DTA (Differential Thermal Analysis)

In case of DTA reference and sample material is heated at the same rate under controlled conditions and the difference of temperature between reference and sample material is continuously measuredagainst time. This difference in temperatures is plotted as a function of temperature or time and called DTA curves or thermo gram. If temperature difference is zero between reference and sample material then sample doesn’t undergo any physical or chemical change, and if there is temperature difference between sample and reference material then physical or chemical change takes place in a sample. These changes result in heat being absorbed (endothermic process) or evolved (exothermic process). Endothermic changes include vaporization,phase changes such as melting, sublimation, transition between two different crystal structures, decomposition and so on; whereas exothermic changes include crystallization, chemisorptions, oxidation – reduction and so on. Thus any change in state can be detected by measuring the temperature difference. By convention, endothermic response is represented by downward peaks whereas exothermic response is shown by upward peaks. Curve obtained from DTA can be used for identification purposes as a fingerprint of material. As an example, DTA can be used to study the point when structural resemblance of different forms of clay complicates the interpretation of diffraction patterns. Area under DTA peaks gives enthalpy change of the sample. Furthermore, DTA and TGA are complimentary techniques.

Types of DTA

On the basis of temperature sensing system DTA are of two types:

1. Heat flux DTA: In case of heat flux DTA thermocouple is placed outside the sample and reference material.

2. Classic DTA: In case of classic DTA thermocouple is immersed into the sample and reference material.

DTA Experimental Factors

Care should be taken while selecting the experimental factors.For example powder decomposition reaction is affected by the specimen environment, size, surface to volume ratio and composition. Although solid state phase changes may not be impacted by these variables. Usually, the experiments involve analysing powder samples so that results do not represent the bulk samples, wherein strain energy builds up to control the transformations. Another factor influencing the decomposition reaction is the packaging of the powders, which leads to large difference in similar samples. Some samples may evolve large amount of heat and may cause saturation of the response capability of measurement systems. To avoid this situation, the sample can be diluted with inert materials. To measure temperature of phase transformations, the maximum temperature should not be varied with sample size. The weight of the sample and the rate of heating do not affect the shape of peaks in DTA. The effect of reducing heating rate is similar to the effect of decreasing the weight of the sample, and both result in sharper peaks with enhanced resolution. However, this is advantageous only in the case when signal to noise ratio is not affected. Studies involving examination of decomposition reactions can benefit from the effects of heating rate on the shape of the peak as well as its disposition. Nonetheless, kinetic studies require minimization of thermal gradients which can be achieved by decreasing either sample size or heating rate.

INSTRUMENTATION

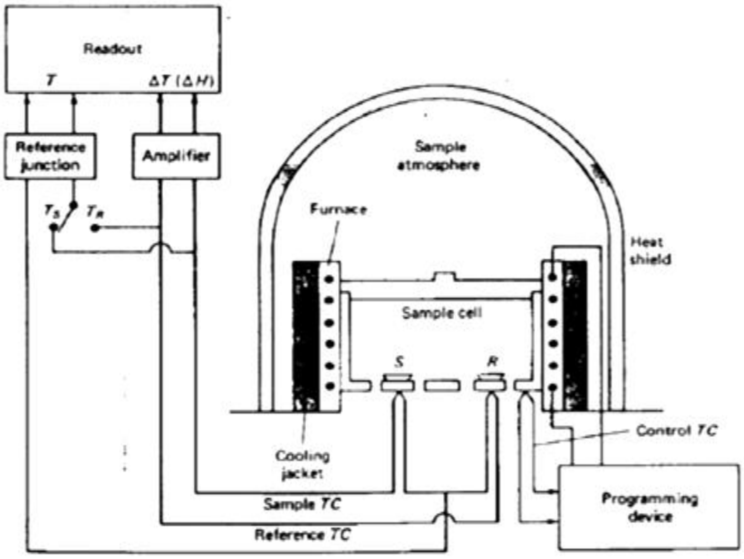

Figure 1: Instrumentation of DTA

1. Sample Holder**:** Sample and reference crucible are generally metallic (al,pt) or ceramic(silica) and may or may not have a lid, for good results area of contacts b/w sample and crucible is maximized. Typically 1-10 mg of sample is required for analytical applications.

