THERMAL METHODS OF ANALYSIS

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Thermal Methods of Analysis (Shetty)

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About the Book

This book on “Introduction to Thermal Methods of Analysis” is dedicated to all the educators who made their educational content freely available during the pandemic (Covid 19). Overnight transition from offline to online mode and limited access to reference books during the pandemic has made many more educators realise the importance of Open Educational Resources (OER).

The internet is flooded with information on basic topics in chemistry. But when it comes to specific topics in chemistry there is a dearth of information. This is an attempt to fill such gap through an interactive textbook on “thermal methods of analysis”. The contents of this book include principles, instrumentation and applications of thermal methods viz thermogravimetry, differential thermal analysis and differential scanning calorimetry. The book is designed in a different way from other books in the sense that there are activities after every topic and the reader will be able to assess their understanding of the topic by taking a simple test or performing a self-assessment activity.

Introduction

Have you ever wondered how the manufacturer of a non-stick pan so confidently offers a warranty on the product? Why silicone baking tray does not melt away even while using the oven at a very high temperature? Was there any study carried out to check the stability of these materials at high temperature? The answer is yes “Thermal Analysis” can give information about stability of the materials at high/low temperature.

Thermal analysis includes a group of techniques in which specific physical properties of a material are measured as a function of temperature. The production of new high technology materials and the resulting requirement for a more precise characterization of these substances have increased the demand for thermal analysis techniques. 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 analysis is useful in both qualitative and quantitative analyses. Samples may be identified and characterized by qualitative investigations of their thermal behavior. 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 temperature of phase changes and reaction as well as heat of reaction are used to determine the purity of materials.

Thermal analysis is valuable in many scientific disciplines ranging from astronomy to zoology-literally from **A to Z** !

Let us learn in detail about “Thermal Methods of Analysis”.

About the Author

Dr. Prabha G Shetty is an Associate Professor and the Head of Chemistry Department at Sophia College for Women, Mumbai, India.

She is specialized in Analytical Chemistry and has been teaching chemistry at undergraduate level for 27 years and at postgraduate level for 14 years.

Dr. Prabha is actively involved in phytochemical research and has published research papers in various reputed journals . She has keen interest in chemistry education and is passionate about developing innovative pedagogy to make chemistry enjoyable.

Acknowledgement

I wish to sincerely thank my student Ms. Maryam Malkani (TYBSc Batch 2023-24) who helped with the few images used in this book.

1: Thermal Analysis

Learning Objectives

After studying this chapter, you should be able to:

- List the different thermal methods of analysis.
- Define the major methods of thermal analysis.
- Identify endothermic and exothermic transitions.

Thermal analysis refers to the group of methods in which some physical property of the sample is continuously measured as a function of temperature, whilst the sample is subjected to a controlled temperature change.

Brain Teaser

Can you write down one similar method, used to characterize solid organic compounds in particular, which depends upon a thermal technique?

Have you guessed it? It is Melting point determination.

The effect of heat can be wide ranging and cause changes in many properties of a sample. In thermal analysis, changes in weight form the basis of Thermogravimetry (TG) while measurement of energy changes form the basis of Differential Thermal Analysis (DTA) and of Differential Scanning Calorimetry (DSC). These techniques are the most important in thermal analysis. Thus, for example, TG tells us when a sample is losing weight (and how much) while DTA or DSC will tell us if that reaction is exothermic or endothermic (and often capable of measuring heat change). These important techniques can be applied to the study of almost any substance. Apart from these, there are some other thermal methods which are listed below:-

Thermomechanical Analysis (TMA): Dimensional changes as a function of temperature.

Thermoacoustimetry: Characteristics of imposed sound waves produced as the material being heated.

Thermoptometry: Study of an optical characteristic of a sample as it undergoes a thermal programme.

Electrothermal analysis: Study of electrical conductivity as a function of temperature.

Thermomagnetometry: Study of variation in a magnetic property of a material with temperature.

Activity 1.1: It is said that **'immediate recall, aids retention'**, so

We have briefly discussed about eight kinds of thermal effects which can occur when a sample is subjected to a controlled temperature programme. Write down as many of these eight effects as you can in the left hand column opposite the name of the corresponding thermal method given in the right hand column.

Fill in the thermal effect/change that is measured in the methods mentioned.

Thermal effect/change	Name of thermal method
	TG
	TMA
	DTA
	Thermoacoustimery
	Thermopotometry
	Electrothermal Analysis
	Thermomagnetometry

(Dodd &Tonge, 2008)

Activity 1.2: Match the following:

Technique	Quantity Measured
1)DSC	a) Weight change
2)DTA	b) Heat and temperature of transition and reactions.
3)EGA	c)Temperature of transitions and reactions.
4)TG	d) Amount of gaseous products of thermally induced reactions.

Answers: 1)____ 2)____ 3)_____ 4) _____

(Dodd &Tonge, 2008)

Let us now learn in detail about some of the frequently used thermal methods. These are listed below:

Thermogravimetry (TG/TGA): TG or TGA is a technique in which the weight of a sample is measured as a function of temperature, whilst it is subjected to a controlled heating programme.

Derivative Thermogravimetry (DTG): DTG is a method of expressing the results of TG by giving the first derivative curve as a function of temperature or time.

Differential Thermal Analysis (DTA): DTA 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 under controlled heating.

Differential Scanning Calorimetry (DSC): DSC is very similar to DTA and gives much the same sort of information but DSC is more often used for quantitative measurement of energy changes.

Evolved Gas Detection (EGD): EGD is a technique in which the evolution of gas from a sample is detected, as a function of temperature, whilst the sample is subjected to controlled thermal programme.

Evolved Gas Analysis (EGA): EGA is a technique whereby the volatile products, released by a sample on decomposition, may be analysed as the sample is heated according to controlled thermal programme. (Dodd & Tonge, 2008)

Pre-requisite:

Before we deep dive into some thermal methods it is essential to check our understanding about the concept of exothermic/endothermic and different transitions accompanied by weight loss or weight gain.

Let us consider an example of different states of water and their inter-conversion,

$Ice_{(s)} \leftrightarrow Water_{(l)} \leftrightarrow Steam_{(g)}$

In each of the above transitions can you tell which one is an endo/exothermic transition? And is there any change in weight during these transitions?

For further explanation please see Introductory Chemistry in *Libretexts*

https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Introductory_Chemistry/03%3A_Matter_and_Energy/3.09%3A_Energy_and_Chemical_and_Physical_Change

Now that you have some idea about endothermic and exothermic transitions, try activity **1.4**

Activity 1.4: Can you assign which of these processes will be endothermic/exothermic?

