Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Third Year)

Subject: Chemistry

Course Code: CHD-103

Course Title: Selected Instrumentation in Chemistry (Section B)

Unit: Analysis of drug in solid state

Module Name: Thermal methods of analysis: Basic principles of Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)

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Notes

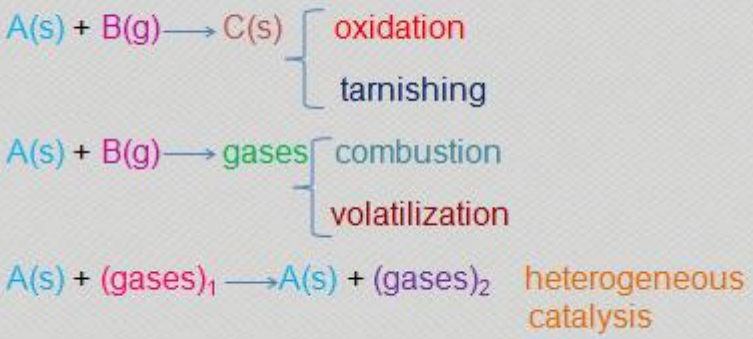
<u>Thermal methods of analysis</u>

- Methods of analysis in which effect of heat on a sample is studied to provide qualitative or quantitative analytical information.
- When matter is heated it undergoes certain physical and chemical changes.
- These physical and chemical changes take place over a wide temperature range.
- Physical changes such as melting or boiling may occur at widely varying temperatures, depending on the material involved.
- Chemical changes, such as decomposition reaction may also take place at very different temperatures.
- The physical and chemical changes a sample undergoes when heated, are characteristic of the material being examined.
- By measuring the temperature at which such reactions occur and the heat involved in the reaction, the compounds present in the material can be characterized.

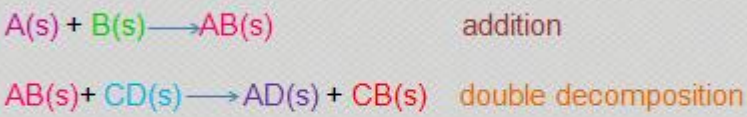
- The physical and chemical changes that take place when an unknown sample is heated provide us with information.
- This enables us to identify the material.
- Thermal analysis is useful in both qualitative and quantitative analysis.
- Samples may be identified and characterized by qualitative investigations of their thermal behaviour.
- Information concerning the detailed structure and composition of different phases of a given sample is obtained from the analysis of thermal data.
- Quantitative results are obtained from changes in weight and enthalpy as the sample is heated.
- The temperatures of phase changes and reactions as well as heats of reaction are used to determine the purity of materials.
- The term 'thermal analysis' incorporates those techniques in which some physical parameter of the system is determined and /or recorded as a function of temperature.
- Current areas of application include environmental measurements, composition analysis, product reliability, stability, chemical reactions and dynamic properties.
- Thermal analysis has been used to determine the physical and chemical properties of polymers, electronic circuit boards, geological materials and coals.
- Thermal events are usually studied by recording the change in thermal property as the temperature is varied to give a thermal analysis curve or thermogram.
- Such curves are characteristic of a sample in both qualitative and quantitative sense.
- The main thermal events are summarized in the table.