2. Furnace: Reference and sample should be thermally matched and symmetrically arranged with the furnace so that both of them are identically cooled or heated, metal block around the wall acts as a heat sink and by using internal heater temperature of the heat sink is slowly increased sink in turn heat the sample and reference material.

3.Sensors and recording system: Pair of matched thermocouple is used; one pair is in contact with the sample while the other pair is in contact with the reference. The output of the differential thermocouple ts-tr is sent to the data acquisition system after amplification. Operating temperature for DTA instruments is generally from room temperature to around 1600 °C. Liquid nitrogen cooling accessories is needed for very low sub ambient temperature. Figure 5 shows instrumentation of DTA.

Interpretation and Presentation of Data

A typical DTAplot consists of several linear portions displaced from abscissa due to: (a) the differences in the heat capacity and thermal conductivity of the reference and test sample; (b)physical or chemical changes taking place in the samples result in either absorption or evolution of heat, which is seen as peaks in DTA plots. It is difficult to measure the transition temperatures from DTA plots. This can be understood as follows: In principle, the onset of a DTA peak signifies the start temperature. However, depending upon the relative position of thermocouple with the reference, test sample, or the DTA block, there might be temperature lag. This can be avoided by calibrating the equipment with materials whose melting point is precisely known. The enthalpy change is related to the peak area A, or the area enclosed between the peak and interpolated baseline. If differential thermocouple is in thermal contact and not in physical with the reference and test material then A can be found using

$$A=\frac{mq}{gK}$$

here, m is mass of sample,q is enthalpy change per unit mass, g is shape factor and K is thermal conductivity of the testspecimen.In case of porous, dense or heaped specimen, the thermal conductivity of the surroundings of DTA container can be altered due to the presence of gas in these pores. The situation further worsens if these gases evolve from the test specimen, leading to a thermal conductivity of the DTA–cell environment which is different from the one used during calibration process. To calibrate the DTA apparatus for enthalpy measurements, area under the peaks of the standard samples is measured over the specified temperature range. A minimum of two samples are required for calibration and both heating and cooling experiments are conducted. The heat capacity at constant pressure (C_P) can be measured as:

$$C_P = K\ \frac{T2 - T1}{mH}$$

here T1 and T2 represent the temperaturedifferencesobtainedby running the DTA apparatus without the testspecimen and with test specimen, respectively. H is the rate of heating and the K is a constant which is measured by calibration against standard materials.

DTA Thermogram

It is a plot of temperature difference versus temperature as shown in Figure 2. Four transitions detect by DTA are as follows:

1. Second order transition in which change in horizontal line is detected (e.g. glass).

2. Narrow endothermic curve due to the melting process.

3. Broad endothermic curve due to the exothermic process.

4. Exothermic curve due to the crystalline phase changes.

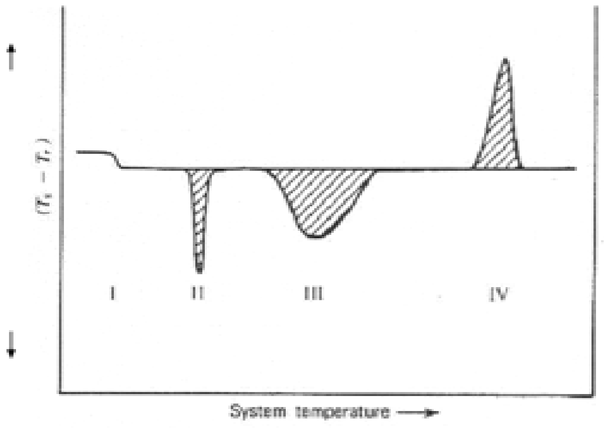

Figure2: DTA Thermogram

Factors affecting DTA curves:

Since DTA is a dynamic technique, a large number of factors can affect the resulting experimental curves. If the DTA curve is used for quantitative purposes, the shape, position, the area enclosed by the curve are of great interest.

For specific heat measurements the baseline deviations become important and such conditions as particle size, system symmetry, sample packing must be taken into account if accurate results are to be obtained .As with the technique of thermogravimetry, the DTA curve is dependent on two general categories of variables: instruments factor and sample characteristics.