Endothermic / Exothermic transitions (please tick)

Phenomenon	Exothermic	Endothermic
Adsorption		
Desorption		
Fusion (melting)		
Vaporization		

Decomposition		
Dehydration		

(Dodd & Tonge, 2008)

Activity 1.5: Can you assign which of these processes will be endothermic/exothermic

and accompanied by weight loss or weight gain. **(Please tick)**

Phenomenon	**Weight gain**	**Weight loss**	**Endothermic**	**Exothermic**
Melting				
Adsorption of gas				
Desorption of gas				
Vaporisation				
Dehydration				
Decomposition				
Sublimation				

(Dodd & Tonge, 2008)

Now that we have an idea about the exothermic, endothermic, weight gain and weight loss process it is important to note that these transitions can be either physical or chemical transitions.

Brain Teaser:

How might you study a sample which, on heating, first melts and then at a later stage decomposes with loss of weight?

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2: Thermogravimetry

Learning Objectives

After completing this chapter, you should be able to:

- Describe the effect of heat on materials.
- Identify physical and chemical transitions.
- Describe the essential features of a thermobalance.
- Draw and interpret thermogravimetric and derivative thermogravimetric curve for a known system.
- Illustrate the range of applications of thermogravimetry.
- Calculate % weight loss at every stage of decomposition and predict stoichiometry.

Thermogravimetry is a technique used to detect any physical or chemical transitions which are accompanied by a weight loss or weight gain as the sample is heated in a controlled manner.

2.1 Effect of heat on matter

We need to first understand the effects of heat on matter. And For further explanation please see Introductory Chemistry in *Libretexts*

https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Introduction_to_General_Chemistry_(Malik)/01%3A_Matter_energy_and_their_measurements/1.09%3A_Heat_and_changes_in_physical_states_of_matter

Now, we have understood the effects of heat on matter and also able to identify the processes involving change in weight on heating through Activity 1D. It is important to keep in mind that the change in weight could be due to physical or chemical transitions. To be able to distinguish between physical and chemical transition, let us go through the next sub-topic.

2.2 Changes in matter: Physical and Chemical Changes

For further explanation please see Introductory Chemistry in *Libretexts*

https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Introductory_Chemistry/03%3A_Matter_and_Energy/3.06%3A_Changes_in_Matter_-_Physical_and_Chemical_Changes#:~:text=3.6%3A%20Changes%20in%20Matter%20%20Physical%20and%20Chemical,4%20Summary%20...%205%20Contributions%20%26%20Attributions%20

Activity 2.1: Can you assign which of these transitions will be physical transitions /chemical transitions? **(please tick)**

Phenomenon	Physical	Chemical
Adsorption		
Dehydration		
Desorption		
Fusion (melting)		
Chemisorption		
Vaporization		
Decomposition		
Redox reactions		
Reduction in gaseous atmosphere		

(Dodd & Tonge, 2008)

2.3 Principle and Instrumentation of TGA

The instrument used to carry out thermogravimetric analysis is known as “thermobalance”.

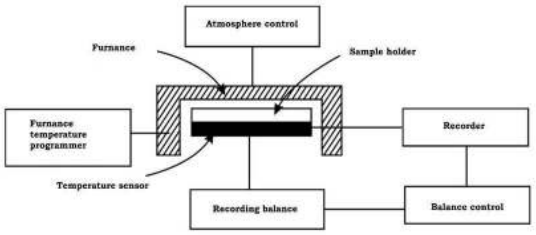

Figure 2.3 Schematic diagram of a thermobalance. (Source: https://images.app.goo.gl/uyRxxbkVNkxLF3nT7)

Working: Please go through the *Chemlibre* link to understand the principle and working of a thermobalance.

https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Instrumental_Analysis_(LibreTexts)/31%3A_Thermal_Methods/31.01%3A_Thermogravimetric_Methods

2.4 Interpretation of thermogravimetric curve

The graphical information obtained from thermogravimetric analysis is known as thermogram/pyrolysis curve. TG curve is a plot of weight (W) decreasing downwards on the y-axis (ordinate), and temperature (T) increasing to the right on the x-axis (abscissa). A typical thermogram for a single step decomposition is shown in Fig. 2.4.

The plateau ‘AB’ indicates no change in weight or the temperature range over which the sample is thermally stable. At point ‘B’ the sample starts decomposing which is indicated by an inflexion.

Please read the following text explaining the interpretation of thermogram and then attempt Activity 2B.

https://chem.libretexts.org/Courses/Franklin_and_Marshall_College/Introduction_to_Materials_Characterization__CHM_412_Collaborative_Text/Thermal_Analysis/Thermogravimetric_analysis_(TGA)

Activity 2.2: A typical thermogram is shown below, observe and fill in the blanks by choosing the most appropriate answer. (Hint: Initial mass at ‘A’ is considered as 100%)

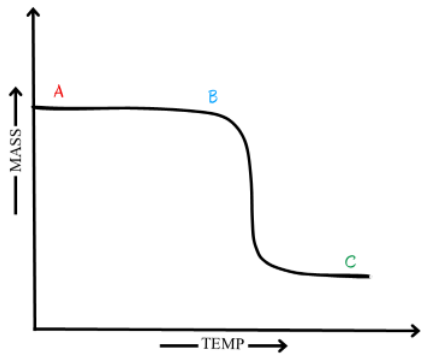

Figure 2.4 Typical TG curve

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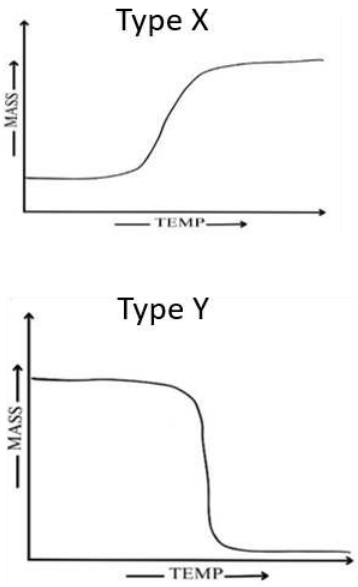
Activity 2.3: For the processes given in the table, predict the nature of thermogram (Type-X /Type-Y or None of these)

Phenomenon	Type
Melting	
Adsorption of gas	
Desorption of gas	
Vaporisation	
Dehydration	
Decomposition	
Sublimation	



2.5 Need for Derivative Thermogravimetry (DTG)

In the above example (Fig. 2.4), we have considered the thermogravimetric curve which represents a single stage decomposition. Figures '1.2.5a' and '1.2.5b' show two-stage and three-stage decompositions respectively. In both these figures (2.5a and 2.5b) there is an overlay of TGA and DTG thermograms, clearly depicting advantages of DTG over TGA thermogram in locating the exact decomposition temperature.

