

G16 - THERMAL ANALYSIS

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Thermal analysis is a group of techniques in which the variation of a physical property of a substance is measured as a function of temperature. The most commonly used techniques are those which measure changes of mass or changes in energy of a sample of a substance.

These techniques have different applications:

- determination of phase changes,
- determination of changes in chemical composition,
- determination of purity.

THERMOGRAVIMETRY

Thermogravimetry is a technique in which the mass of a sample of a substance is recorded as a function of temperature according to a controlled temperature programme.

Apparatus. The essential components of a thermobalance are a device for heating or cooling the substance according to a given temperature program, a sample holder in a controlled atmosphere, an electrobalance and a recorder.

Temperature calibration. The temperature sensor close to or in contact with the sample is calibrated using certified reference materials such as indium, tin or zinc. The Curie temperature of a ferromagnetic substance such as nickel may also be used for temperature calibration, based on the occurrence of an apparent mass change at the Curie point. In the case of an apparatus capable of simultaneously conducting differential scanning calorimetry (DSC) and differential thermal analysis (DTA), the same certified reference materials as those for DSC and DTA may be used.

Calibration of the electrobalance. Place an appropriate quantity of a suitable certified reference material (for example, calcium oxalate monohydrate) in the sample holder and record the mass. Set the heating rate according to the manufacturer's instructions (e.g. 5 °C/min) and start the temperature increase. Record the thermogravimetric curve as a graph with temperature, or time, on the abscissa, increasing from left to right, and mass on the ordinate, decreasing downwards. Stop the temperature increase at about 250 °C. Measure the difference on the graph between the initial and final mass-temperature plateaux, or mass-time plateaux, which corresponds to the loss of mass. The declared loss of mass for the certified reference material is stated on the label.

Method. Apply the same procedure to the substance to be examined, using the conditions prescribed in the monograph. Calculate the loss of mass of the substance to be examined from the difference measured in the graph obtained. Express the loss of mass as $\Delta m/m$ (%).

If the apparatus is in frequent use, carry out temperature calibration regularly. Otherwise, carry out such checks before each measurement.

38 Since the conditions are critical, the following parameters are noted for each measurement:
 39 pressure or flow rate, composition of the gas, sample size, heating rate, temperature range,
 40 sample pre-treatment including any isothermal period.

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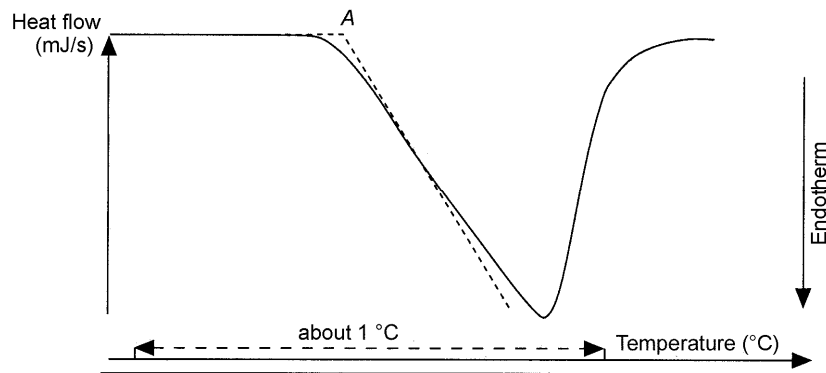
42 DIFFERENTIAL SCANNING CALORIMETRY

43 Differential Scanning Calorimetry (DSC) is a technique that can be used to demonstrate the
 44 energy phenomena produced during heating (or cooling) of a substance (or a mixture of
 45 substances) and to determine the changes in enthalpy and specific heat and the temperatures at
 46 which these occur.

47 The technique is used to determine the difference in heat flow (with reference to the
 48 temperature) evolved or absorbed by the test sample compared with the reference cell, as a
 49 function of the temperature. Two types of DSC apparatuses are available, those using power
 50 compensation to maintain a null temperature difference between sample and reference and
 51 those that apply a constant rate of heating and detect temperature differential as a difference in
 52 heat flow between sample and reference.

53 **Apparatus.** The apparatus for the power compensation DSC consists of a furnace containing
 54 a sample holder with a reference cell and a test cell. The apparatus for the heat flow DSC
 55 consists of a furnace containing a single cell with a sample holder for the reference crucible
 56 and the test crucible.

57 A temperature-programming device, thermal detector(s) and a recording system which can be
 58 connected to a computer are attached. The measurements are carried out under a controlled
 59 atmosphere.



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Figure 1. – *Thermogram*

62 **Calibration of the apparatus.** Calibrate the apparatus for temperature and enthalpy change,
 63 using suitable certified materials.

64 *Temperature calibration.* It can be performed using certified reference materials having an
 65 intrinsic thermal property, such as melting point of pure metals or organic substances, or
 66 phase transition point of crystalline inorganic salts or oxides. Melting points of indium and/or
 67 tin are usually employed for calibration.