Thermal Events

Thermal Events



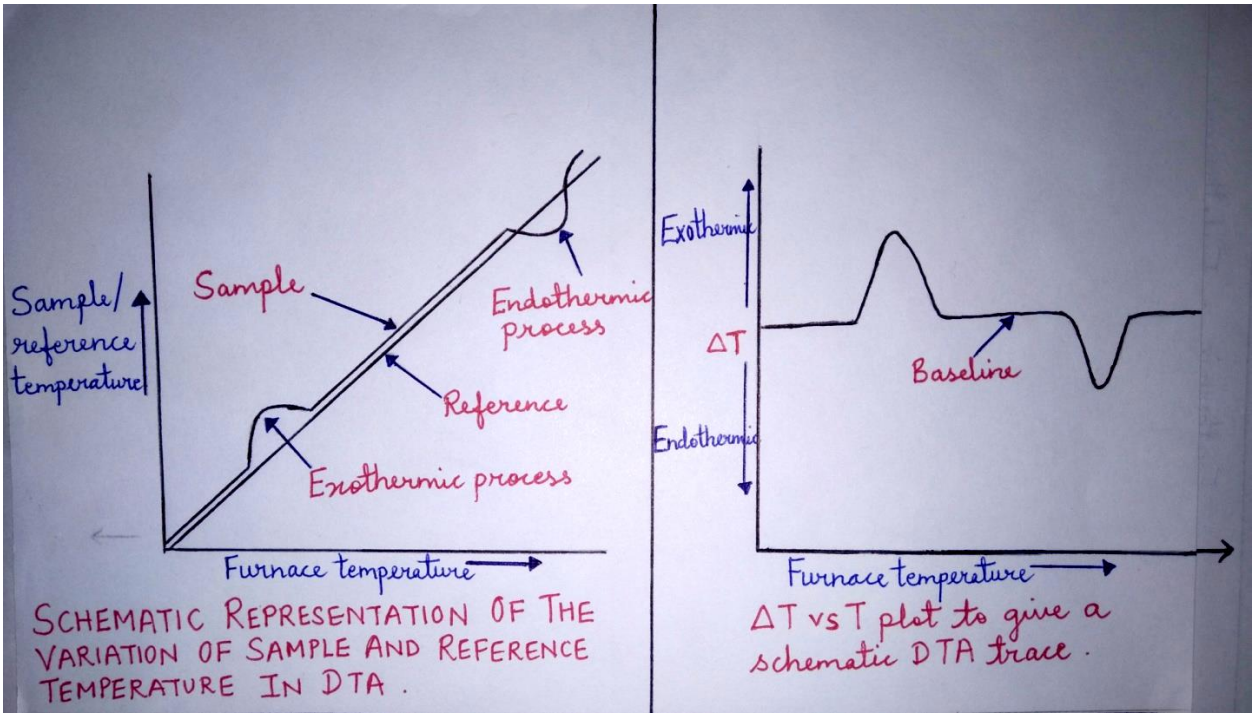
Thermal Events



Differential Thermal Analysis (DTA)

Principle:

- Monitoring of the temperature difference between a sample and an inert reference as they are heated uniformly.
- Endothermic or exothermic changes in the sample lead to characteristic deviations in temperature.
- This can be used for qualitative and quantitative analysis.
- Differential thermal analysis (DTA) is based upon the measurement of the temperature difference (ΔT) between the sample and an inert reference such as glass or Al_2O_3.
- They both are subjected to the same heating programme.
- The temperature of the reference will thus rise at a steady rate determined by its specific heat, and the programmed rate of heating.
- Similarly with the sample, except that when an exothermic or endothermic process occurs a peak or trough will be observed.
- Typical behaviour is shown in the schematic diagram.
- The figure shows a curve for the DTA examination of calcium oxalate monohydrate exemplifying also the effect of changing the atmosphere from nitrogen to air.



SCHEMATIC REPRESENTATION OF THE VARIATION OF SAMPLE AND REFERENCE TEMPERATURE IN DTA.

ΔT vs T plot to give a schematic DTA trace.

