CH 2252 Instrumental Methods of Analysis

Unit – III

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Thermogravimetry

M. Subramanian

Assistant Professor
Department of Chemical Engineering
Sri Sivasubramaniya Nadar College of Engineering
Kalavakkam – 603 110, Kanchipuram (Dist)
Tamil Nadu, India
msubbu.in@gmail.com

Thermal Analysis Methods

- The analytical techniques used to study changes in physical properties with temperature are called thermal analysis techniques

- They include thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermometric titration (TT), and direct injection enthalpimetry, dynamic mechanical analysis (DMA), and thermomechanical analysis (TMA).

- Thermal analysis techniques are used in the characterization of inorganic and organic compounds, polymers, pharmaceuticals, metals, alloys, glasses, ceramics, and many manufactured products.

Thermogravimetry

- Thermogravimetry or thermogravimetric analysis (TGA) measures the mass (weight) of a sample in a specified atmosphere as the temperature of the sample is programmed.

- The most common temperature program is a linear increase in temperature with time, although isothermal programs, stepped temperature programs, and so on can be used.

- The output from a TGA experiment is a plot of mass (or mass%) vs. temperature. The TGA plot is called a thermal curve.

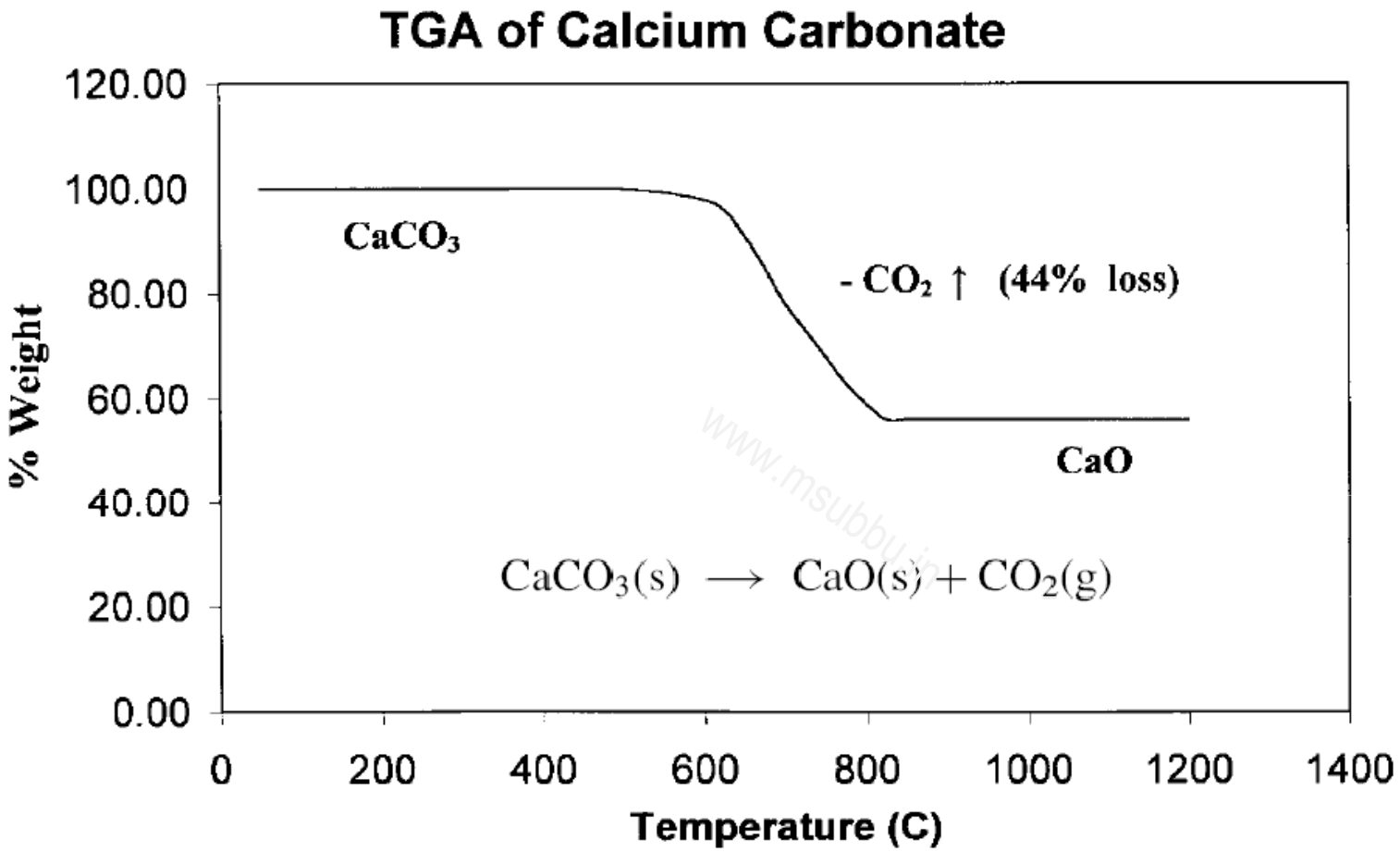


Figure 16.1 TGA thermal curve for pure anhydrous calcium carbonate, $CaCO_3$. The loss in mass is due to the loss of CO_2 (g) and the compound remaining is CaO.

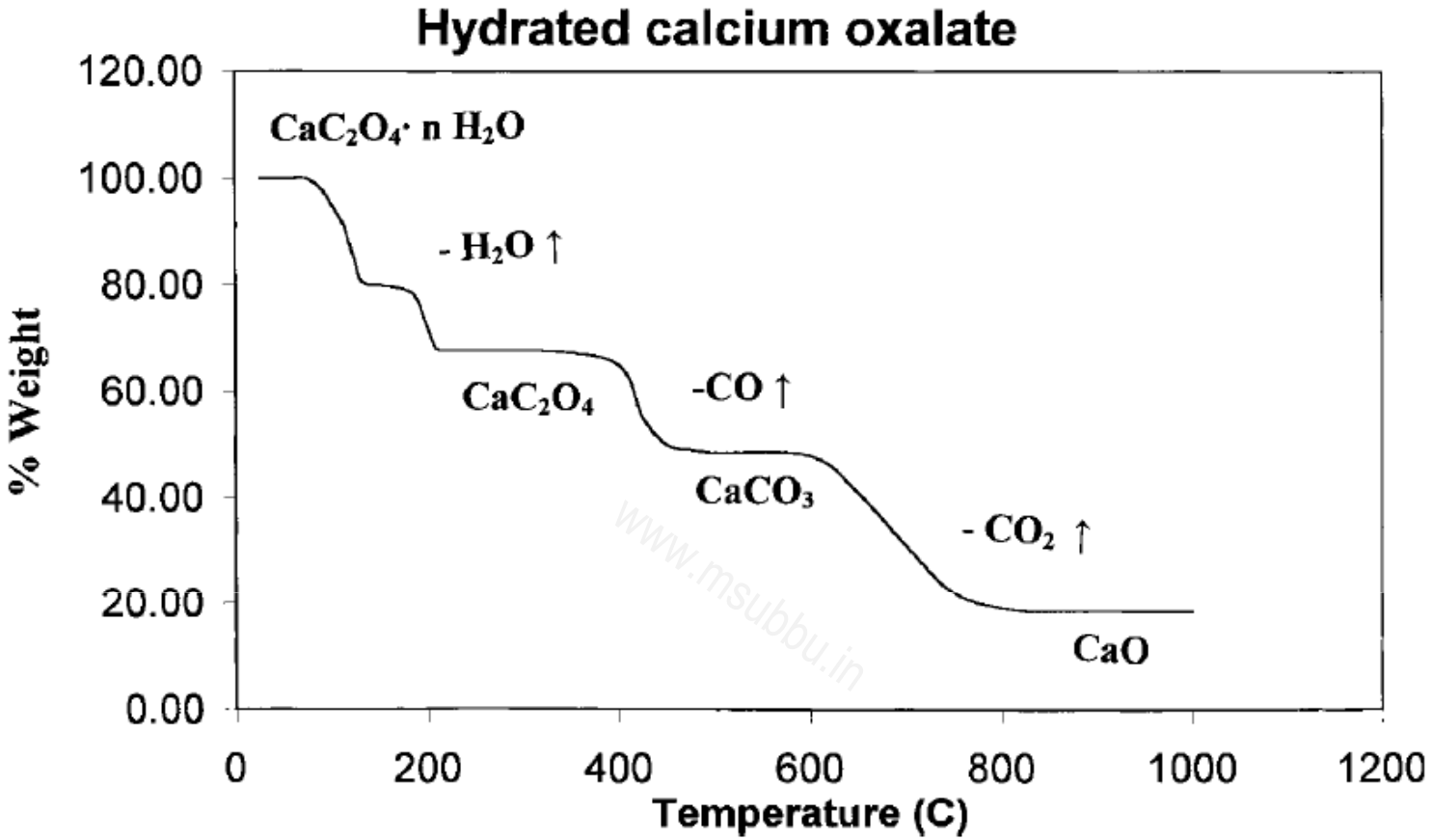


Figure 16.2 TGA thermal curve of hydrated calcium oxalate, $Ca(COO)_2 \cdot xH_2O$, with both adsorbed water from the precipitation process and water of crystallization. There is a loss of adsorbed water starting at about 90°C, and loss of bound water at about 150°C. The stable compound above 225°C is anhydrous calcium oxalate, $Ca(COO)_2$. This loses CO at about 450°C to form $CaCO_3$. The calcium carbonate is stable until approximately 600°C, when it loses CO_2 to form CaO. (Compare this step with Fig. 16.1.)

