Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Third Year)

Subject: Chemistry

Course Code: CHD103 (SECTION B)

Course Title: Selected Instrumentation in Chemistry

Unit: 3 Analysis of drugs in solid state

Module Name: Factors affecting DTA results, quantitative DTA, interpretation of results

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Notes

Factors affecting DTA results, quantitative DTA, interpretation of results

The DTA curve of a substance is not strictly reproducible, probably due to the factors caused by the instrument and those depending upon the characteristics of the sample. The factors caused by instrument are furnace atmosphere, size and shape of the furnace, sample holder material, sample holder geometry, heating rate, speed and response of recording device, and thermocouple location in the sample chamber. Particle size, thermal conductivity, heat capacity, packing density, amount of sample, swelling or shrinkage of the sample, effect of diluent and degree of crystallinity are the factors which depend upon the sample characteristics.

Each of these factors plays an important role in determining the shape of the curve peaks and positions in relation to the temperature axis.

The DTA technique is very sensitive to the gaseous environment around the sample. The gaseous atmosphere may react with the sample, and as a result, extra peaks may be obtained in the curve. For example, oxygen of the air may cause oxidation giving rise to an exothermic peak. The gaseous atmospheres in DTA may either be static gaseous atmosphere or dynamic gaseous atmosphere. The shapes of the curve, however, remain similar in both the atmospheres, but in dynamic gaseous atmosphere, the peak minimum temperature is shifted to lower temperatures, while static gaseous atmosphere is not easy to reproduce, because of the fact that atmosphere surrounding the sample changes in concentration chemically as a result of evolved gases and physically due to convection currents. The results in dynamic atmosphere may be reproduced because gases (either inert or reactive) are swept past the sample in a controlled way. For example, when lignite is studied by DTA, it has been observed that it pyrolyses and distils off volatile matter in the dynamic nitrogen atmosphere, but it undergoes oxidation in dynamic oxygen atmosphere, giving rise to exothermic peaks instead of endothermic peaks.

The resolution, size and shape of the DTA curve peaks are dependent on geometry and material used in the preparation of sample holder.

Sharp exothermic peaks, but flat endothermic peaks, are usually obtained if the sample holder is fabricated from metals or other materials of high thermal conductivity.

Opposite effect is observed, if the sample holder is made of ceramics or other poor thermal conductivity material. For good resolution, the size of the sample holder and amount of sample used should be as small as possible.

If the wires used in temperature sensing devices are much thick, more distortion of the peak heights and peak temperatures are expected to take place, while reverse is the case if thin wires are used for the same purpose. A compromise is made here because of the fact that thin wires have much higher resistance and they are also not suitable in impedance matching.

The intensity of the peaks, shapes of the peaks and base line are greatly influenced by the position of the temperature measuring and differential thermocouples. Best results are, however, obtained by plotting differential temperature against the sample temperature. The base line, is greatly affected with non-uniform winding used in the furnace. The commercially available instruments employ machine-wound furnace windings and so this problem is much solved there.

The DTA curves are also influenced by heating rate. Higher the heating rates, higher the peak temperature and deeper the peaks. The most appropriate rate is 10-20^{o} per minute.

Usually the area of DTA peak does not change with the heating rate, but there is a great change if the sample is diluted with some inert substance. The curves both in heating as well as cooling cycles are obtained while studying phase transformations. This is due to the fact that some transitions, if missing in the heating cycle, may appear in the cooling cycle.

DTA curves are also influenced by the type, span, chart speed and pen response of a recorder. The DTA peaks get flattened out in case of faster chart speeds. For transient heat effects a rapid pen response is desirable.

In quantitative DTA, to keep heat capacity as constant as possible, an excess of an inert material is mixed with a small amount of the sample, but this creates other serious problems.

Thermal conductivity and hence the rate of flow of heat is highly influenced by packing density. Reproducible packing densities are, however, difficult to obtain.

The particle size of the sample also affects the packing density and thermal conductivity of the sample. The peak area is found to decrease with increasing particle size. The peak temperature increases generally, as the particle size increases.

Peak area also depends upon the quantity of the sample. But in case of cylindrical sample holders and fixed location of thermocouple, no increase in peak area is observed with an increase in the amount of the sample.