1. Instrumental parameters: It includes furnace atmosphere, size and shape of furnace, sample holder materials, sample holder geometry, heating rate, and location of thermocouple in sample chamber, speed and response of recording device.

2. Characteristics of sample: It includes particle size of sample, amount of sample, packing density, swelling or shrinkage characteristic of sample, degree of crystallinity, presence of diluents, thermal conductivity and heat capacity.

The effect of furnace atmosphere is similar to that discussed in the thermogravimetry section and is significant for equilibrium reactions. An increase of the heating rate would cause the spreading of the DTA curve. Since the return of the signal to the baseline is a time function, this will happen at a higher actual temperature with more rapid heating tis is shown in fig 3

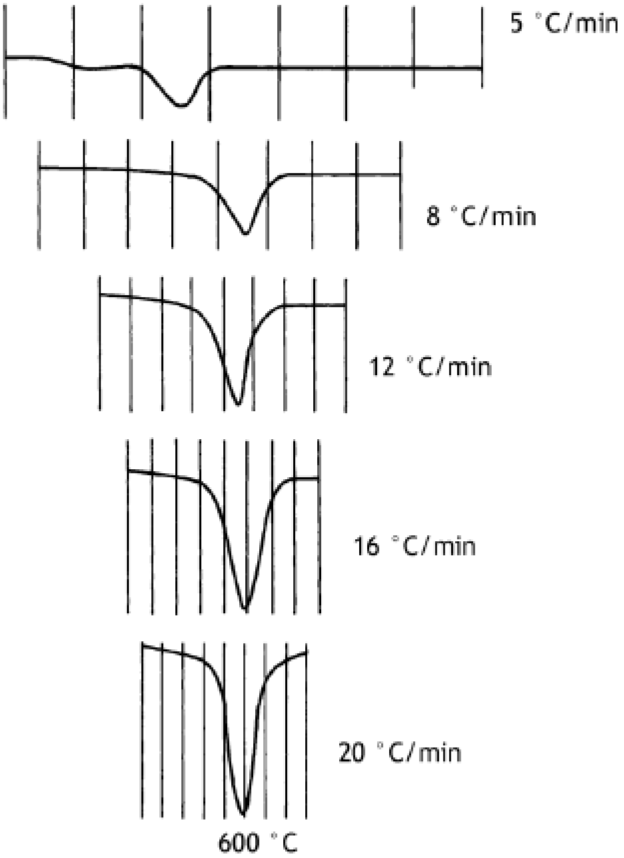

Figure 3: Variation of dta peak temperature with heating rate for kaolinite

It is also found that increasing the heating rate will decrease the resolution between two adjacents peaks. The amount of the sample and the heating rate are critical in the dta analysis as well.

A small amount of sample

- yiels maximum resolution of the peaks,
- yields best quantitative results,
- yields more regular peak shapes,
- permits best thermal contacts with the sample holder,
- allow quick removal of volatiles,
- minimizes thermal gradients within the sample,
- permits the use of higher heating rates.
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A large amount of sample

- allows detection of small thermal effects,
- provides more precise qualitative results,
- provides greater quantities of volatiles for evolved gas analysis.
- The heating rate is normally in the 5-10 C range.

Quantitative aspects of dta

Determination of the heat of tranformation (reaction), or the mass of the reactive components of the sample ,is made from the curve peak area :

$$A=\int_{t1}^{t2}\Delta T\,\mathrm{d}t=\frac{\mathrm{m}\Delta \mathrm{H}}{\mathrm{gk}}$$

Where

A is the curve peak area

Dh is the molar enthalpy change

M is the mass of the reactive component

K is the thermal conductivity of the sample,

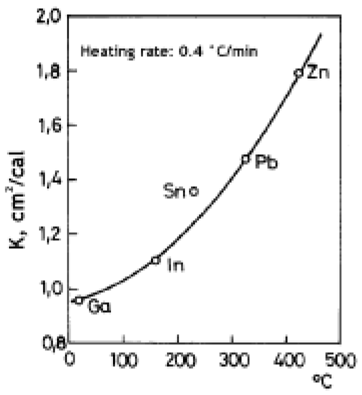
G is a contant related to the geometry of the sample holder ,

In practice a simplified expression is used: A = mΔH K, where

A is the curve peak area,

K is the callibration coefficient.