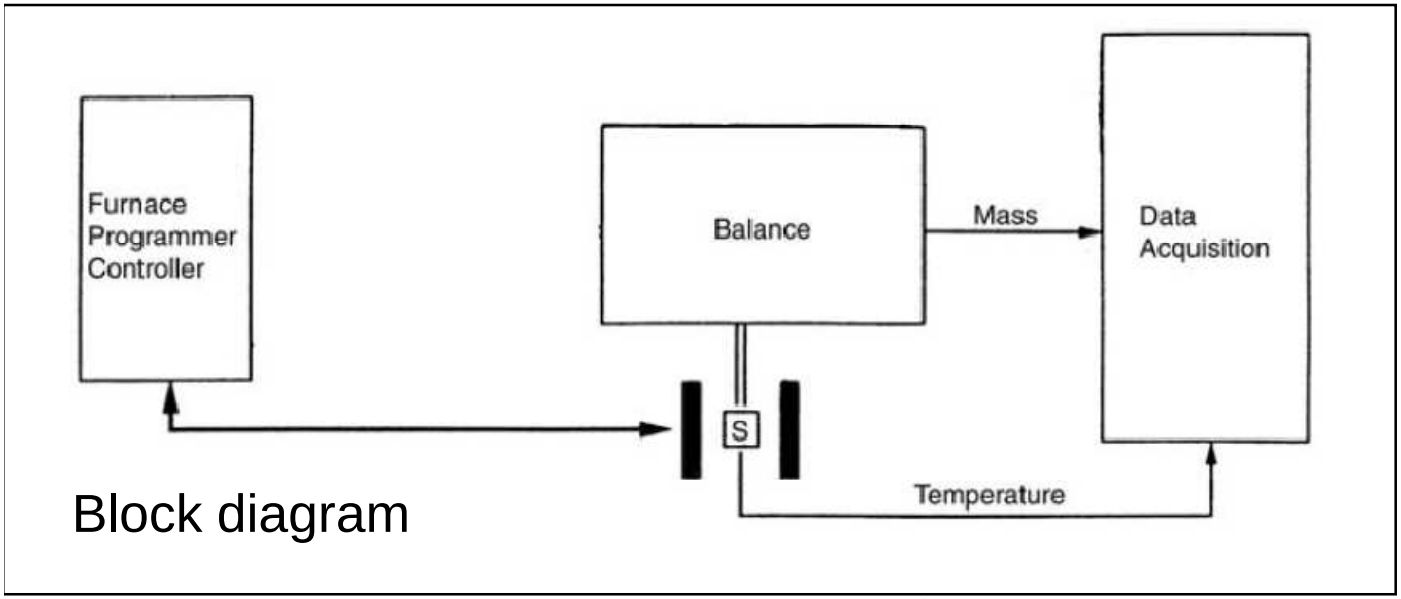
Interpretations from TGA curve

- The weight loss at a temperature is helpful to determine the composition of a compound and follow reactions in its decomposition

- It also enables to identify crystals of unknown composition

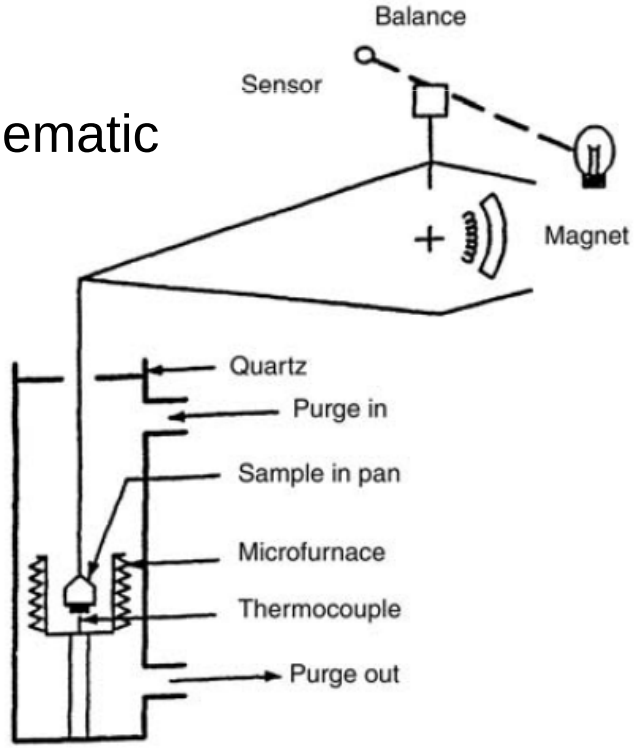
TGA Instrumentation

- Consists of:
  - sensitive balance (usually a microbalance) for continuously measuring sample weight
  - furnace surrounding a sample holder
  - purge gas system for providing inert or reactive atmospheres
  - computer to control the furnace temperature, data collection and data processing
  - auto-samplers

