

**M.Sc.- II Semester-I**

# **Introduction to thermal methods**

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## **Introduction to thermal methods**

- The effects of heat on materials have fascinated and benefited humanity since the very earliest times.
- The use of fire to cook foods, and of ice to preserve foods, probably contributed greatly to the settlement and welfare of early peoples and cooking was perhaps the very first 'chemical experiment'.
- The production of both organic and inorganic pigments by heating natural materials allowed the decorative arts to develop.
- The skills which people first acquired in the controlled use of heat allowed the manufacture of ceramics, mortars, glass and metals.

- Primitive apparatus dating from around 2500 BC is known and the problems that arose with burning materials and the damage caused by fire are frequently seen in early years.
- However, with the spread of information through travel, the methods were transmitted to people in other countries, who added their expert knowledge to improve the methods still further.
- Jabir Hayyan wrote a *Book of Furnaces* and a *Book of Balances* around AD 800
- In studying the history of materials, we also come to realize the effects that made changes in their properties.

- As the study of chemistry became more disciplined, the range of substances studied increased and it became necessary for scientists to be able to distinguish between different substances and materials.
- By studying their properties and reactions, it became possible to identify not only the constituents of a substance, but often the particular source from which it came. This is the beginning of the discipline known as *analytical chemistry*.
- The modern student of chemistry or materials science may well start his or her experimental study of the subject by observing the nature of a range of materials, their appearance, mechanical properties and density and may then choose to heat the materials as a first attempt at classification.
- A small sample, heated in a test tube, may undergo both physical and chemical changes and may alter in a large number of ways, or it may be completely stable. Table 1.1 gives some examples of behaviour that may be observed when solid substances are heated in air.

**Table 1.1** The effects of heat on solid materials

Effect	Possible conclusion	Example
<i>Colour change</i>		
Charring, burning with little residue	Organics, polymer	Paper, burning
Blackening with large residue	Metal oxide formed	$\text{CuCO}_3 = \text{CuO} + \text{CO}_2$
Metal changes to powder	Oxidation	$2\text{Mg} + \text{O}_2 = \text{MgO}$
Colour change	Transition metal salt or phase transition	$\text{HgI}_2$ , red $\rightarrow$ yellow
<i>Substance melts</i>		
Melts at low temperature	Covalent?	Organics
Melts at high temperature	Ionic salts	NaCl
<i>Substance sublimates</i>		
White sublimate	Volatile solid Ammonium salts	$\text{NH}_4\text{Cl}$
Violet sublimate	Iodine	$\text{I}_2$
<i>Vapours evolved (and characterised by additional tests)</i>		
Water vapour (droplets)	Hydrates	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Oxygen	Nitrates, chlorates	$2\text{KNO}_3 = 2\text{KNO}_2 + \text{O}_2$
Oxides of nitrogen (brown fumes)	Nitrates	$2\text{AgNO}_3 = 2\text{Ag} + 2\text{NO}_2 + \text{O}_2$
Carbon dioxide	Carbonates	$\text{ZnCO}_3 = \text{ZnO} + \text{CO}_2$
<i>Physical changes</i>		
Becomes more pliable	Plastics above $T_g$	
Expansion: (a) gradual (b) abrupt	General expansion Phase change	
Swelling	Some intumescent materials	Polyphosphates
Shrinkage	Some strained polymers	Fibres
<i>No effect</i>	Stable oxides or temperature too low	$\text{MgO}$ , $\text{Al}_2\text{O}_3$

- It must be noted that a single observation is often not complete in itself, but requires additional chemical or physical measurements.

- For example, we cannot know what gas is evolved without a simple chemical test or physical measurement, such as a spectrum.

- The need to use complementary analytical techniques must be recognized throughout any investigation. The addition of some simple apparatus to determine accurately the temperature of the event, and to control the heating, or to measure colour, change in weight, or the extent of expansion or the nature of the volatiles evolved, gives a great deal more information to the analyst.

## Historical development

- The definition of thermometric scales and the start of practical calorimetry in the eighteenth century, particularly by Lavoisier and Laplace really brought about practical approach to studying the effects of heat.
- It led directly to the work of Fourier on heat conduction and to the experiments of Joule on electrical heating and calorimetry.
- The chief drawbacks of their equipment were that it often required large samples and a long time to complete the experiment.

- The development of scientific instruments during the earlier part of the twentieth century allowed the principles of thermal measurements to be established - for example, the measurement of the coefficients of expansion of silica using an optical method led to the development of modern interferometric dilatometers.

- In the second half of the twentieth century, vast improvements in instrumentation, sensors, data acquisition, storage and processing have been made, especially with the advent of microprocessors.



- The precision, sensitivity and reproducibility of modern instruments are high, and their range of temperature of operation has extended and quality of temperature control.
- Thermal methods of analysis are now used in a very large range of scientific investigations.
- Besides the more 'chemical' areas, such as polymers, fine organic chemicals and pharmaceuticals, they have applications to electronics, in construction, geology and engineering, in materials science and in quality control.
- Very often, a complex material, such as a polymer composite, will show definite and characteristic effects on heating which relate to its nature, composition and history.