The callibration coefficient is determined by the use of compounds having known heat of transformation, most standard used involve the heat of fusion,dhf or that of a solid (1) solid (2) transition. The calibration coefficient , k is temperature dependent as shown in fig 4



Temperature

Figure 4: Calibration constant vs Temperature

Temperature dependence of calibration constant k

This means that the calorimetric sensitivity of the dta apparatus decreases with temperature , i.e more heat is required per unit area. The peak area can be converted into mass or enthalpy change only if the value of k at the transformation temperature is known , precise determination of the curve peak area is often a problem , since the heat capacity and the thermal conductivity of the sample changes in the course of transformation, as a result, the shifting baseline in the area determination is assumed to be linear (which is not true), or an equivalent peak area is determined which is also an approximation(fig 5).

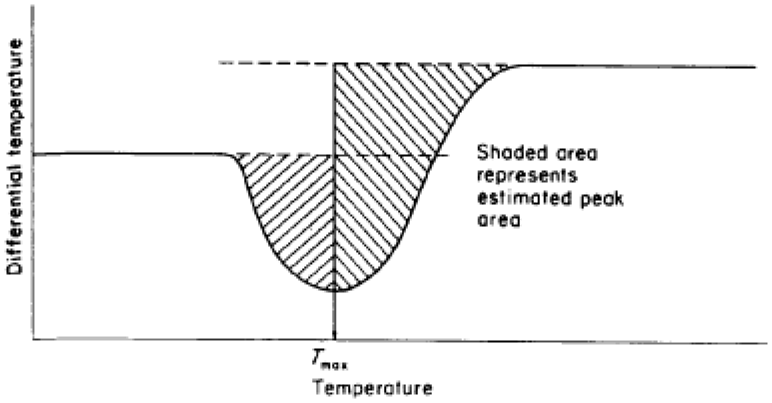


Figure 5: Calculation of the DTA peak area in the case of shifted baselines(change in heat capacity)

Applications of DTA (Differential Thermal Analysis)

1. Analysis of characteristic decomposition patterns.
2. Studies of degradation mechanisms and reaction kinetics.
3. Determination of organic content and inorganic content in a sample.
4. Study of materials, chemical analysis.
5. Any change which is associated with enthalpy change.

References :

1. Bhadeshia H.K.D.H. "Thermal analyses techniques. Differential thermal analysis". University of Cambridge, Material Science and Metallurgy. www.msm.cam.ac.uk/phase-trans/2002/Thermal1.pdf.
2. K. S. Chou, M. J. Hwang, M. Y. Shu, Thermochimica Acta, **233**, (1994) 141.
3. K. Cho, T. F. Irvine, J. Karni, Intl. J. Heat Mass Transfer, **35**, (1992) 957.
4. H. R. Brunner, B. J. Curtis, *Journal of Thermal Analysis*, **5**, (1973) 111.
5. T. Hatakeyama, and F. X. Quinn John wiley & Sons Publications 1999 Thermal Analysis Fundamentals and Applications to Polymer Science Thermogravimetry, 2nd Ed.
6. Coats , A.W: Redfern Jp, 1963 Thermogravimetric Analysis. A Review.
7. Fleming Polymer Testing and Consultancy. http://www.flemingptc.co.uk/our-services/dsc-tga/.
8. Analytical Compendium, Chapter 5 Section 2. https://iupac.org/publications/analytical_compendium/.
9. Gudeep R Chatwal , Sham K . Anand, Himalaya Publishing House, 2002, Instrumental Methods Of Chemical Analysis: Thermal Methods, 5th Ed.
10. D.A Skoog et al, Principles of instrumental analysis, fifth edition, Harcourt publishers, 2001.
11. Sharma B.K Goel Publishing House "Instrumental Methods of Analysis".
12. E.N. Kaufmann (Ed), Characterization of Materials, Wiley –Inter Science, 2003.
13. M.E. Brown, Introduction to thermal analysis : Techniques and application , second edition, Springer, 2007.