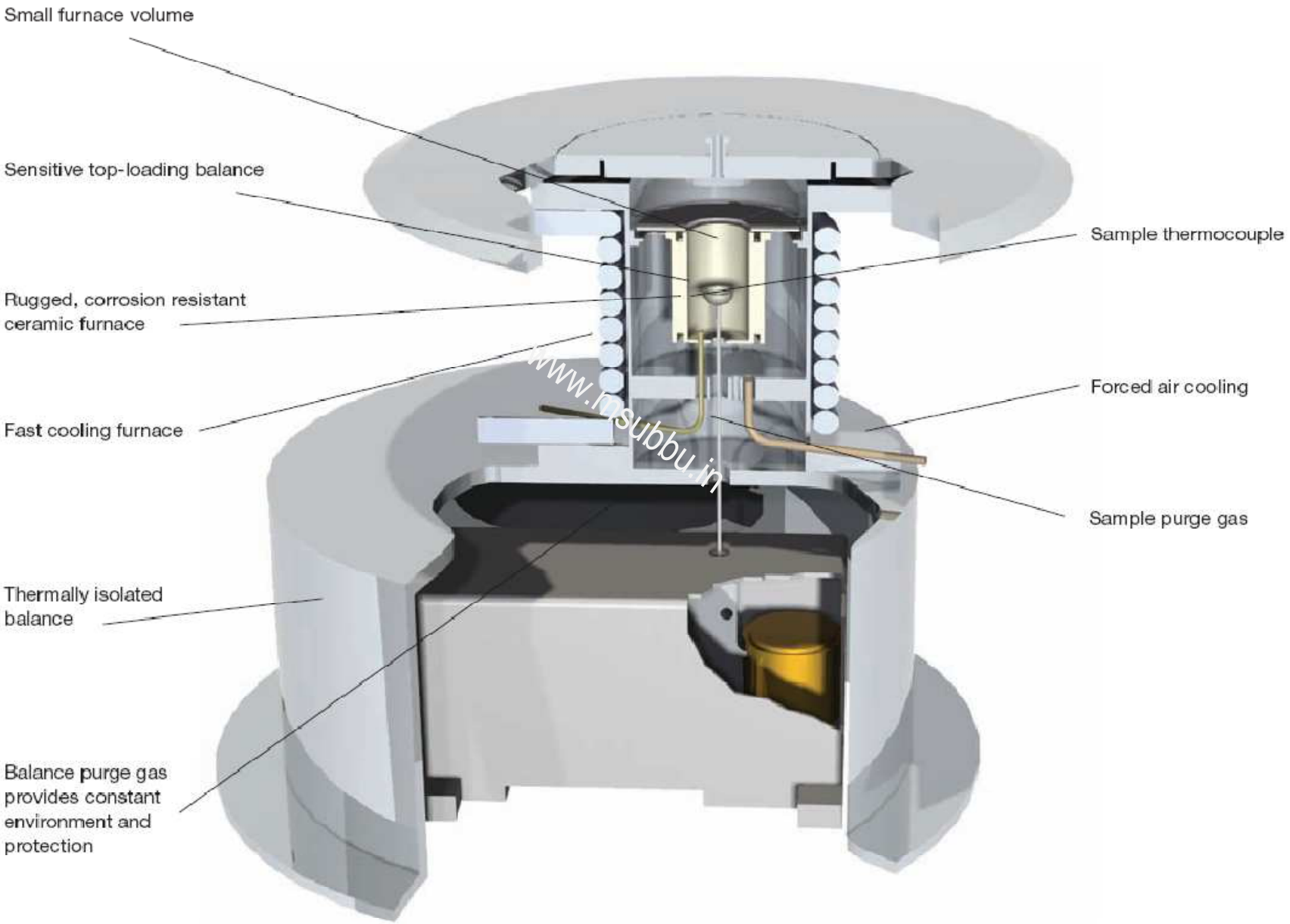


Block diagram

Schematic



Thermogravimetric Analyzer

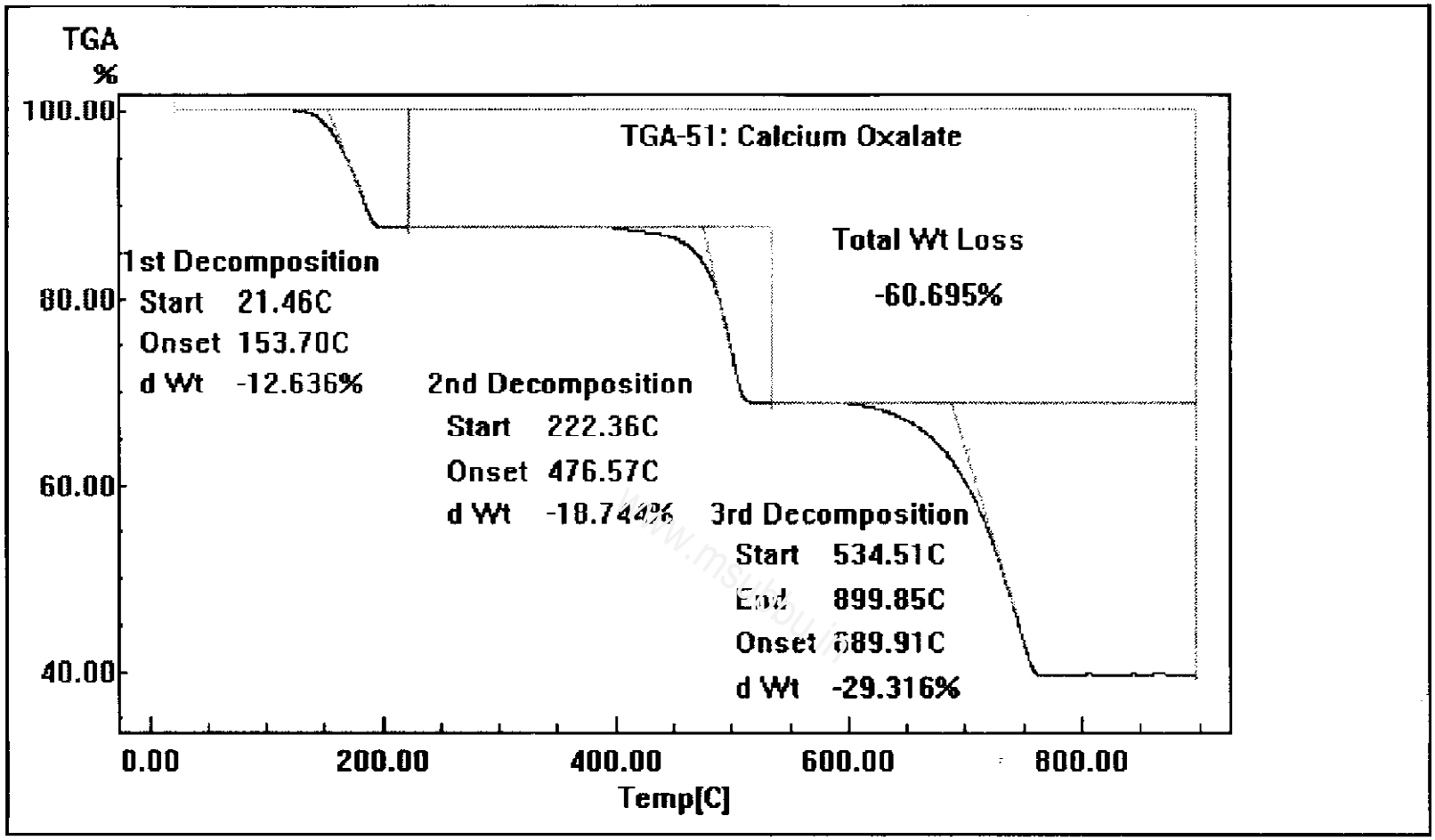


Instrumentation details

- Balance: 1 to 1000 mg, with typical sample size of 5 to 20 mg
- Furnace: heating rates up to 1000°C/min (typically 200°C/min); cooling at ~50°C/min through forced air circulation. Furnace upper temperatures: 1500°C, 1700°C, or 2400°C.
- Purge gas: argon or nitrogen for providing inert atmosphere; air for combustion or oxidation studies; hydrogen for reducing atmopshere
- Sample holder: quartz, platinum, and various ceramics
- Thermocouple is made as small as possible and placed close to the sample holder

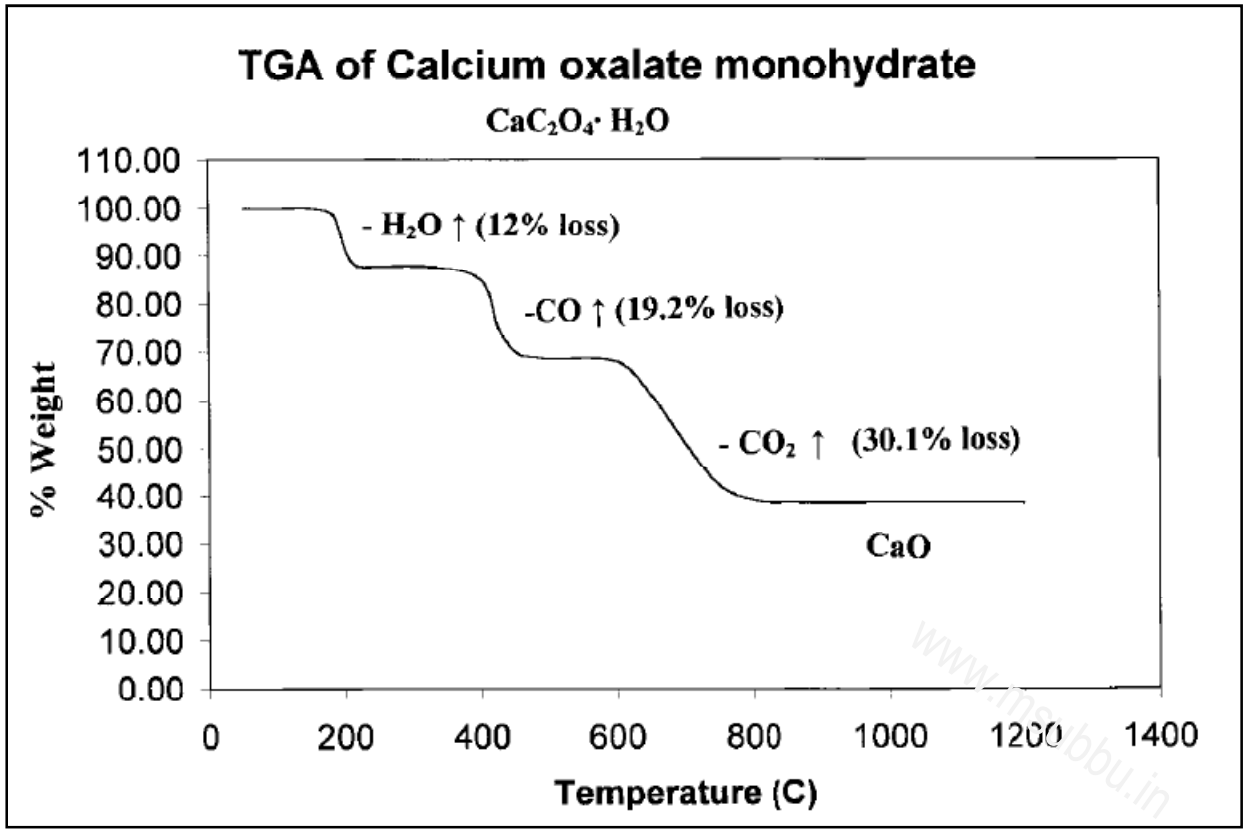
Analytical Applications of TGA

- Determination of correct drying temperatures for precipitates used in gravimetric analysis
- Identification of gases given off while a sample's temperature is increased
- By determining the residues by techniques such as XRD, and gases by IR spectroscopy, the identification of material is possible
- TGA is very important in determining the upper use temperatures of materials such as polymers by identifying the temperature at which oxidative degradations occur on heating in air