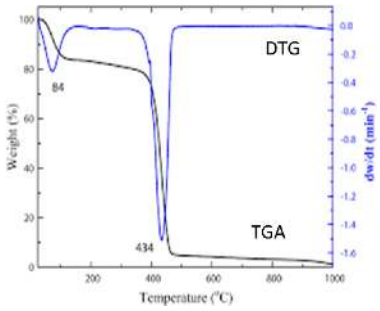


Figure 2.5a. Thermogravimetric (TG) and Derivative thermogravimetry (DTG) curves for PVP at a heating rate of 10°C/min. (Source: Al-Hada et al., 2014) https://images.app.goo.gl/fWChwNJi9uxfHZAJ7

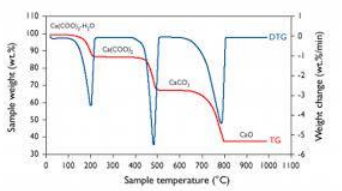


Figure 2.5b. TGA test result of calcium oxalate monohydrate (Source: Chegg.com) https://images.app.goo.gl/1Hbp2vSV2rBjeFc4A

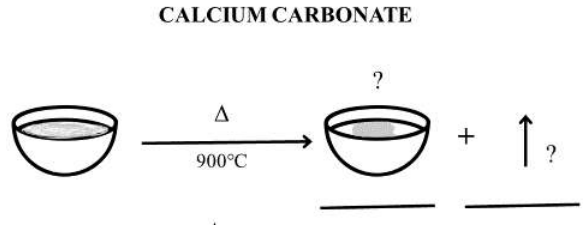
Figure '2.5b' is for the decomposition of calcium oxalate monohydrate, the weight loss commences just above 100°C and continues up to 200°C. Between about 400 °C and 500°C further decomposition occurs, to give a product which is stable up to

700°C before decomposing to give another stable compound at 800°C. Every process of decomposition continues over a range of temperature hence the DTG curve is useful in providing information regarding precise decomposition temperature at every stage.

Activity 2.4: (James & Tonge, 2008)

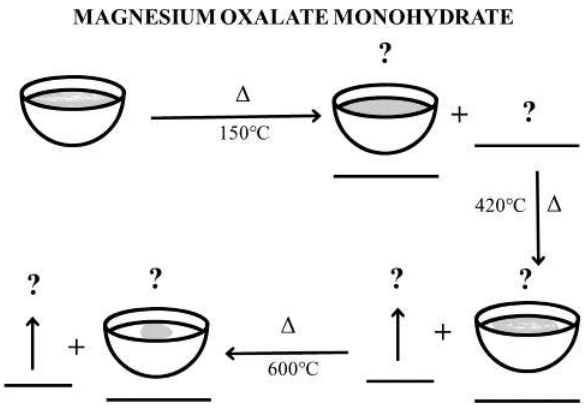
Activity 2.5: Complete the following reaction for the decomposition of calcium carbonate.

- Identify the volatile and stable compound/s remaining in the crucible post decomposition and indicate these on a thermogram.



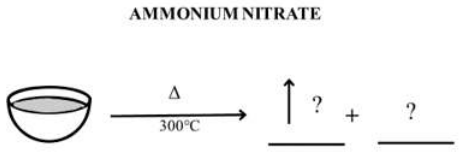
Activity 2.6: Observe the image given below for the decomposition of magnesium oxalate monohydrate ($MgC_2O^4.H_2O$)and complete the activity.

1. Identify the volatile product and the residue remaining in the crucible at each stage of decomposition.
2. Write the decomposition reaction taking place at each stage.
3. Draw a thermogram for the decomposition of magnesium oxalate monohydrate.



Activity 2.7: Observe the image given below for the decomposition of ammonium nitrate (NH_4NO_3) and complete the activity.

1. Identify the volatile product/s and the residue remaining (if any) in the crucible after decomposition.
2. Write the decomposition reaction.
3. Draw a thermogram for the decomposition of ammonium nitrate.



2.6 Applications of Thermogravimetric analysis

I. Thermogravimetric analysis of a binary mixture of calcium and magnesium oxalates:

Following thermogram shows decomposition curve for a mixture of oxalates.

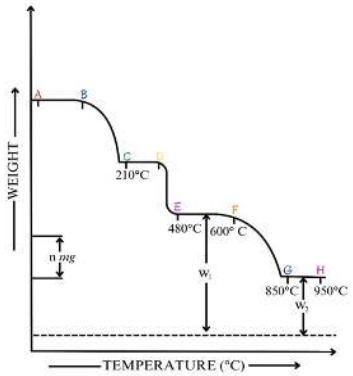


Figure 2.6a. Decomposition curve for a mixture of calcium and magnesium oxalate dihydrate

- There is a significant loss which occurs before 210°C- due to loss of water from the sample.
- The mixture of anhydrous carbonate then shows some weight loss by about 480 °C owing to the reaction

$$MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{2(g)}$$

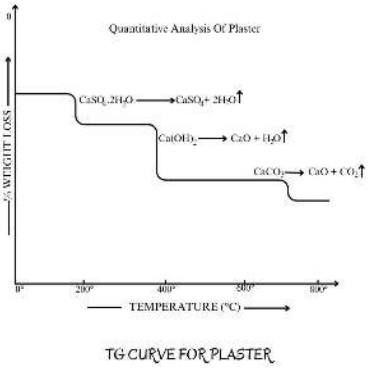
- No further weight loss occurs before 600 °C. (EF)
- $CaCO_3$ decomposes between about 600 °C and 900 °C. (FG)

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

- Thus, EF represents a mixture of MgO and $CaCO_3$
- The plateau GH represents the residue of MgO and CaO

Activity 2.8: Construct separate decomposition curves for calcium oxalate dihydrate and magnesium oxalate dihydrate based on the above information.

