



Designation: E 794 – 01

# Standard Test Method for Melting And Crystallization Temperatures By Thermal Analysis<sup>1</sup>

This standard is issued under the fixed designation E 794; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the determination of melting (and crystallization) temperatures of pure materials by differential scanning calorimetry (DSC) and differential thermal analysis (DTA).

1.2 This test method is generally applicable to thermally stable materials with well-defined melting temperatures.

1.3 The normal operating range is from  $-120$  to  $600^{\circ}\text{C}$  for DSC and  $25$  to  $1500^{\circ}\text{C}$  for DTA. The temperature range can be extended depending upon the instrumentation used.

1.4 Computer or electronic based instruments, techniques, or data treatment equivalent to those in this test method may be used.

1.5 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.6 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

E 473 Terminology Relating to Thermal Analysis<sup>2</sup>

E 793 Test Method for Heats of Fusion and Crystallization by Differential Scanning Calorimetry<sup>2</sup>

E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers<sup>2</sup>

E 1142 Terminology Relating to Thermophysical Properties<sup>2</sup>

## 3. Terminology

3.1 Definitions—Specialized terms used in this test method are defined in Terminologies E 473 and E 1142.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Test Methods and Recommended Practices.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 14.02.

## 4. Summary of Test Method

4.1 The test method involves heating (or cooling) a test specimen at a controlled rate in a controlled environment through the region of fusion (or crystallization). The difference in heat flow (for DSC) or temperature (for DTA) between the test material and a reference material due to energy changes is continuously monitored and recorded. A transition is marked by absorption (or release) of energy by the specimen resulting in a corresponding endothermic (or exothermic) peak in the heating (or cooling) curve.

NOTE 1—Enthalpies of fusion and crystallization are sometimes determined in conjunction with melting or crystallization temperature measurements. These enthalpy values may be obtained by Test Method E 793.

## 5. Significance and Use

5.1 Differential scanning calorimetry and differential thermal analysis provide a rapid method for determining the fusion and crystallization temperatures of crystalline materials.

5.2 This test is useful for quality control, specification acceptance, and research.

## 6. Interferences

6.1 Test specimens need to be homogeneous, since milligram quantities are used.

6.2 Toxic or corrosive effluents, or both, may be released when heating the material and could be harmful to personnel and to apparatus.

## 7. Apparatus

7.1 Apparatus shall be of either type listed below:

7.1.1 *Differential Scanning Calorimeter*, capable of heating (or cooling) at rates up to at least  $10^{\circ}\text{C}/\text{min}$  and of automatically recording the differential energy input between a specimen and a reference material both to the required sensitivity and precision.

7.1.2 *Differential Thermal Analyzer*, capable of heating (or cooling) at rates up to at least  $10^{\circ}\text{C}/\text{min}$  and of automatically recording the differential temperature between a specimen and a reference material both to the required sensitivity and precision.

7.2 *Specimen Capsules or Pans*, for DSC, composed of aluminum or other inert material of high thermal conductivity. For DTA, sample cups or tubes composed of borosilicate glass, alumina, or quartz may be used. The specimen capsules, pans, cups, or tubes must not react with the sample.

7.3 *Nitrogen*, or other inert purge gas supply.

7.4 *Analytical Balance*, with a capacity greater than 100 mg, capable of weighing to the nearest 0.01 mg.

## 8. Sampling

8.1 Powdered or granular materials should be mixed thoroughly prior to sampling and should be sampled by removing portions from various parts of the container. These portions, in turn, should be combined and mixed well to ensure a representative specimen for the determination. Liquid samples may be sampled directly after mixing.

8.2 In the absence of information, samples are assumed to be analyzed as received. If some heat or mechanical treatment is applied to the sample prior to analysis, this treatment should be noted in the report. If some heat treatment is applied, record any mass loss as a result of this treatment.

## 9. Calibration

9.1 Using the same heating rate, purge gas, and flow rate as that to be used for analyzing the specimen, calibrate the temperature axis of the instrument using the procedure in Practice E 967.

## 10. Procedure

10.1 Weigh 1 to 15 mg of material to an accuracy of 0.01 mg<sup>3</sup> into a clean, dry specimen capsule. The specimen mass to be used depends on the magnitude of the transition enthalpy and the volume of the capsule. For comparing multiple results, use similar mass ( $\pm 5\%$ ) and encapsulation.