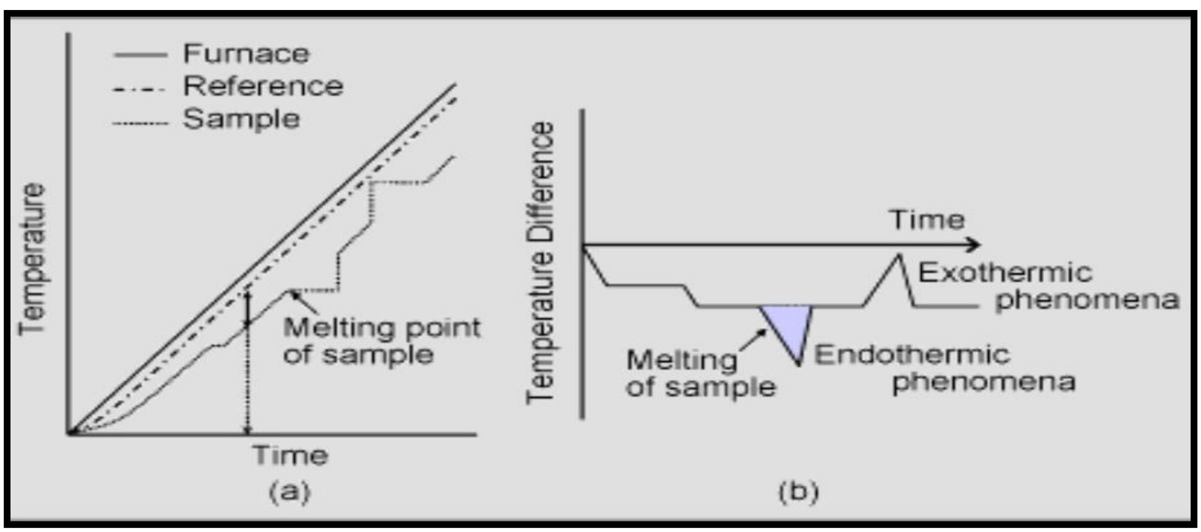
The peak intensity as well as temperature increase with increasing weight of the sample.

Other factors, such as degree of crystallinity of the sample, chemical reactivity of the sample, the thermocouple material, the ambient gaseous environment, etc. greatly influence the DTA peaks.

DTA involves heating or cooling a test sample and an inert reference under identical conditions, while recording any temperature difference between the sample and reference.

The differential temperature is then plotted against time, or against temperature. Changes in the sample which lead to the absorption or evolution of heat can be detected relative to the inert reference.

A DTA curve can be used as a fingerprint for identification purposes.

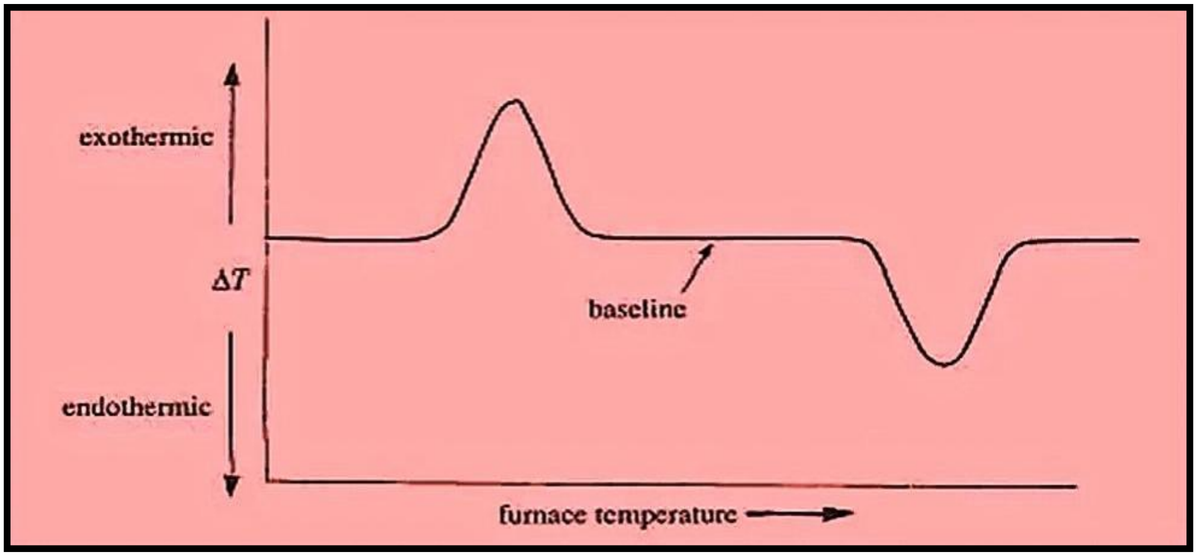


Graph (a) shows the temperature change of the furnace, the reference and the sample against time.

Graph (b) shows the change in temperature difference (ΔT) against time detected with the differential thermocouple.

ΔT signal is referred to as the DTA signal.

DTA Curve or Thermogram



An upward peak in DTA thermogram represents an **exothermic change** whereas a downward peak represents an **endothermic change.**

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

DTA Curve Information

Endothermic	Exothermic
Heat absorbed by the sample	Heat evolved by the sample
Phase changes Meting (fusion), vaporization, sublimation, some transitions between two crystal structures	**Phase changes** Freezing (crystallization), some transitions between two crystal structures
Chemical reactions Dehydration, decomposition, oxidation-reduction	**Chemical reactions** Decomposition, oxidation-reduction and chemisorption