The TGA-51 plot of CaC_2O_4 shows the three stage decomposition of CaC_2O_4. Chemically these decomposition stages are:

1. $CaC_2O_4 \cdot H_2O \rightarrow C_2O_4 + H_2O$
2. $CaC_2O_4 \rightarrow CaCO_3 + CO$
3. $CaCO_3 \rightarrow CaO + CO_2$



$$CaCO_3(s) \longrightarrow \underset{44}{CaO(s) + CO_2(g)\uparrow}$$

The $\%W$ lost from the original compound

$$= (44/146) \times 100 = 30.1\%$$

$$\underset{\text{Molecular weights (g/mol)}}{Ca(COO)_2 \cdot H_2O(s)} \longrightarrow \underset{128}{Ca(COO)_2(s)} + \underset{18}{H_2O(g)\uparrow}$$
146

$$\%W \text{ lost} = (18/146) \times 100 = 12.3\%.$$

$$Ca(COO)_2(s) \longrightarrow \underset{28}{CaCO_3(s)} + CO(g)\uparrow$$

$\%W$ lost from the initial compound $= (28/146) \times 100 = 19.2\%$.

Identification of compounds in a mixture

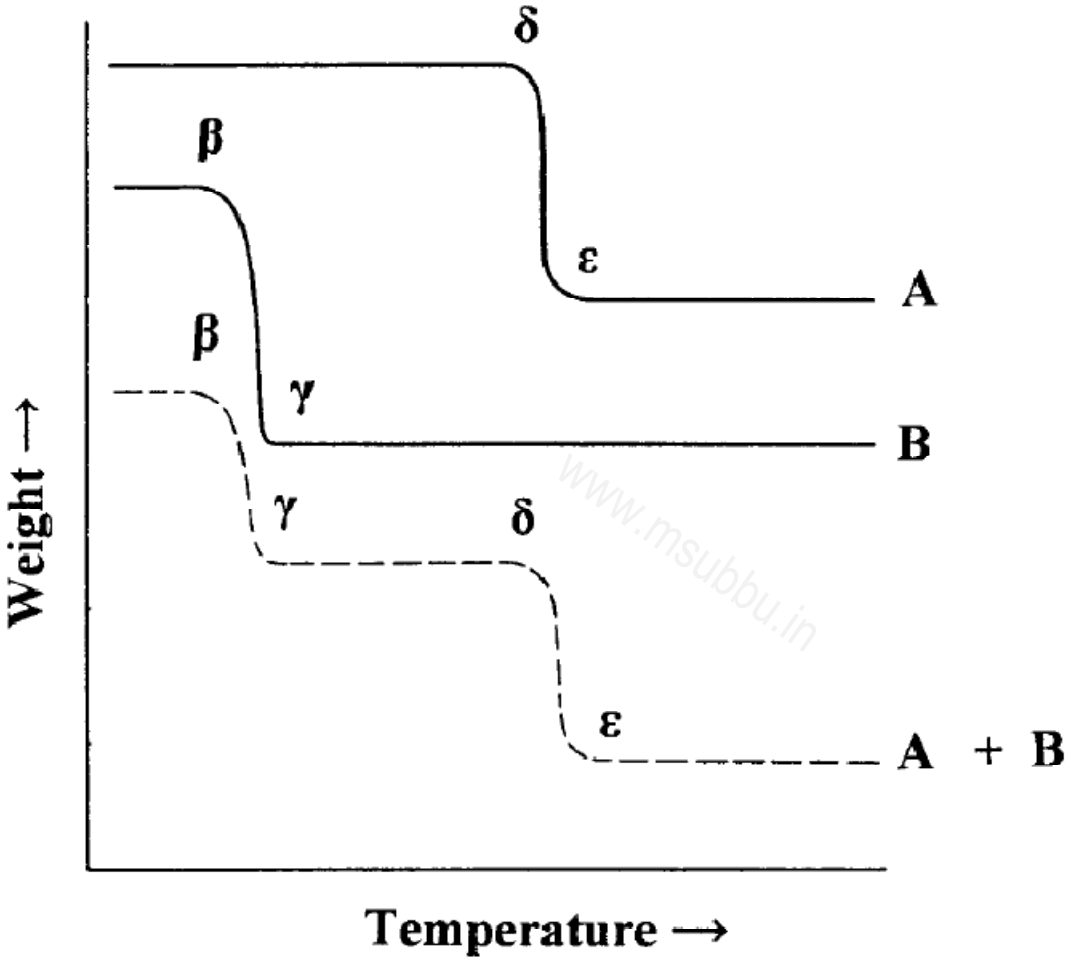


Figure 16.7 TGA thermal curves for (top) pure A, (middle) pure B, and (bottom dotted line) a mixture of A and B. Because A and B have unique temperatures at which mass is lost, the composition of the mixture may be determined.

Estimating Magnesium Oxide in a mixture of Magnesium Oxide [MgO] and Magnesium Oxalate [$Mg(COO)_2.2H_2O$]

$$Mg(COO)_2 \cdot 2H_2O \longrightarrow MgO(s) + CO + CO_2 + 2H_2O$$

Molecular weights (g/mol)	148	40	28	44	18

The final weight loss is therefore: $\%W = ([28 + 44 + 2(18)]/148) \times 100 = 73\%$

Temperature = 500^{o}C

The following data were obtained from our TGA curve:

Original weight of sample	25.00 mg
Weight of sample after heating to 500°C	10.40 mg
Loss in weight	14.60 mg

But we have already calculated that $Mg(COO)_2 \cdot 2H_2O$ loses 73% of its mass upon heating to 500°C; therefore the weight of $Mg(COO)_2 \cdot 2H_2O$ in the original sample was:

$$\text{mg } Mg(COO)_2 \cdot 2H_2O = (14.60 \text{ mg lost}) \frac{100 \text{ mg } Mg(COO)_2 \cdot 2H_2O}{73 \text{ mg lost}} = 20 \text{ mg}$$

Then the concentration of $Mg(COO)_2 \cdot 2H_2O$ in the original sample was:

$$\%Mg(COO)_2 \cdot 2H_2O = \frac{\text{mg } Mg(COO)_2 \cdot 2H_2O}{\text{total sample weight in mg}} \times 100$$

$$\%Mg(COO)_2 \cdot 2H_2O = \frac{20 \text{ mg}}{25.00 \text{ mg}} \times 100 = 80\%$$

Thus the other 20% of the starting mixture is MgO.