II. Thermogravimetric analysis of plaster for safety screening:



TG CURVE FOR PLASTER

Figure 2.6b. TG curve for plaster

Plaster contains following ingredients,

Gypsum--- $CaSO_4.2H_2O$

Lime--- $Ca(OH)_2$

Chalk--- $CaCO_3$

From the weight loss at each step on the curve, the quantity of each ingredient can be determined in the original sample. In the manufacture of Portland cement, 5% gypsum is added to reduce the rate of setting. The gypsum is added to the fused clinker during processing, and the two components are subsequently milled to obtain uniform mixing and the required particle size. During milling, the thermal energy generated may cause partial dehydration of gypsum to hemihydrate $CaSO_4$ .1/2 H_2O which adversely affects (increases) the rate of setting of the cement. Hence it is important to monitor the presence of each hydrate in the final cement. In order to provide quantitation at the required levels, this problem can be solved by TGA and DTA or DSC.

The dehydration of gypsum occurs as a two-stage endothermic process.

$CaSO_4.2H_2O \rightarrow CaSO_4.1/2\ H_2O \rightarrow CaSO_4$

So, if there is conversion of gypsum to hemihydrate, the TG curve in Fig. 2.6b will show two step decomposition for gypsum instead of one.

Activity 2.9: (James &Tonge, 2008)

A manufacturer wishes to incorporate a plastic coating on the inside of a utensil. One factor to be evaluated is the stability of the following polymer.

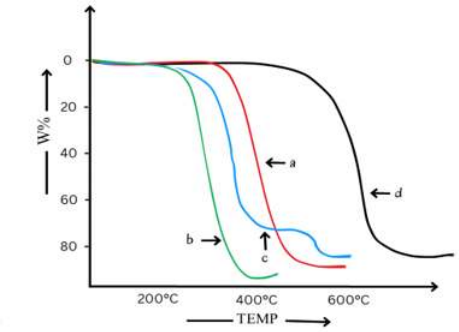
a. Polyethylene

b. Polypropylene

c. PVC

d. Polytetrafluoroethylene

Figure below gives TG curves for the above polymers.



So far, we have discussed qualitative applications of TGA. Let us see some quantitative applications of thermogravimetric measurement.

Activity 2.10: Solve the following numerical problems.

1) Calculate the percent weight changes W% for each of the following reactions which occur on heating the parent material.

a) $Ca(OH)_{2^{(S)}} \rightarrow CaO_{(s)} + H_2O_{(g)}$

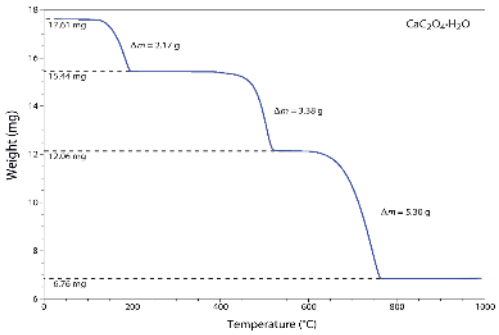
b) $6PbO_{(s)} + O_{2(g)} \rightarrow 2Pb_3O_{4(s)}$

[Ca=40.1, H=1.0, O=16.0, Pb=207.2]

2) A mixture of calcium oxide and calcium carbonate is analysed by thermogravimetry. The resultant curve indicates one decomposition only between 600-900° C during which the weight of sample decreases from 250.6 mg to 190.8 mg. What is the percentage of calcium carbonate in mixture by weight?

[Atomic mass: H=1.0, Pb=207.2, C=12.0, O=16.0, Ca= 40.1]

3) The thermogram given below shows the mass of a sample of calcium oxalate monohydrate, $CaC_2O_4.H_2O$, as a function of temperature. The original sample of 17.61 mg was heated from room temperature to 1000°C at a rate of 20°C per minute. Calculate the % weight loss at each step.



Activity 2.11: Solve the puzzle

https://thewordsearch.com/puzzle/6923734/thermal-analysis/

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3: Differential Thermal Analysis

Learning Objectives

After completing this chapter, you should be able to:

- Explain the principle and working of a differential thermal analyser.
- Draw and interpret DTA thermogram.
- Compare and contrast TG and DTA results.
- Explain the applications of DTA and simultaneous TG-DTA analysis.

When a molecule undergoes a physical or chemical transition, heat is either absorbed or liberated. Two thermal methods, DTA and DSC are particularly useful for investigating these physical and chemical changes.

3.1 Principle and Instrumentation:

In DTA, difference in temperature between the sample and an inert reference (ΔT) is measured as the sample and the reference are heated or cooled in a controlled manner.

$$\Delta T = T_S - T_R \tag{3.1}$$

with T_S as the temperature of sample and T_R is temperature of reference which is thermally stable.

Please go through the *Chemlibre* link to understand the principle and working of DTA.

https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Instrumental_Analysis_(LibreTexts)/31%3A_Thermal_Methods/31.02%3A_Differential_Thermal_Analysis

Instrumentation and working: A typical DTA set up is shown in the figure given below.

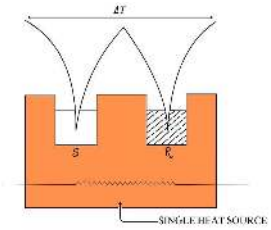


Figure 3.1 DTA set up

In differential thermal analysis (DTA), the difference in temperature between the sample and a thermally inert reference material is measured as a function of temperature (usually the sample temperature). Any transition that the sample undergoes results in the liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. A plot of the differential temperature, ΔT, versus the programmed temperature, T, indicates the transition temperature(s) and whether the transition is exothermic or endothermic. DTA and thermogravimetric analyses (measurement of the change in weight as a function of temperature) are often run simultaneously on a single sample.

3.2 DTA curve and its interpretation

$$\Delta T = T_S - T_R \tag{3.2}$$

T_S= temperature of sample

T_R = temperature of thermally stable reference

A typical DTA curve is represented below

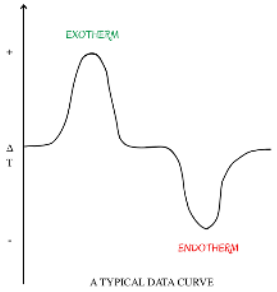


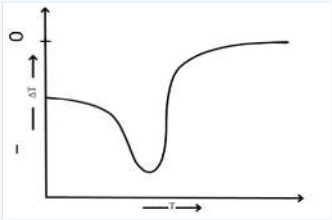
Figure 3.2 DTA curve

Brain Teaser:

Can you suggest why we adopt $\Delta T > 0$ for exothermic and $\Delta T < 0$ for endothermic transition?