## Definitions

- Definitions necessary to agree on a common terminology, and the International Confederation for Thermal Analysis and Calorimetry (ICTAC)
- Thermal analysis-** Thermal analysis (TA) is defined as: A group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.
- The programme may involve heating or cooling at a fixed rate of temperature change, or holding the temperature constant, or any sequence of these.

- The word sample is interpreted to mean the substance placed into the apparatus at the beginning of the experiment, and its reaction products.
- The graphical results obtained are called the 'thermal analysis curve', or by the specific name of the method.
- The property used for study may be chosen from an extensive list, shown in part in Table 1.2.

**Table 1.2 Thermal methods**

Technique	Abbreviation	Property	Uses
1. Thermogravimetry (Thermogravimetric analysis)	TG TGA	Mass	Decompositions Dehydrations Oxidation
2. Differential thermal analysis	DTA	Temperature difference	Phase changes Reactions
3. Differential scanning calorimetry	DSC	Power difference	Heat capacity Phase changes Reactions Calorimetry
4. Thermomechanical analysis	TMA	Deformations	Mechanical changes Expansions
5. Dynamic mechanical analysis	DMA	Moduli	Phase changes Polymer cure
6. Dielectric thermal analysis	DETA	Permittivity	Phase changes Polymer changes
7. Evolved gas analysis	EGA	Gases	Decompositions Catalyst and surface reactions
8. Thermooptometry		Optical	Phase changes Surface reactions Colour changes

*Less frequently used techniques*

9. Thermosonimetry	TS	Sound	Mechanical and chemical changes
10. Thermomagnetometry	TM	Magnetic	Magnetic changes Curie points
11. Thermoluminescence	TL	Light emitted	Trap depths
12. Emanation thermal analysis	ETA	Gas released	Structural changes

*Also used*

13. Simultaneous thermal analysis	STA	Two or more techniques used on the same sample at the same time.	
14. Controlled-rate thermal analysis	CRTA	The rate of change of the property is held constant	

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- In Table 1.2 careful distinction should be made between the terms derivative and differential.
- Differential techniques involve the measurement of a difference in the property between the sample and a reference - for example, in differential thermal analysis (DTA) where the difference in temperature between the sample and a reference is measured.
- Derivative techniques imply the measurement or calculation of the mathematical first derivative, usually with respect to time. For example derivative thermogravimetry (DTG) is the measurement of the rate of mass loss ( $dm/dt$ ) plotted against temperature T.

- In discussing the theories and results of thermoanalytical studies, we shall always use the 'SI' system of units and symbols and, where necessary, conversion from older units will be made with the occasional exception of temperature which may be quoted in the (more familiar) degree Celsius ( $^{\circ}\text{C}$ ).

- The principal symbols and units to be used are given in Table 1.3. The usual prefixes are used, e.g.  $10^{-3} \text{ m} = 1 \text{ mm}$ ,  $10^6 \text{ Pa} = 1 \text{ MPa}$ ,  $10^3 \text{ g} = 1 \text{ kg}$ , etc.

**Table 1.3** SI units and symbols for thermal methods [14, 18]

Quantity	Symbol	Unit(s) and abbreviation(s)
<i>Basic units</i>		
length	<i>l</i>	metre m
mass	<i>m</i>	kilogram kg
time	<i>t</i>	second s
electric current	<i>I</i>	ampere A
temperature	<i>T</i>	kelvin K
amount of substance	<i>n</i>	mole mol
<i>Derived units</i>		
energy	<i>E</i>	joule J = kg m <sup>2</sup> /s <sup>2</sup>
power	<i>P</i>	watt J/s
force	<i>F</i>	newton N(= kg m/s <sup>2</sup> )
pressure	<i>p</i>	pascal Pa (= N/m <sup>2</sup> )
concentration	<i>c</i>	molarity mol/dm <sup>3</sup>
frequency	<i>v</i>	hertz s <sup>-1</sup>



*Combined units*

heat	$q$	J
heat capacity	$C$	J/K
internal energy	$U$	J
enthalpy	$H$	J
free energy	$G$	J
entropy	$S$	J/K
thermal conductivity	$k$	J/(s m K)
density	$\rho$	kg/m <sup>3</sup>
rate of reaction	$v$	mol/(m <sup>3</sup> s)
order of reaction	$n$	
fractional extent of reaction	$\alpha$	
rate constant of $n$ th-order reaction	$k$	s <sup>-1</sup> (mol/m <sup>3</sup> ) <sup><math>n-1</math></sup>
activation energy	$E$	J/mol
molar gas constant	$R$	J/(K mol)
stress	$\sigma$	Pa
strain	$\epsilon$	–
bulk modulus	$K$	Pa
tensile modulus	$E$	Pa
shear modulus	$G$	Pa

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