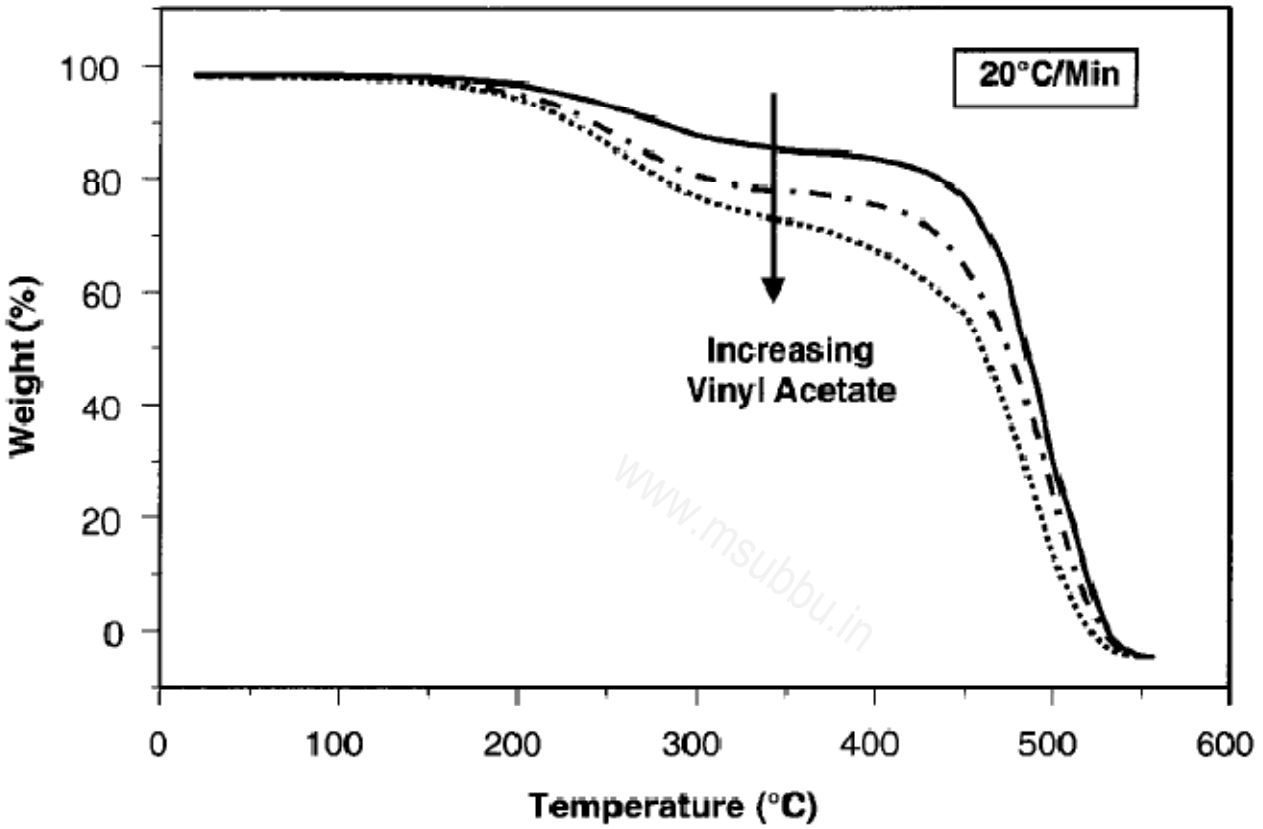


Figure 16.9 TGA thermal curves of vinyl acetate copolymers. The weight loss at 340°C is due to loss of acetic acid and gives a quantitative measure of the amount of vinyl acetate in the polymer. (Courtesy of TA Instruments, New Castle, DE, www.tainst.com.)

Robinson, Undergraduate Instrumental Analysis 6th Edition, Marcel Dekker, New York

Determination of Stability of Polymers

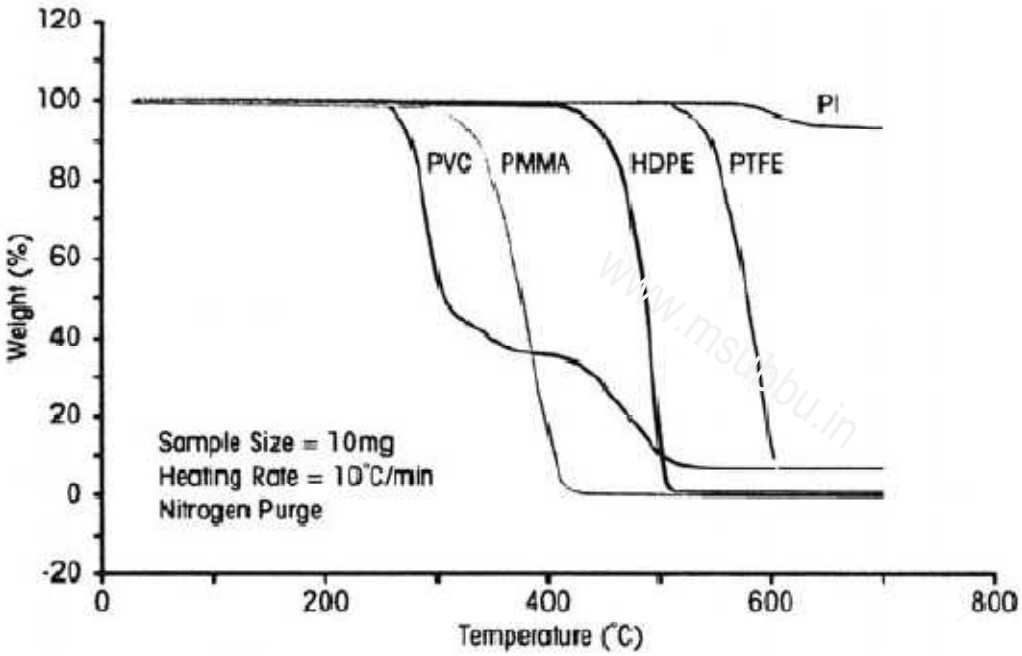


Figure 16.10 TGA thermal curves showing the decomposition temperatures of some common polymers: PVC, polyvinylchloride; PMMA, polymethylmethacrylate; HDPE, high-density polyethylene; PTFE, polytetrafluoroethylene; PI, polyimide. (Courtesy of TA Instruments, New Castle, DE, www.tainst.com.)

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Derivative Thermogravimetry

- Examination of a TGA curve will show that a sample's weight loss associated with a particular decomposition occurs over a considerable temperature range, not at a single temperature.
- When TGA is used to identify an unknown compound, this wide range is a handicap because the uncertainty of identification is increased.
- This problem can be partially overcome by derivative thermogravimetry (DTG). In DTG, the first derivative of the TGA curve is plotted with respect to temperature.
- In this method, temperature increase slows as weight loss increases. This is done so that the exact temperature at which a peak occurs can be more accurately identified.

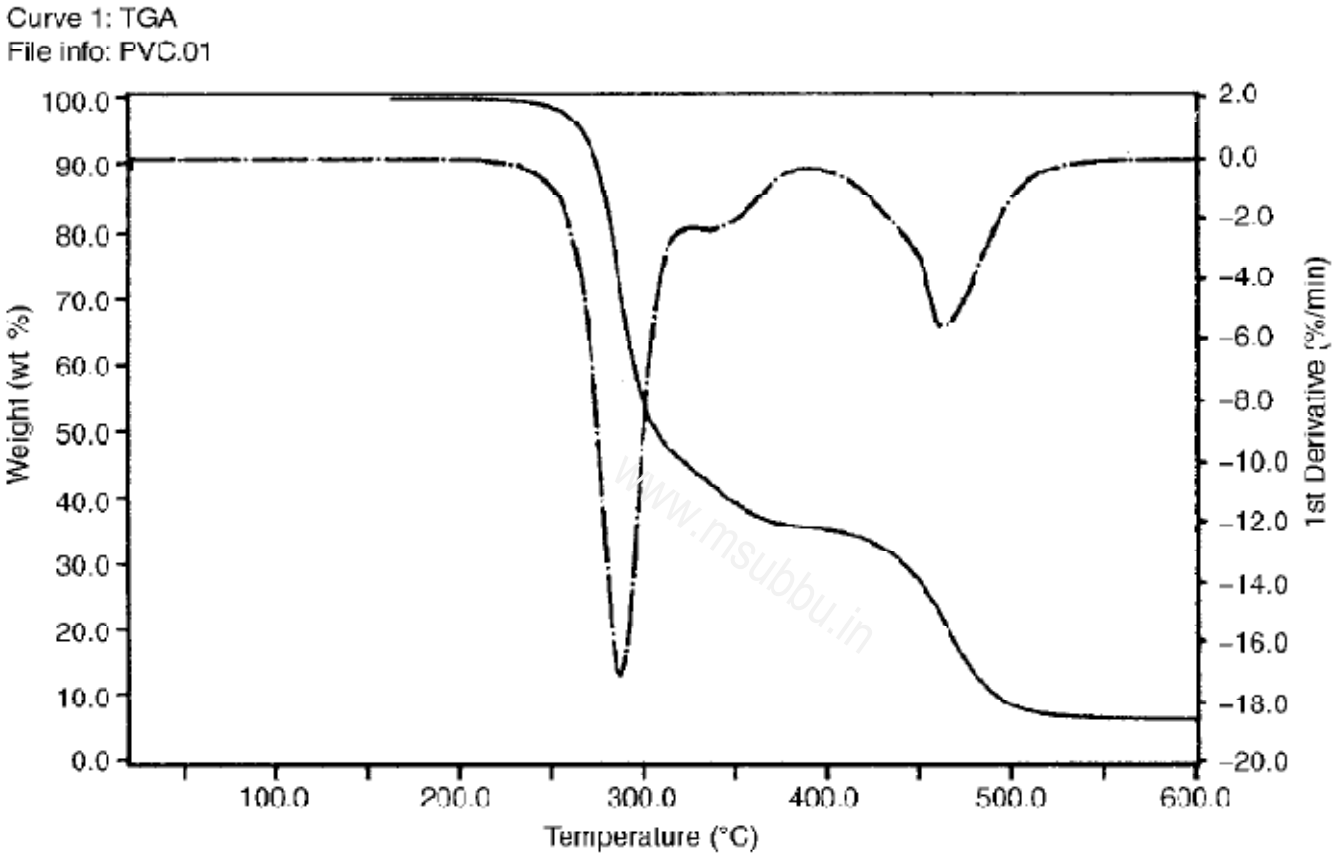

Figure 16.14 TGA (solid line) and DTG (dotted line) thermal curves of polyvinylchloride polymer heated under nitrogen. The first mass loss at 280°C is due to loss of HCl. (Courtesy of PerkinElmer, Inc. Shelton, CT, www.perkinelmer.com.)