? Activity 3.1

The following figure represents thermal investigation. Fill in the blanks by choosing the correct option. (James & Tonge, 2008)



The record shown is that of a_____ experiment since the_____ plot ΔT which is a _____temperature. The _____direction of the peak indicates that a _____reaction has occurred. This in turn implies that the corresponding _____ change ΔH must have been _____ ie the value of enthalpy _____the thermal effect was _____ than its value _____.This means that the sample _____ heat during the reaction. Furthermore, there is evidence of a change _____in the temperature is increased beyond the thermal transition. This is shown by the _____of the just beyond the end.

Answer

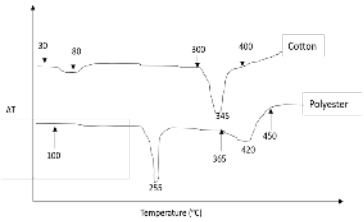
Select from the following list

[upward/downward, free energy/heat capacity, greater/less, DTG/DTA, base-line/background, derivative/differential, took in/gave out, negative/positive, enthalpy/entropy, before/after/during, exothermic/endothermic/isothermal, abscissa/ordinate, distortion/displacement.]

Activity 3.2: (James & Tonge, 2008)

During the Falklands campaign in 1982 many naval personnel suffered serious burns. In 1985 the Admiralty decreed that all men on active service in Navy should be issued cotton uniforms instead of polyester ones which had been issued in 1982. Does the thermal data suggest a reason for the decision? Justify your answer.

[Hint: Cotton decomposes at 345 °C whereas polyester melts at 255 °C and decomposes at 420 °C]



3.3 Comparison with TGA

	TGA	DTA
1	It measures change (loss or gain) in weight as the sample is subjected to controlled heating program	It is a technique in which the difference in temperature between the sample and an inert reference material, is measured as a function of temperature
2	It will detect only those physical and chemical transitions which are accompanied by change in weight.	It can detect all physical and chemical transitions.
3	This does not require an inert reference.	This requires an inert reference material.
4	It is a quantitative method	It is a semi-qualitative method.
5	This technique is generally used to study decomposition reactions.	This technique is used to study phase transitions

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4: Differential Scanning Calorimetry (DSC)

Learning Objectives

After completing this chapter, you should be able to:

- Explain the principle and working of DSC.
- Draw and interpret DSC curves.
- Compare and contrast DSC with TG and DTA.
- Calculate heat of any reaction from the given data.
- Explain the applications of DSC to polymeric materials and pharmaceuticals.
- Explain the applications of simultaneous TG-DTA-DSC analysis.

Differential scanning calorimetry (DSC) has become the most widely used thermal analysis technique. In this technique, the sample and the reference materials are subjected to a precisely programmed temperature change. DSC is very similar to DTA and gives much the same sort of information but DSC is more often used for quantitative measurement of energy changes.

4.1 Principle

In DSC, the difference in temperature (ΔT) between the sample and an inert reference is maintained at zero as they are subjected to controlled heating or cooling. The instrument is provided with a separate heater for the sample and the reference. When a thermal transition occurs in the sample, thermal energy is added to either the sample or the reference container in order to maintain both the sample and the reference at the same temperature. Because the energy transferred is exactly equivalent in magnitude to the energy absorbed or evolved in the transition, the balancing energy yields a direct calorimetric measurement of the transition energy. Since DSC can measure directly both temperature and the enthalpy of a transition or the heat of a reaction, it is often substituted for differential thermal analysis as a means of determining these quantities except in certain high temperature applications.

4.2 Instrumentation and working

A typical DSC cell uses a constantan (Cu-Ni) disk as the primary means of transferring heat to the sample and the reference positions and also as one element of the temperature-sensing thermoelectric junction. The sample and a reference are placed in separate pans that sit on raised platforms on the disk. Heat is transferred to the sample and reference through the disk. The differential heat flow to the sample and reference is monitored by the chromel/constantan thermocouples formed by the junction of the constantan disk and the chromel wafer covering the underside of each platform. Chromel and alumel wires connected to the underside of the wafers form a chromel/alumel thermocouple, which is used to directly monitor the sample temperature.

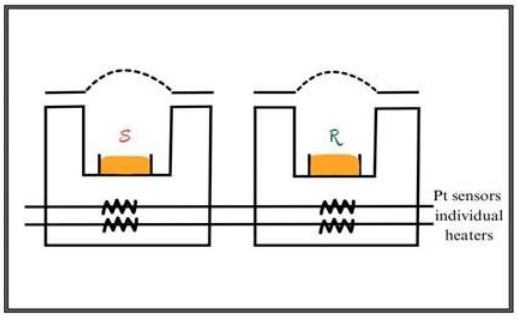

Figure 4.2a. DSC set up

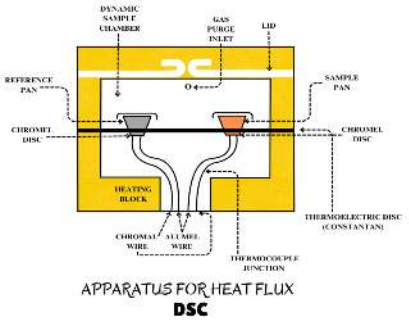

Figure 4.2b. DSC cell cross section

Activity 4.1: Read each of the statements and mark them as **True or False**

(i) In DSC the sample and reference positions are provided with their own separate heating sources, so that the assembly may be operated on a 'null balance' basis.

(ii) In DTA the equipment is so designed that the temperature of the sample is equal to that of the reference material at every point in the heating programme.

(iii) Chemical decompositions which give rise to weight changes may be detected by DTA and DSC.

(iv) The main components of a conventional differential thermal analyser consist of following

1. The sample/reference holder
2. The thermocouple
3. The furnace
4. The amplifier
5. The recorder

4.3 DSC curves and its interpretation

The enthalpy of a sample refers to its heat content. Exothermic/Endothermic changes in a sample give rise to enthalpy changes. Enthalpy changes may be taken to correspond to a heat of reaction are usually written as ΔH.