68 *Heat-quantity calibration.* For accurate estimation of a quantity of heat change (enthalpic
 69 change) of a test sample, caused by a certain physical change accompanying a temperature

70 change, it is necessary to calibrate the apparatus using suitable certified reference materials.
71 Similarly to temperature calibration, heat-quantity calibration may be performed using
72 suitable certified reference materials showing a known definite enthalpic change caused by
73 physical changes, such as melting of pure metals and/or organic substances, or phase
74 transition of crystalline inorganic salts. Melting points of indium and/or tin are usually
75 employed for calibration.

76 **Operating procedure.** Weigh in a suitable crucible an appropriate quantity of the substance
77 to be examined; place it in the sample holder. Set the initial and final temperatures, and the
78 heating rate according to the operating conditions prescribed in the monograph.

79 Begin the analysis and record the differential scanning calorimetric curve, with the
80 temperature or time on the abscissa (values increasing from left to right) and the energy
81 change on the ordinate (specify whether the change is endothermic or exothermic).

82 The temperature at which the phenomenon occurs (the onset temperature) corresponds to the
83 intersection (A) of the extension of the baseline with the tangent at the point of greatest slope
84 (inflexion point) of the curve (see Figure 1). The end of the thermal phenomenon is indicated
85 by the peak of the curve.

86 The enthalpy of the phenomenon is proportional to the area under the curve limited by the
87 baseline; the proportionality factor is determined from the measurement of the heat of fusion
88 of a known substance (e.g., indium) under the same operating conditions.

89 Each thermogram may be accompanied by the following data: conditions employed, record of
90 last calibration, sample size and identification (including thermal history), container,
91 atmosphere (identity, flow rate, pressure), direction and rate of temperature change,
92 instrument and recorder sensitivity.

93 **Applications**

94 *Phase changes.* Determination of the temperature, heat capacity change and enthalpy of phase
95 changes undergone by a substance as a function of temperature.

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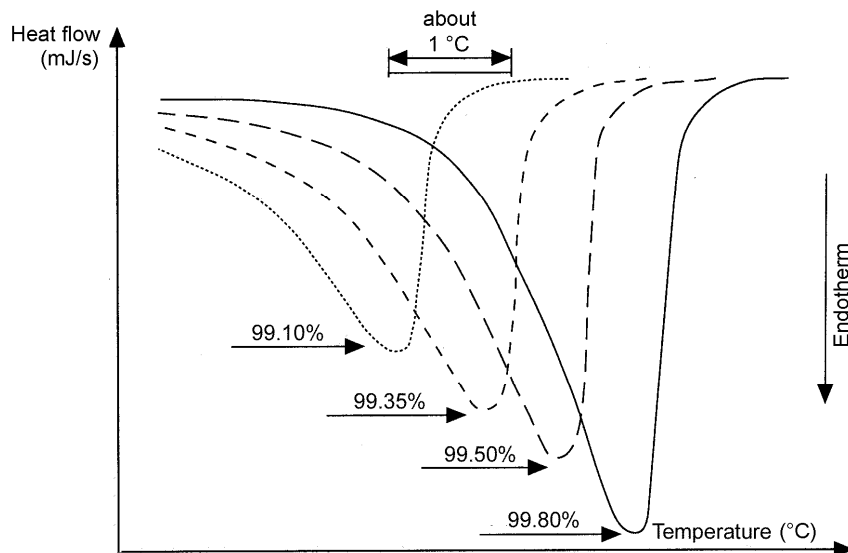
solid - solid transition	allotropy – polymorphism glass transition desolvation amorphous-crystalline
solid - liquid transition	melting
solid - gas transition	sublimation
liquid - solid transition	freezing recrystallisation
liquid - gas transition	evaporation

98 *Changes in chemical composition.* Measurement of heat and temperatures of reaction under
 99 given experimental conditions, so that, for example, the kinetics of decomposition or of
 100 desolvation can be determined.

101 *Application to phase diagrams.* Establishment of phase diagrams for solid mixtures. The
 102 establishment of a phase diagram may be an important step in the preformulation and
 103 optimisation of the freeze-drying process.

104 *Determination of purity.* The measurement of the heat of fusion and the melting point by DSC
 105 enables the impurity content of a substance to be determined from a single thermal diagram,
 106 requiring the use of only a few milligrams of sample with no need for repeated accurate
 107 measurements of the true temperature.

108 In theory, the melting of an entirely crystalline, pure substance at constant pressure is
 109 characterised by a heat of fusion ΔH_f in an infinitely narrow range, corresponding to the
 110 melting point T_0 . A broadening of this range is a sensitive indicator of impurities. Hence,
 111 samples of the same substance, whose impurity contents vary by a few tenths of a per cent,
 112 give thermal diagrams that are visually distinct (see Figure 2).