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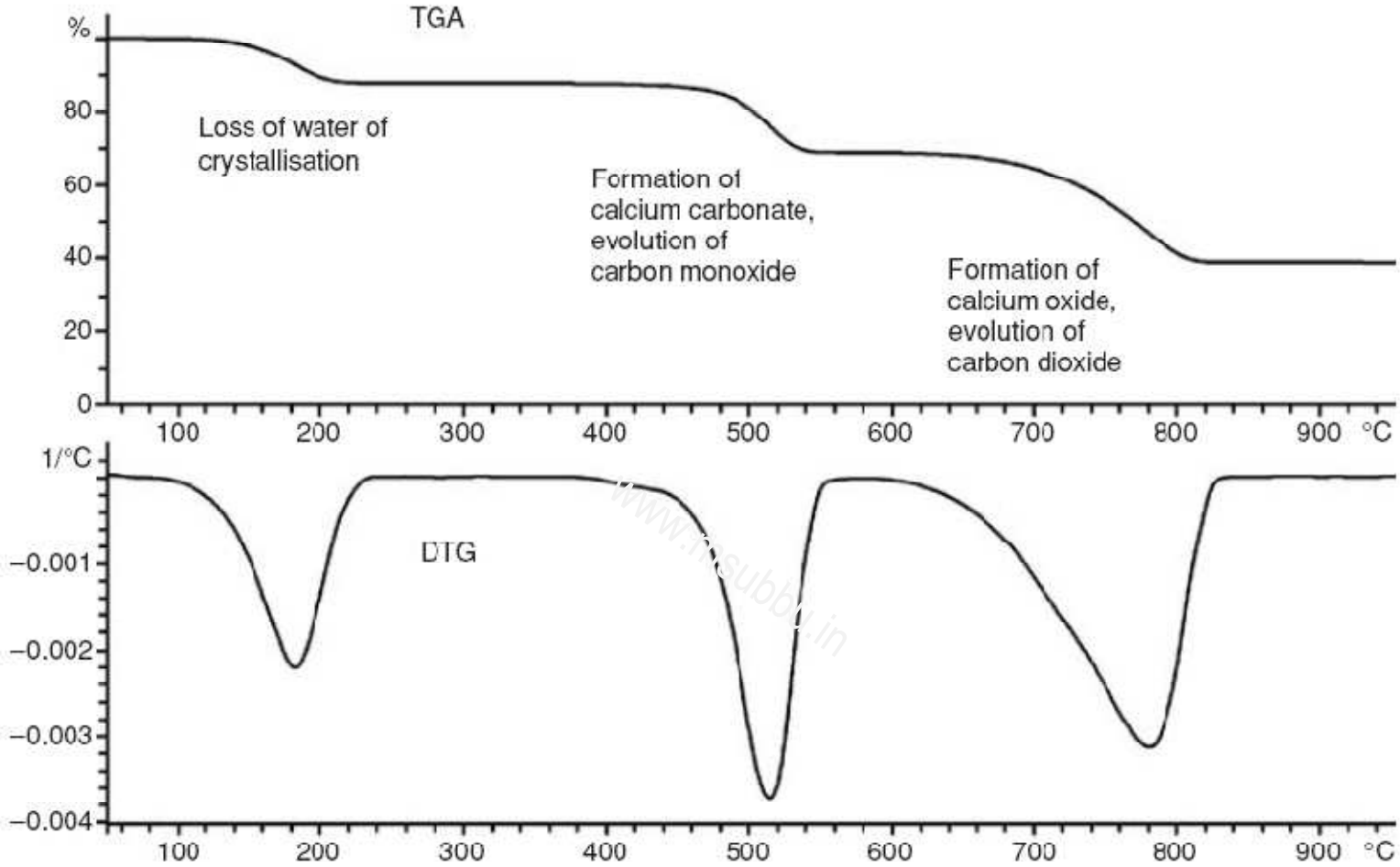
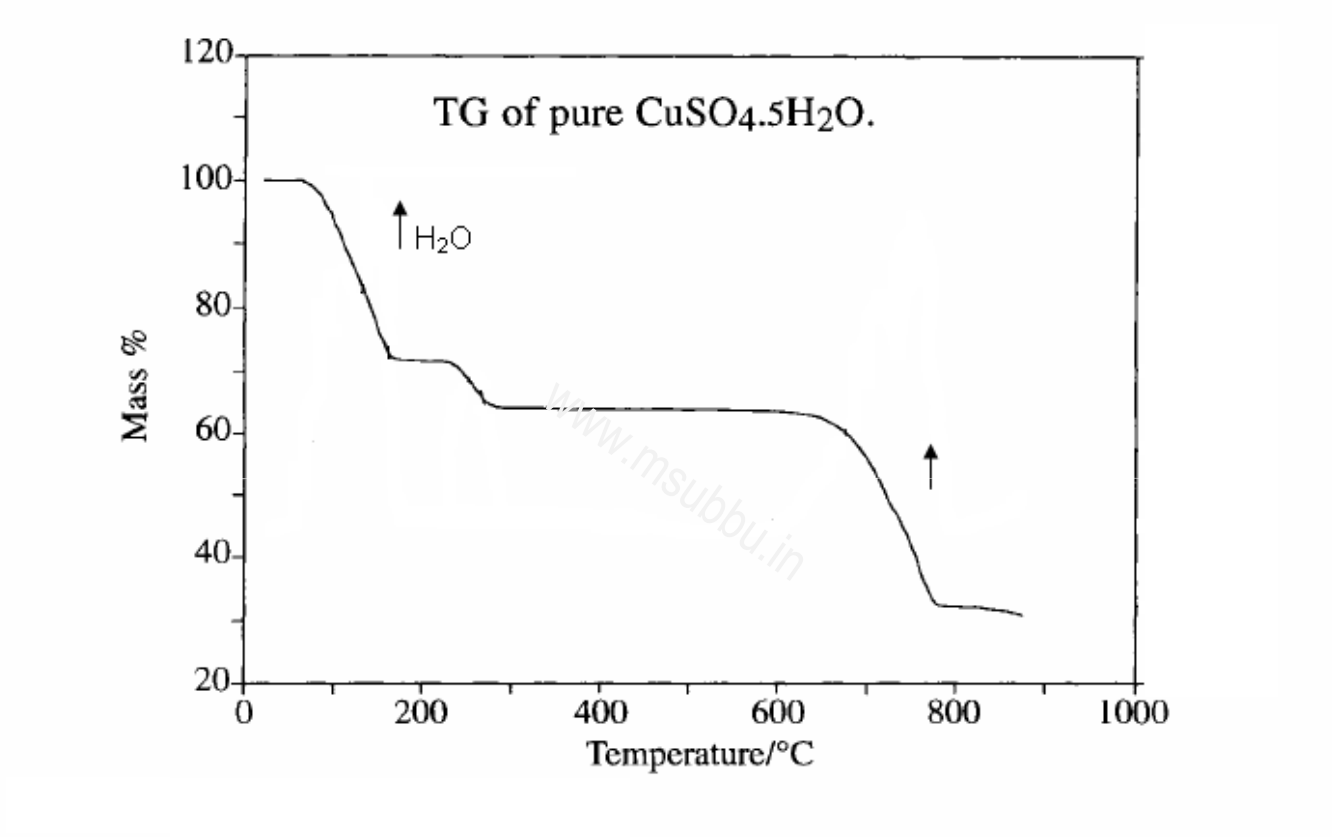