$\Delta H = Hp - HR$

Hp = Enthalpy of products

HR = Enthalpy of Reactants

A typical DSC curve is shown in Figure 4.3

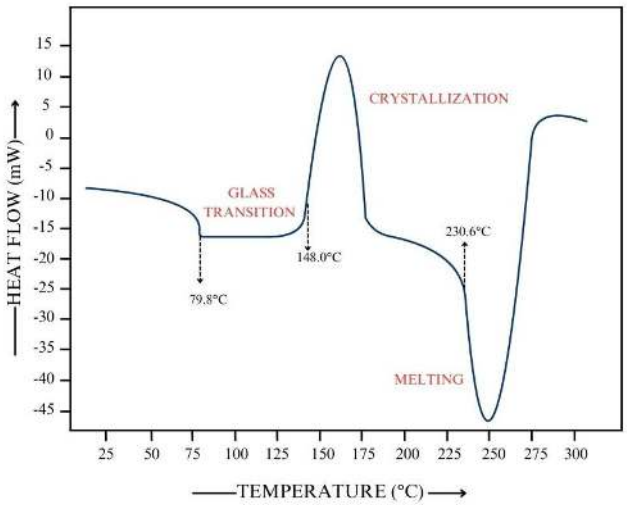

Figure 4.3. DSC of PET

Activity 4.2: Choose the correct option (James and Tonge, 2008)

1. If ΔH < 0, the system has undergone an endothermic/ exothermic change which means

   Ts __ TR [Choose the correct option: =, <, >]

2. Conversely ΔH > 0, means _____change and Ts ___ TR [Choose the correct option: =, <, >]

3. In order to keep ΔT = 0 [ΔT = Ts – TR],

- In case of an endothermic reaction we must provide heat to sample/reference.
- In case of an exothermic reaction we must provide heat to sample/reference

Activity 4.3: Observe the DSC curve given in 'figure **4.3**.' and answer the following questions.

- How many transitions are seen in the above diagram?
- Do you see any endotherm or exotherm? If yes, how many?
- What does an endo or exothermic nature of the transition tell you about the transition or ΔH value?
- Do you see a shift in the base line post glass transition temperature?
- Is the DSC curve of PET useful in predicting stability of the polymer? Justify your answer.

In the above figure, the shift in baseline is due to the change in heat capacity (Cp) of the polymer post glass transition temperature.

Let us learn more about heat capacity, glass transition temperature and the role of DSC in characterization of polymeric materials.

Definition: Heat Capacity

What does change in **Cp** means?

Heat Capacity (specific heat) is denoted as C_p . It is the energy required to raise the temperature of one mole of material through one degree kelvin.

4.4 Applications of DSC

I. Characterisation of polymeric materials: The 'glass transition temperature' (Tg) is an important parameter for many polymeric, ceramics and glasses. On cooling the material from the liquid state, there is (at the Tg) a change from the liquid state to amorphous state or glassy state. At this point there is discontinuity in the rate of change of the volume. There is also a change in the specific heat which allows study by DSC. Both these effects are illustrated in the figure 4.4a and 4.4b respectively.

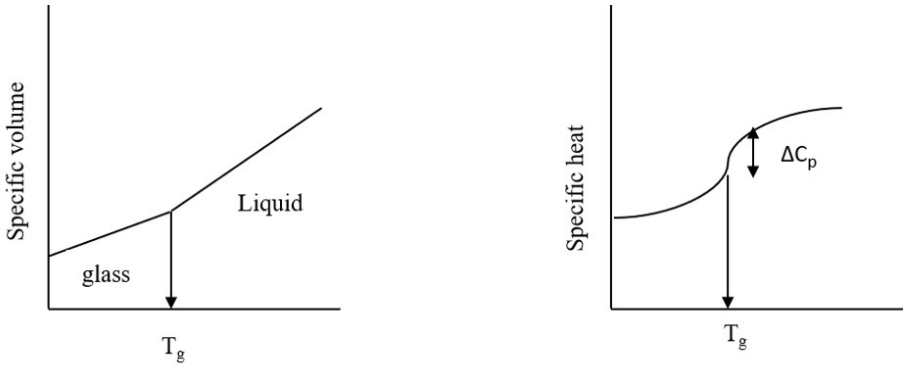

Figure 4.4a. Figure 4.4b.

II. Drug analysis for purity assessment: DSC analysis can be used to assess purity of drug. Fig 4.4c shows comparative melting points of 98%, 99% and 100 mole % phenacetin. Since melting is an endothermic process but does not involve change in weight, it cannot be detected by TGA. DTA or DSC is the most suitable technique in such cases.

Pure compounds give sharp endothermic peak in DSC, which is evident from the peaks observed for 98% and 100% mole phenacetin. Impure compounds will melt at a temperature lower than the corresponding pure compounds. Hence, melting point and nature of peak can be used to comment on the purity of any drug.

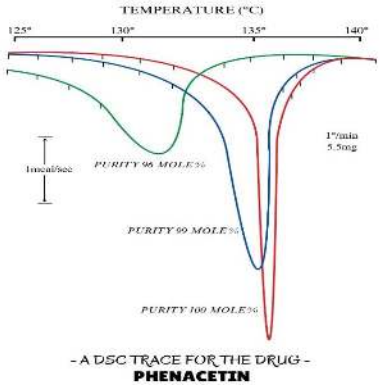

Figure 4.4c. DSC of Phenacetin

4.5 Comparison of DSC with DTA

	DSC	DTA
1	It involves measurement of energy changes whilst the sample is subjected to controlled heating.	It is a technique in which the difference in temperature between the sample and inert reference material, is measured as a function of temperature.
2	It can detect all chemical and physical transitions including change in heat capacity.	It can detect all physical and chemical transitions.
3	It is a quantitative method.	It is a semi-quantitative method.
4	This technique is used to study purity of compounds, heat of reaction and characterization of polymers.	This technique is used to study phase transitions.

Activity 4.4: Solve the puzzle

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5: Summary

You must have realized that thermal methods are extremely versatile as far as their applications are concerned. It is applied in industries as diverse as aerospace and pharmaceuticals. It can be used to investigate samples of all kinds of materials-inorganic, organic, plastics, metallic, ceramic and glass.

We have illustrated the application of thermal methods to some, but not all, of these kinds of materials. Summarize this by entering the reference number of the appropriate figure in the text against the corresponding type of material. Where there is no Figure to illustrate the application of thermal methods to a particular material enter a dash (-)

Activity 5:

Sr. No	Material	Figure
1	Biological material eg Kidney stones	
2	Inorganic compounds	
3	Plastics	
4	Textiles and fibre	
5	Pharmaceuticals	
6	Metals and alloys	
7	Building materials eg. Cement	

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6: Self Assessment Activities- Answer Key

Activity 1.1:

Thermal effect/change	Name of thermal method
Weight	TG
Dimension	TMA
Energy (difference in temperature)	DTA
Acoustic property	Thermoacoustimery
Optical property	Thermoptometry
Electrical conductivity	Electrothermal Analysis
Magnetic property	Thermomagnetometry

Activity 1.2:

Technique	Quantity Measured
1)DSC	Heat and temperature of transition and reactions
2)DTA	Temperature of transitions and reactions.
3)EGA	Amount of gaseous products of thermally induced reactions.
4)TG	Weight change