10.2 Load the encapsulated specimen into the instrument chamber, and purge the chamber with dry nitrogen (or other inert gas) at a constant flow rate of 10 to 50 mL/min throughout the experiment. The flow rate should be measured and held constant for all data to be compared. The use of 99.99 % purity purge gas and a drier is recommended.

10.3 Select the appropriate sensitivity for energy input or temperature difference axis to yield a 25 to 95 % deflection on the output plot.

NOTE 2—Preliminary analysis on a similar specimen may be run to yield this information.

10.4 When a DSC is used, heat the specimen rapidly to 30°C (60°C in a DTA) below the melting temperature, and allow to equilibrate. For some materials, it may be necessary to start the scan substantially lower in temperature, for example, below the glass transition in order to establish a baseline where there is no evidence of melting or crystallization.

10.5 Heat the specimen at 10°C/min through the melting range until the baseline is reestablished above the melting endotherm. Other heating rates may be used but shall be noted in the report. To allow the DSC system to achieve steady state, provide at least 3 min of scanning time both before and after

the peak. For DTA instrumentation, allow at least 6 min to ensure reaching a steady state. Record the accompanying thermal curve.

10.6 Hold the specimen at this temperature for 2 min. Other periods may be used but shall be noted in the report.

10.7 Cool the specimen at 10°C/min through the exotherm until the baseline is reestablished below the crystallization exotherm. Other cooling rates may be used but must be indicated in the report. To allow the system to achieve steady state, provide at least 3 min of scanning time (six for DTA) both before and after the peak. For some materials, it may be necessary to scan several tens of degrees below the peak maximum in order to attain a constant baseline. Record the accompanying thermal curve.

10.8 Reweigh the specimen after completion of the analysis and discard. Report any mass loss observed.

NOTE 3—Mass loss is only one indication of suspected sample degradation or decomposition. An accurate determination of mass loss may not be easily accomplished for tests in which the measuring thermocouple is embedded in the specimen. For these cases, other decomposition indications, such as color change, will suffice and should be reported.

10.9 From the resultant curve, measure the temperatures for the desired points on the curve:  $T_p$ ,  $T_m$ ,  $T_f$ ,  $T_n$ ,  $T_c$ . Report  $T_m$  and  $T_n$ , (see Fig. 1) for a pure crystalline, low molecular weight compound. For such a material  $T_m$  is the best determination of the discrete thermodynamic melting temperature, and  $T_n$  indicates the onset of crystallization. For polymers, alloys or mixtures of materials, report the relevant descriptive parameter (see Fig. 2). Report multiple  $T_p$ s and  $T_c$ s, if observed.

where:

$T_m$  = melting temperature,  
 $T_p$  = melting peak maximum, °C,  
 $T_f$  = return to baseline, °C,  
 $T_n$  = extrapolated crystallization onset °C, and  
 $T_c$  = crystallization onset, °C.

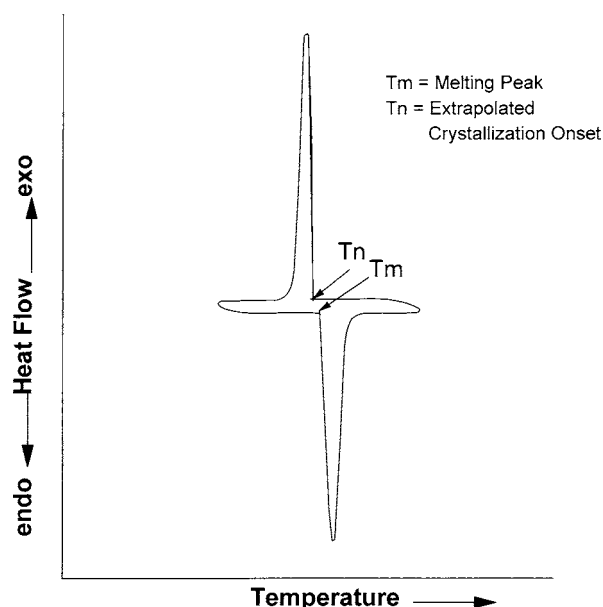


FIG. 1 Fusion and Crystallization Temperatures for Pure Crystalline Material