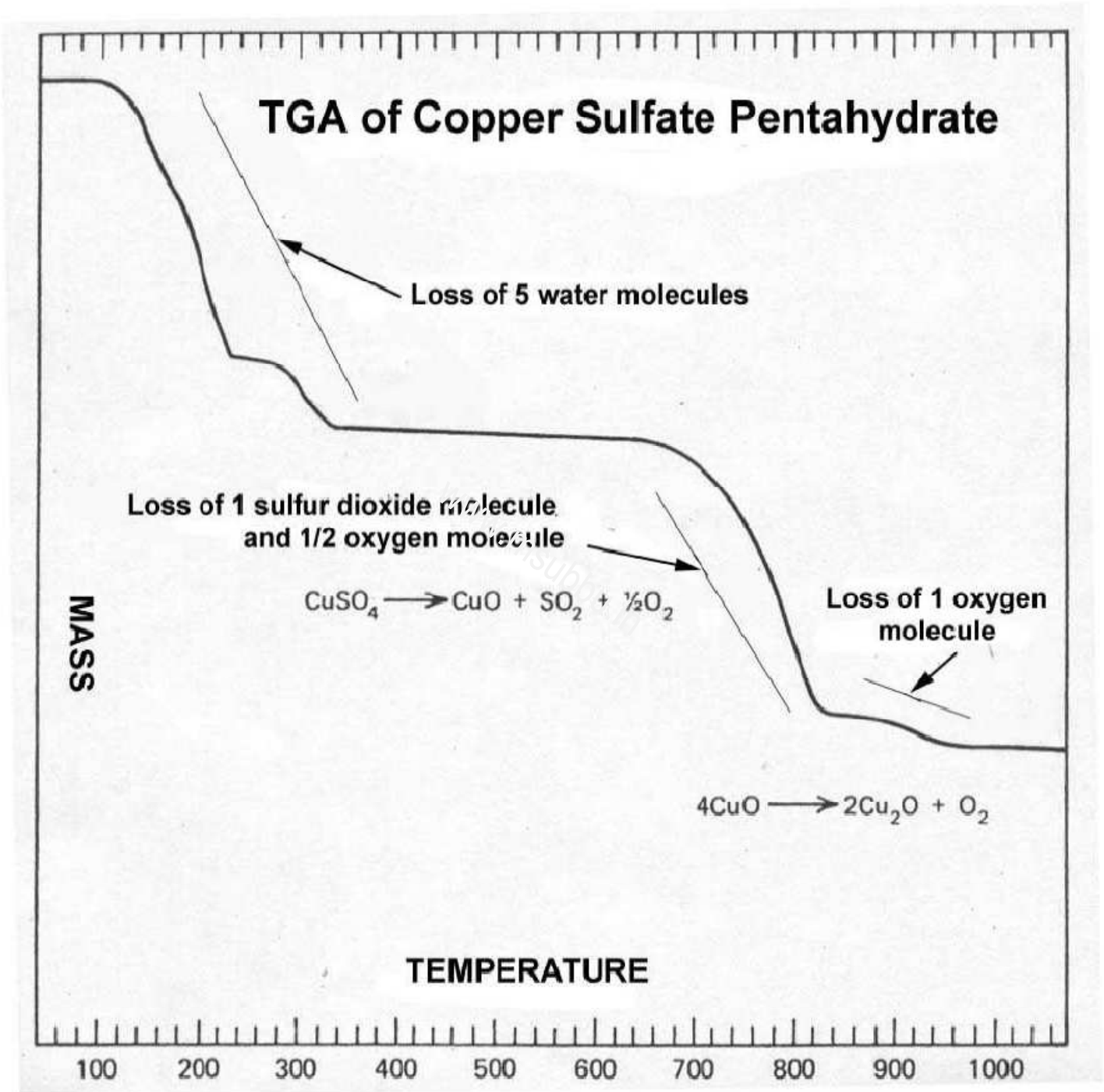
Figure 3.1 Stepwise decomposition of calcium oxalate monohydrate: sample mass 19 mg, heating rate 30 K/min, nitrogen. The TGA curve has been normalised (divided by the sample weight) and therefore begins at 100%. The temperature range of the three mass losses is particularly clear in the normalised first derivative or DTG curve.

TGA of $CuSO_4.5H_2O$



Formation of anhydrous copper sulfate takes between 75 and 300°C; and that of copper oxide takes between 400 and 575°C.

Ref: Brown, M.E., (ed), Handbook of Thermal Analysis and Calorimetry, Vol.1, Elsevier, pp.515, 1998.


TGA of Copper Sulfate Pentahydrate
Loss of 5 water molecules
Loss of 1 sulfur dioxide molecule
and 1/2 oxygen molecule
$CuSO_4 \rightarrow CuO + SO_2 + \frac{1}{2}O_2$
Loss of 1 oxygen molecule
$4CuO \rightarrow 2Cu_2O + O_2$
MASS
TEMPERATURE
100
200
300
400
500
600
700
800
900
1000

Desorption Studies

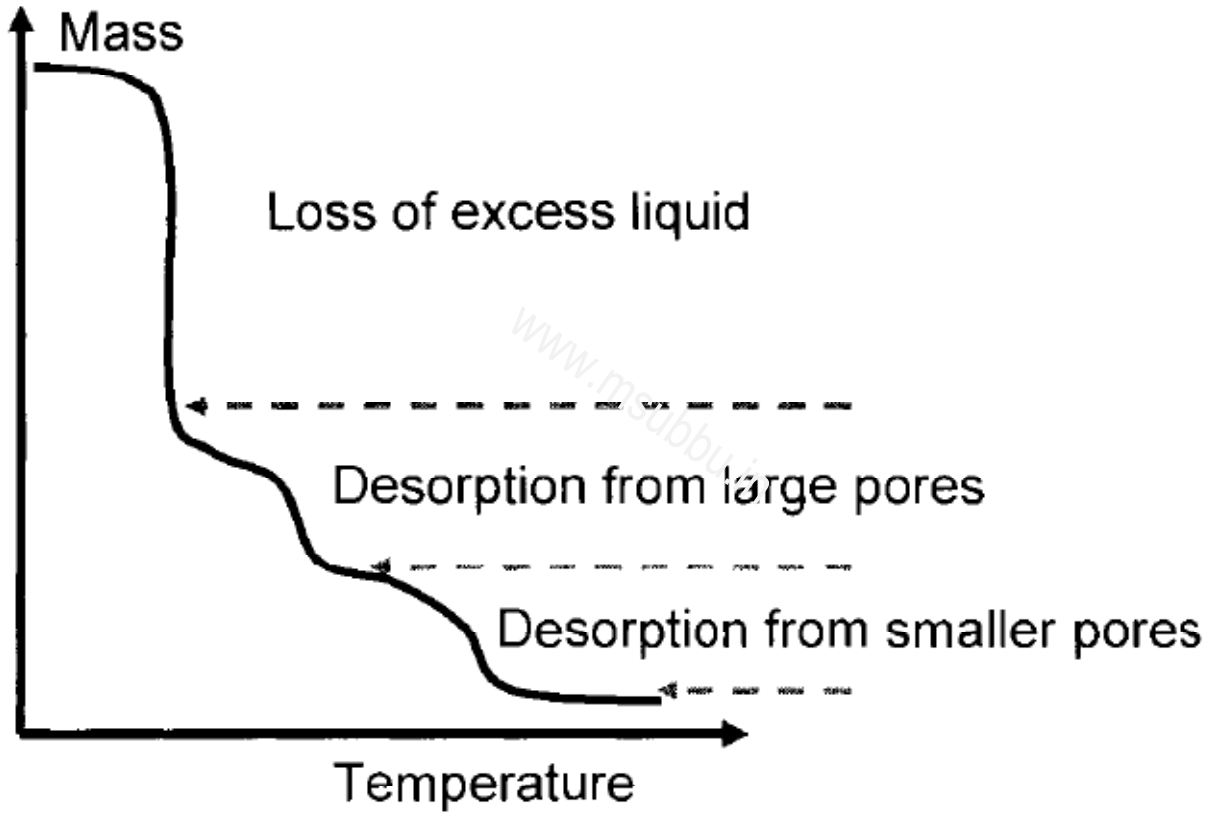


Figure 12. Schematic representation of a curve obtained from a quasi-isothermal gravimetric experiment with a solid with a bimodal pore size distribution.