Activity 1.4:

Phenomenon	Exothermic	Endothermic
Adsorption	✔	
Desorption		✔
Fusion (melting)		✔
Vaporization		✔
Decomposition	✔	✔
Dehydration		✔

Activity 1.5:

Phenomenon	Weight gain	Weight loss	Endothermic	Exothermic
Melting			✔	
Adsorption of gas	✔			✔
Desorption of gas		✔	✔	
Vaporisation		✔	✔	
Dehydration		✔	✔	
Decomposition		✔	✔	✔
Sublimation		✔	✔	

Activity 2.1:

Phenomenon	Physical	Chemical
Adsorption	✔	
Dehydration		✔
Desorption	✔	
Fusion (melting)	✔	
Chemisorption		✔
Vaporization	✔	
Decomposition		✔
Redox reactions		✔
Reduction in gaseous atmosphere		✔

Activity 2.2:

a. The part of the TG curve where the mass is essentially constant – Plateau AB

b. The temperature at which cumulative mass change reaches a magnitude that the thermobalance can detect -Point B

c. The temperature at which the cumulative mass change reaches a maximum-Point C

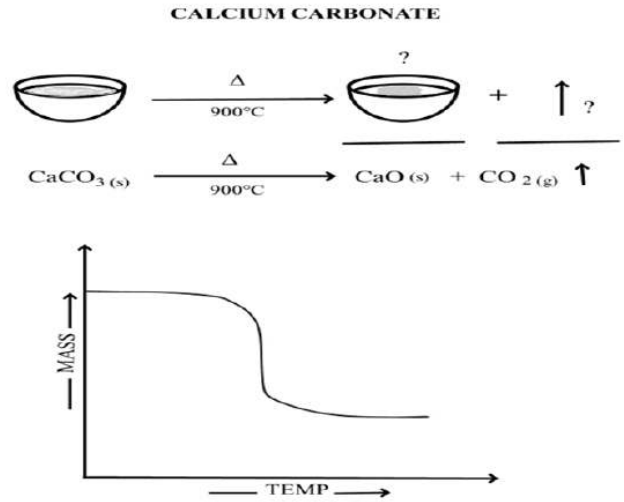
Activity 2.3:

Phenomenon	Type
Sublimation	Y
Adsorption of gas	X
Desorption of gas	Y
Vaporisation	Y
Dehydration	Y
Decomposition	Y
Melting	None

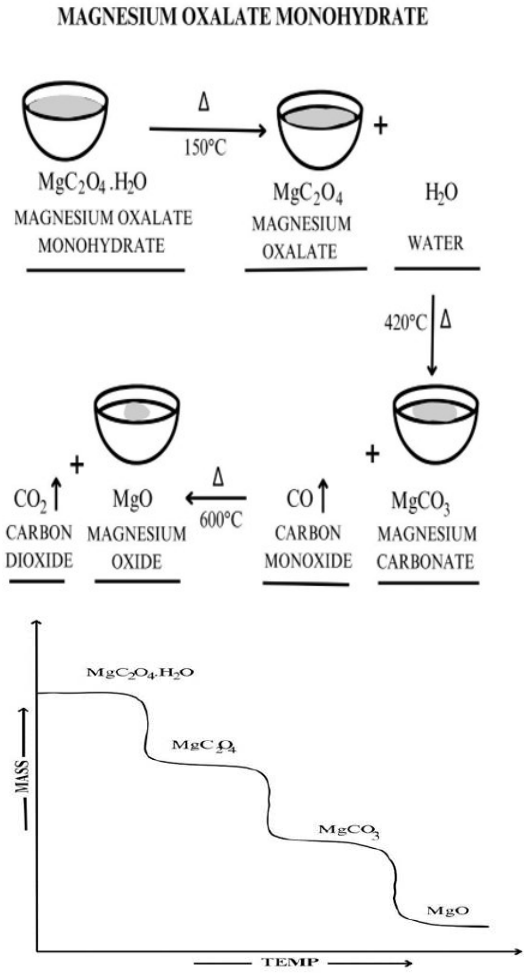
Activity 2.4:

1. A derivative thermogravimetric (DTG) curve represents a plot of mass of sample, as a function of temperature. **F**
2. A point of inflection on a thermogravimetric (TG) curve will correspond to a minimum on the DTG curve for a given chemical decomposition. **T**
3. A ‘plateau’ on a TG curve will not necessarily correspond to a zero ordinate value of the DTG curve. **F**
4. Thermal decomposition which overlap are often indicated more clearly by DTG curves than by the corresponding TG curves. **T**

Activity 2.5:

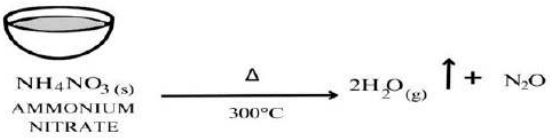


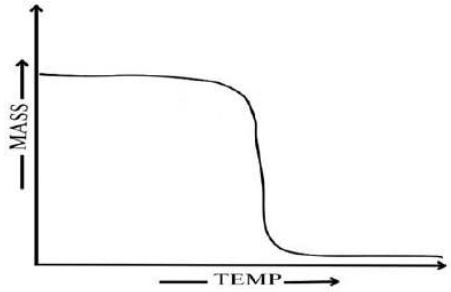
Activity 2.6:



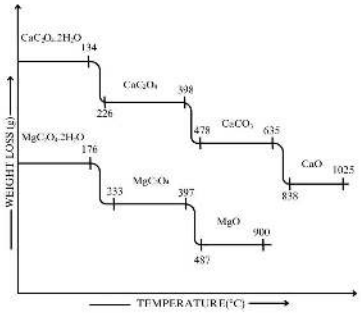
Activity 2.7:

AMMONIUM NITRATE





Activity 2.8: Will you be able to construct separate decomposition curves for calcium oxalate dihydrate and magnesium oxalate dihydrate based on the above application.



