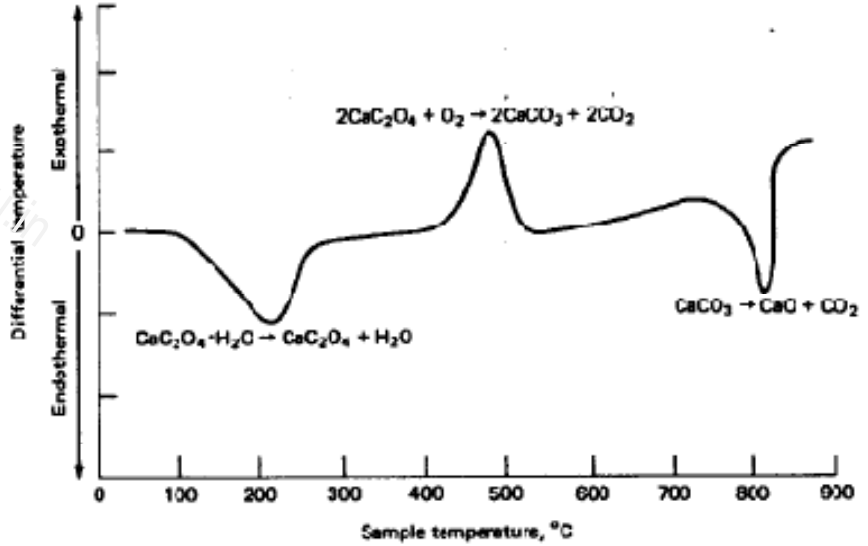


FIGURE 23-4 Differential thermogram of $CaC_2O_4 \cdot H_2O$ in the presence of O_2; the rate of temperature increase was 8°C/min. (From *Handbook of Analytical Chemistry*, ed. L. Meites. New York: McGraw-Hill, 1963, p. 8–14. With permission.)

Skoog - Principles of Instrumental Analysis 2nd Edition, 1980, Saunders College, Philadelphia

Inferences from DTA plot

- Any chemical or physical change that results in a change in ΔH gives a peak in the DTA thermal curve.
- There are some types of changes that do not result in a peak in the thermal curve but only a change in the baseline. These types of changes do not undergo a change in ΔH, but a change in their heat capacity, Cp.
- The most common process that gives rise to a change in baseline but not a peak in the DTA is a "glass transition" in materials such as polymers or glasses.
- The peak area in a DTA thermal curve is related to the enthalpy change for the process generating the peak

Analytical Applications of DTA

- 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.

- The main use of DTA is to detect thermal processes and characterize them as exothermic or endothermic, reversible or irreversible, but only qualitatively.

- DTA thermal curves can be used to provide the information required to construct phase diagrams 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