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Figure 2. – *Thermal diagrams according to purity*

115 The determination of the molar purity by DSC is based on the use of a mathematical
 116 approximation of the integrated form of the van't Hoff equation applied to the concentrations
 117 (not the activities) in a binary system

$$118 \quad [\ln(1 - x_2) \approx -x_2 \text{ and } T \times T_0 \approx T_0^2]:$$

119

$$120 \quad T = T_0 - \frac{RT_0^2}{\Delta H_f} \times x_2 \quad (1)$$

121 T = temperature of the sample, in kelvins,

122 T_0 = melting point of the chemically pure substance, in kelvins,

123 R = gas constant for ideal gases, in joules·kelvin⁻¹·mole⁻¹,

124 ΔH_f = molar heat of fusion of the pure substance, in joules·mole⁻¹,

125 x_2 = mole fraction of the impurity i.e. the number of molecules of the impurity divided by the
 126 total number of molecules in the liquid phase (or molten phase) at temperature T (expressed in
 127 kelvins),

128 Hence, the determination of purity by DSC is limited to the detection of impurities forming a
 129 eutectic mixture with the principal compound and present at a mole fraction of typically less
 130 than 2 per cent in the substance to be examined.

131 This method cannot be applied to:

132 — amorphous substances,

133 — solvates or polymorphic compounds that are unstable within the experimental temperature
134 range,

135 — impurities forming solid solutions with the principal substance,

136 — impurities that are insoluble in the liquid phase or in the melt of the principal substance.

137 During the heating of the substance to be examined, the impurity melts completely at the
138 eutectic temperature. Above this temperature, the solid phase contains only the pure substance.
139 As the temperature increases progressively from the eutectic temperature to the melting point
140 of the pure substance, the mole fraction of impurity in the liquid decreases, since the quantity
141 of liquefied pure substance increases. For all temperatures above the eutectic point:

$$x_2 = \frac{1}{F} \times x_2^* \quad (2)$$

142 F = molten fraction of the analysed sample,

143 x_2^* = mole fraction of the impurity in the analysed sample.

144 When the entire sample has melted, $F = 1$ and $x_2 = x_2^*$.

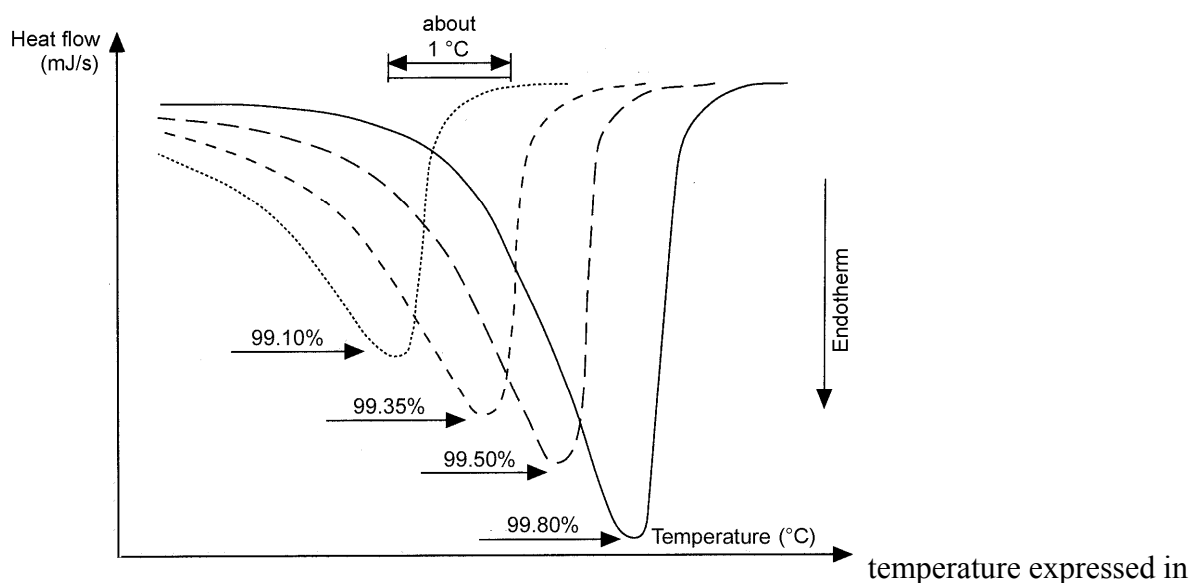
145 If equation (2) is combined with equation (1), the following equation is obtained:

$$T = T_0 - \frac{RT_0^2}{\Delta H_f} \times \frac{1}{F} \times x_2^*$$

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148 The value of the heat of fusion of the pure substance is obtained by integrating the melting
149 peak.

150 The melting point T_0 of the pure substance is extrapolated from the plot of $1/F$ versus the



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- 152 kelvins. The slope α of the curve, obtained after linearisation, if necessary, corresponding to
- 153 $\frac{RT_0^2}{\Delta H_f} x_2^*$ allows x_2^* to be evaluated.
- 154 The fraction x_2^* multiplied by 100 gives the mole fraction in per cent for the total eutectic
- 155 impurities.
- 156