Activity: 2.10

1. Ans: a

$Ca(OH)_{2(s)} \rightarrow CaO_{(S)} + H_2O_{(g)}$

74.1g 56.1g 18g

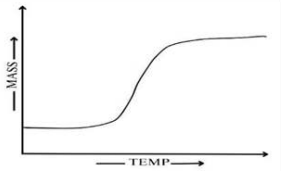
% weight loss = $\frac{74.1 - 56.1}{74.1}$ x 100 = **24.3%**

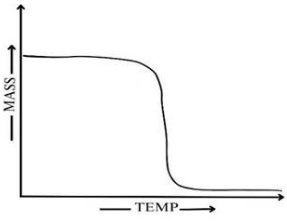
Ans: b

$6PbO_{(s)} + O_{2(g)} \rightarrow 2Pb_3O_{4(S)}$

1339.2 g 1371.2 g

% weight gain = $\frac{1371.2 - 1339.2}{1339.2}$ x 100 = **2.4%**





TG for ‘b’ TG for ‘a’

2. Ans:

The decrease in weight corresponds to the amount of carbon dioxide lost due to the decomposition of calcium carbonate present in the mixture as per the following reaction:

$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}\uparrow$

Weight loss = 250.6-190.8 = 59.8 mg

1mol of $CaCO_3 \equiv$ 1 mol of CO_2

100.1mg of $CaCO_3 \equiv$ 44mg of CO_2

? ≡ 59.8 mg of CO_2

$= \frac{100.1 \times 59.8}{44}$ = 136.05 mg of $CaCO_3$

Weight of the sample = 250.6 mg = mixture of $CaCO_3$ &CaO

250.6 mg of mixture = 136.05 mg of $CaCO_3$

100 mg of mixture = $\frac{136.05 \times 100}{250.6}$

= **54.29%** of $CaCO_3$

3.Ans: $CaC_2O_4.H_2O_{(s)} \rightarrow CaC_2O_{4(s)} + H_2O\uparrow$

$CaC_2O_{4(s)} \rightarrow CaCO_{3(s)} + CO_{(g)}\uparrow$

$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}\uparrow$

ii. Calculate the % weight loss at each step.

% weight loss = $\frac{\text{initial weight} - \text{final weight}}{\text{initial weight}}$ x 100

% weight loss at step 1 = $\frac{17.61 - 15.44}{17.61} x\ 100$ = **12.32**

% weight loss at step 2 = $\frac{15.44 - 12.06}{15.44} x\ 100$ = **21.89**

% weight loss at step 3 = $\frac{12.06 - 6.76}{12.06} x\ 100$ = **43.95**

Activity 3.1:

The record shown is that of a **DTA** experiment since the **ordinate** plot ΔT which is a **differential** temperature. The **downward** direction of the peak indicates that a **endothermic** reaction has occurred. This in turn implies that the corresponding **enthalpy** change (ΔH) must have been **positive** ie the value of enthalpy **after** the thermal effect was **greater** than its value **before**. This means that the sample **took in** heat during the reaction. Furthermore, there is evidence of a change in the **heat capacity** as the temperature is increased beyond the thermal transition. This is shown by the **displacement** of the **baseline** just beyond the end.

Answers: Select from the following list

[upward/**downward**, free energy/**heat capacity**, **greater**/less, DTG/**DTA**, **base-line**/background, derivative/**differential**, **took in**/gave out, negative/**positive**, **enthalpy**/entropy, **before/after**/during, exothermic/**endothermic**/isothermal, abscissa/**ordinate**, distortion/**displacement**.]

Activity 3.2:

Yes, they do offer an explanation. The curve for polyester shows that it melts at 255°C. Molten polymer in contact with the skin is a real hazard. Cotton, on the other hand, does not melt. It decomposes at 345°C.

Activity 4.1: Read each of the statements and mark them as **True or False**

(i) In DSC the sample and reference positions are provided with their own separate heating sources, so that the assembly may be operated on a ‘null balance’ basis. **T**

(ii) In DTA the equipment is so designed that the temperature of the sample is equal to that of the reference material at every point in the heating programme. **F**

(iii) Chemical decompositions which give rise to weight changes may be detected by DTA and DSC. **T**

(iv) The main components of a conventional differential thermal analyser consist of following: **F (programmer missing)**

a) The sample/reference holder

b) The thermocouple

c) The furnace

d) The amplifier

e) The recorder

Activity 4.2:

If $\Delta H < 0$, the system has undergone an endothermic/ **exothermic** change which means

$T_s > T_R$ [Choose the correct option: =, <, >]

Conversely $\Delta H > 0$ means **endothermic** change and $T_s < T_R$ [Choose the correct option: =, <, >]

In order to keep $\Delta T = 0$ [$\Delta T = T_s - T_R$]

- In case of an endothermic reaction we must provide heat to **sample**/reference.
- In case of an exothermic reaction we must provide heat to sample/**reference**

Activity 4.3: Observe the DSC curve given in 'figure **4.3a**.' and answer the following questions.

➢ How many transitions are seen in the above diagram?

Ans: Two

➢ Do you see any endotherm or exotherm? If yes, how many?

Ans: One endotherm and one exotherm.

➢ What does the endo or exothermic nature of the transition tell you about transition or ΔH value?

Ans: Endotherm: + ve ΔH (heat is absorbed) Exotherm: -ve ΔH (heat is given out)

➢ Do you see a shift in the baseline post glass transition temperature?

Ans: Yes, due to change in heat capacity

➢ Is the DSC curve of PET useful in predicting stability of the polymer? Justify your answer.

Ans: Yes, the melting point of any polymer is an important characteristic. It is the minimum temperature for processing the polymer and maximum temperature for using it. In addition, the glass transition temperature is useful since beyond this there is change in some of the physical properties of the polymer.

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Index

T

Glossary

Derivative Thermogravimetry | DTG is a method of expressing the results of TG by giving the first derivative curve as a function of temperature or time.

Differential Scanning Calorimetry | DSC is very similar to DTA and gives much the same sort of information but DSC is more often used for quantitative measurement of energy changes.

Differential Thermal Analysis | DTA 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 under controlled heating.

Electrothermal analysis | Study of electrical conductivity as a function of temperature.

Evolved Gas Analysis | EGA is a technique whereby the volatile products, released by a sample on decomposition, may be analysed as the sample is heated according to controlled thermal programme. (Dodd & Tonge, 2008)

Evolved Gas Detection | EGD is a technique in which the evolution of gas from a sample is detected, as a function of temperature, whilst the sample is subjected to controlled thermal programme.

Thermoacoustimetry | Characteristics of imposed sound waves produced as the material being heated.

Thermogravimetry | TG or TGA is a technique in which the weight of a sample is measured as a function of temperature, whilst it is subjected to a controlled heating programme.

Thermomagnetometry | Study of variation in a magnetic property of a material with temperature.

Thermomechanical Analysis | Dimensional changes as a function of temperature.

Thermoptometry | Study of an optical characteristic of a sample as it undergoes a thermal programme.

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