Examples

1. Calcium oxalate monohydrate ($CaC_2O_4.H_2O$)

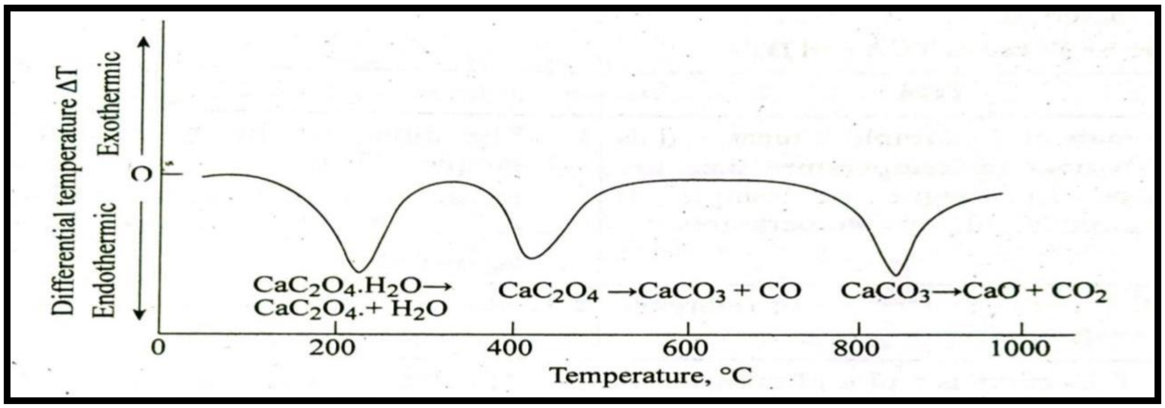


Figure: Dfferential thermogram for the decomposition of calcium oxalate (CaC_2O_4. H_2O) in inert nitrogen atmosphere

The **three minima** indicate that the sample becomes cooler than the reference material as a result of the **three endothermic reactions**.

When calcium oxalate is heated, it first loses its water of crystallisation and forms CaC_2O_4.

$$\mathbf{CaC_2O_4.H_2O \rightarrow CaC_2O_4 + H_2O}$$

On further heating (up to about 400°C), the reaction

$$\mathbf{CaC_2O_4 \rightarrow CaCO_3 + CO\uparrow}$$

occurs and CO is given off.

At even higher temperatures (about 800°C), $CaCO_3$ decomposes to form CaO and CO_2 is given off.

$$\mathbf{CaCO_3 \rightarrow CaO + CO_2\uparrow}$$

2. Copper sulphate pentahydrate ($CuSO4.5H_2O$)

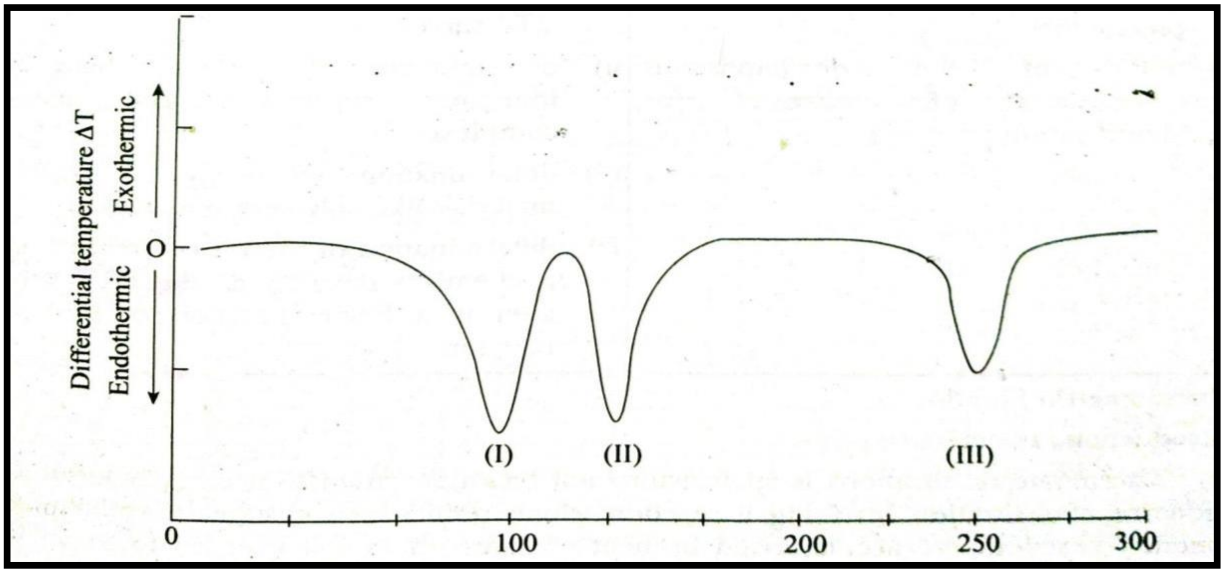


Figure: Differential thermogram for the dehydration of $CuSO_4.5H_2O$

When $CuSO_4.5H_2O$ is heated, it undergoes following dehydration reactions:

$CuSO_4.5H_2O \rightarrow CuSO_4.3H_2O + 2H_2O$ (81-96°C)

$CuSO_4.3H_2O \rightarrow CuSO_4.H_2O + 2H_2O$ (111-120°C)

$CuSO_4.H_2O \rightarrow CuSO_4 + H_2O$ (220-250°C)

This results in three endothermic peaks in DTA thermogram.