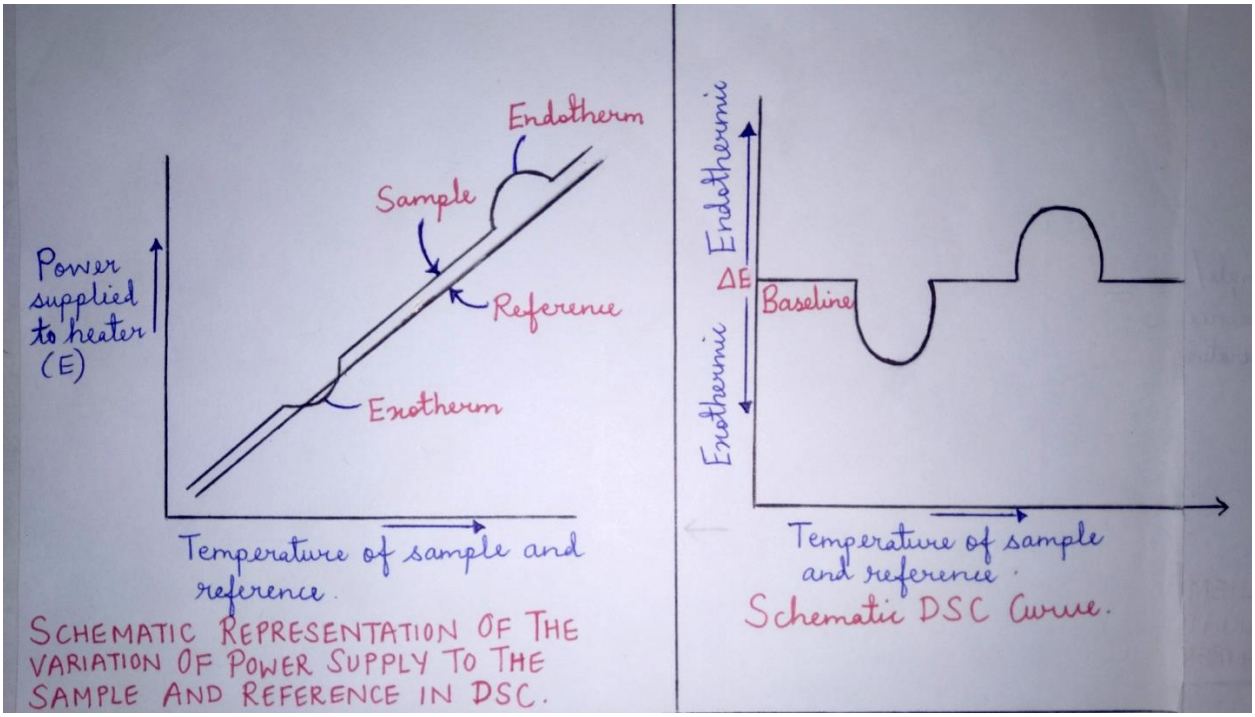
- In practice ΔT vs furnace temperature is plotted giving a thermogram.
- Mostly, the convention with exothermic peaks (exotherms) shown as positive and endothermic peaks (endotherms) as negative is accepted.
- However there are exceptions and care should always be exercised in the interpretation of recorded data.

Differential Scanning Calorimetry (DSC)

Principle:

- Sample and an inert reference heated separately, with the power supply to the sample heater variable so that the temperature difference can be maintained at zero even when endothermic or exothermic changes occur.
- The difference in power supplied to the two heaters is monitored as the analytical sign (ΔE).
- Differential scanning calorimetry (DSC) is a technique which aims to study the same thermal phenomena as DTA, but does so on a rather different principle.
- Hence, although the data obtained are very similar, they may differ in detail.

- In principle, like DTA, DSC involves the heating of the sample and an inert reference in parallel.
- However, for power compensated DSC, the two are heated quite separately with separate electrical heaters.
- The heaters are programmed to ensure that the temperatures of both sample and reference advance at exactly the same rate.
- It follows that when exotherms or endotherms occur in the sample, the power to the heater will need to be varied in order to maintain $\Delta T=0$.
- Thus by monitoring the difference in power supplied to the heaters (ΔE) the thermal changes in the sample may be followed.
- The measurement of ΔE is effectively a direct measurement of the energy change in the sample.
- This makes DSC particularly appropriate as a technique for the measurement of ΔH values.
- Heat flux DSC attains similar results by heating sample and reference from the same disc.
- Thermocouples are used to sense the differential heat flow(supply) to the sample and standard.
- The figure illustrates a typical DSC thermogram schematically.



SCHEMATIC REPRESENTATION OF THE VARIATION OF POWER SUPPLY TO THE SAMPLE AND REFERENCE IN DSC.

Schematic DSC Curve.

Comparison of DTA and DSC Technique

Aspect	DTA	DSC
➢ Size of sample	2 –10 mg	50 – 20.0 mg
➢ Sensitivity of measurement of heat of transition	a few joule/mol	0.5 kJ/mole
➢ Heating and cooling cycles	Programmed	Programmed
➢ Second order phase transition	Observed with a sample size of 200 mg	It is not observed
➢ Specific heat measurement	Accurate	Not accurate

Summary of Thermal Analysis Techniques

Technique	Parameter measured	Graph	Application
➢ Differential Thermal Analysis (DTA)	ΔT	ΔT vs temp.	Phase diags. thermal stability
➢ Differential Scanning Calorimetry (DSC)	dH.dt	dH/dt vs temp	Reaction kinetics, purity analysis

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