Determination of Stoichiometry of Oxides

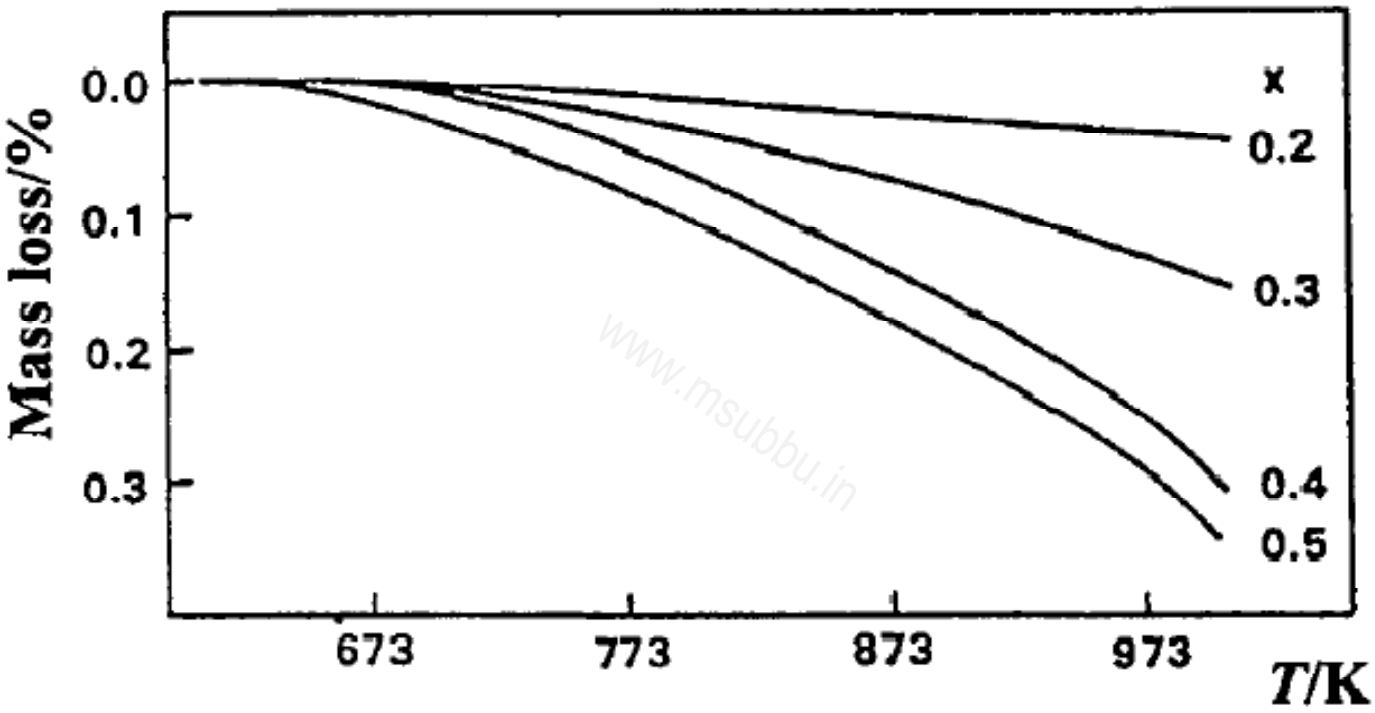


Figure 16. Percentage mass loss as a function of temperature for the $Ba_xLa_{1-x}CoO_3$

Buoyancy Correction

- Due to changes in density of a gas as the temperature changes, buoyancy corrections must be made in TGA experiments
- Without corrections every sample will appear to show a mass increase during a heating experiment
- TGA experiments are usually corrected for the effect of buoyancy by performing blank experiment

Table 3.1 Density of several gases at 25, 500 and 1000°C at a standard pressure of 101.3 kPa

Gas	Density (mg/mL) at 25°C	Density (mg/mL) at 500°C	Density (mg/mL) at 1000°C
Dry air	1.184	0.457	0.269
Nitrogen	1.146	0.441	0.268
Oxygen	1.308	0.504	0.306
Argon	1.634	0.630	0.383
Helium	0.164	0.063	0.038
Carbon dioxide	1.811	0.698	0.424

$$\rho = \rho_0 \frac{T_0}{T}$$

From Table 3.1 it follows that a body with a volume of 1 mL experiences a buoyancy force in dry air of 1.184 mg at 25°C or 0.269 mg at 1000°C. This means that the body appears to become 0.915 mg heavier, i.e. to weigh more, when it is heated from 25 to 1000°C.

Influence of Heating Rate

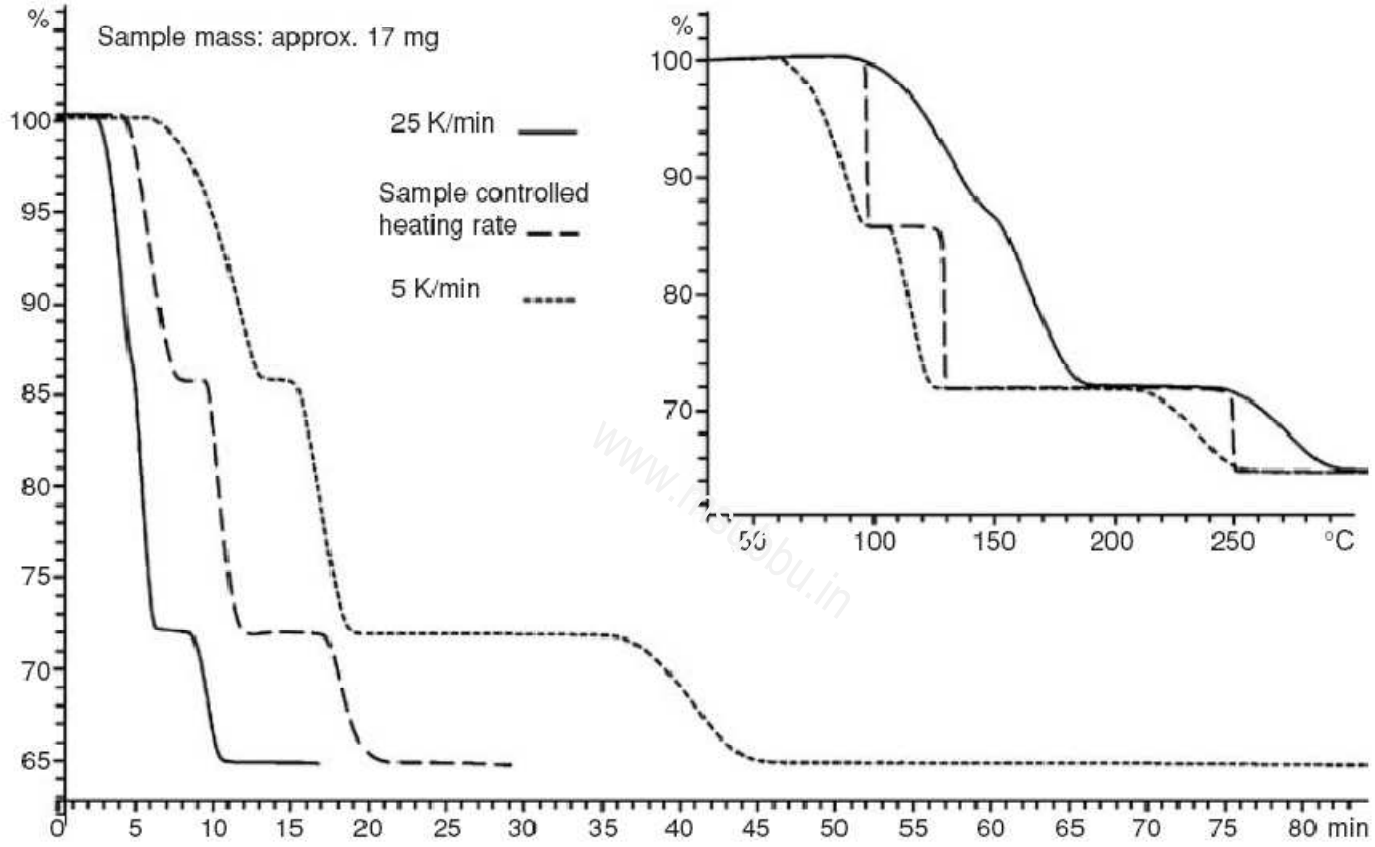


Figure 3.5 Influence of the heating rate on the resolution of partial reactions. In the inserted diagram on the right, the dotted and solid TGA curves of copper sulphate pentahydrate were measured conventionally at 5 and 25 K/min, whereas the dashed curve was recorded using the sample controlled heating rate. In this presentation of mass against temperature, the steps in the curve appear to be nearly vertical because, at low heating rates, the reaction takes place almost isothermally. In contrast, in the mass against time presentation (main diagram), the shapes of the three curves at first sight appear similar. On closer inspection, the better separation obtained using sample controlled heating rates – especially in the first two steps – becomes apparent.

Influence of Heating Rate

- If the sample undergoes chemical reactions, the temperature region in which the reaction occurs is very much dependent on the heating rate.

- In general, higher heating rates cause reactions to shift to higher temperatures

- *Sample controlled TGA: a* quite different approach for separating overlapping reactions makes use of rate of change in sample weight to automatically control the heating rate: the faster the change in mass, the slower the heating rate.