Designation: E794 − 06 (Reapproved 2012)

Standard Test Method for
Melting And Crystallization Temperatures By Thermal Analysis[1]

This standard is issued under the fixed designation E794; 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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method describes 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°C for DSC and 25 to 1500°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 standard. No other units of measurement are included in this standard.

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:*[2]

E473 Terminology Relating to Thermal Analysis and Rheology

E793 Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry

E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

E1142 Terminology Relating to Thermophysical Properties

3. Terminology

3.1 *Definitions*—Specialized terms used in this test method are defined in Terminologies E473 and E1142.

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 E793.

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 (DSC) or Differential Thermal Analyzer (DTA)*—The essential instrumentation required to provide the minimum differential scanning calorimetric or differential thermal analyzer capability for this method includes:

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[1] This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Calorimetry and Mass Loss.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

7.1.1.1 *Test Chamber* composed of:

(1) A *furnace* or *furnaces* to provide uniform controlled heating (cooling) of a specimen and reference to a constant temperature or at a constant rate within the applicable temperature range of this method.

(2) A *temperature sensor* to provide an indication of the specimen or furnace temperature to within ±0.01°C.

(3) Differential *sensors* to detect a heat flow difference (DSC) or temperature difference (DTA) between the specimen and reference with a range of at least 100 mW and a sensitivity of ±1 μW (DSC) or 4°C and a sensitivity of 40 μ°C (DTA).

(4) A means of sustaining a *test chamber environment* with a purge gas of 10 to 100 ± 5 mL/min.

NOTE 2—Typically 99.9+% pure nitrogen, argon or helium is employed when oxidation in air is a concern. Unless effects of moisture are to be studied, use of dry purge gas is recommended and is essential for operation at subambient temperatures.

7.1.1.2 A *temperature controller*, capable of executing a specific temperature program by operating the furnace or furnaces between selected temperature limits at a rate of temperature change of 10°C/min constant to within ±0.1°C/min or at an isothermal temperature constant to ±0.1°C.

7.1.2 A *recording device*, capable of recording and displaying on the Y-axis any fraction of the heat flow signal (DSC curve) or differential temperature Signal (DTA Curve) including the signal noise as a function of any fraction of the temperature (or time) signal on the X-axis including the signal noise.

7.2 Containers (pans, crucibles, vials, lids, closures, seals, etc.) that are inert to the specimen and reference materials and that are of suitable structural shape and integrity to contain the specimen and reference in accordance with the requirements of this test method.

NOTE 3—DSC containers are commonly composed of aluminum or other inert material of high thermal conductivity. DTA containers are commonly composed of borosilicate glass (for use below 500°C), alumina, or quartz (for use below 1200°C).

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

7.4 Auxiliary instrumentation and apparatus considered necessary or useful for conducting this method includes:

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

7.4.2 Cooling capacity to hasten cooling down from elevated temperatures, to provide constant cooling rates or to sustain an isothermal subambient temperature.

7.4.3 A means, tool or device, to close, encapsulate or seal the container of choice.

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 E967.

10. Procedure

10.1 Weigh 1 to 15 mg of material to an accuracy of 0.01 mg 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 (±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 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.

10.4 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

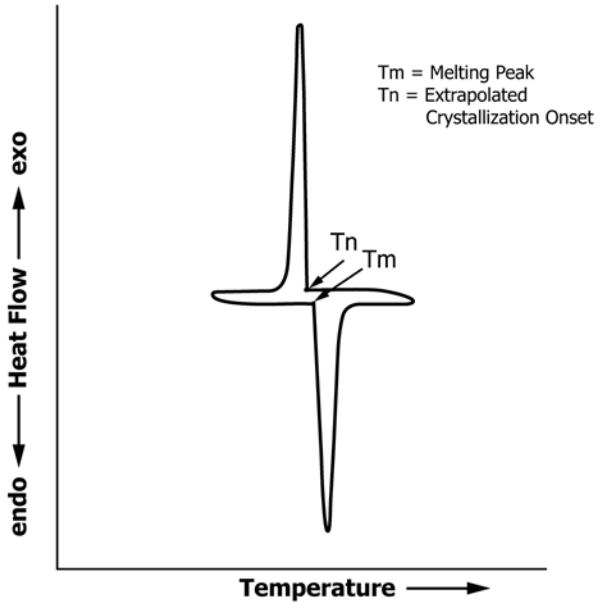

FIG. 1 Fusion and Crystallization Temperatures for Pure Crystalline Material

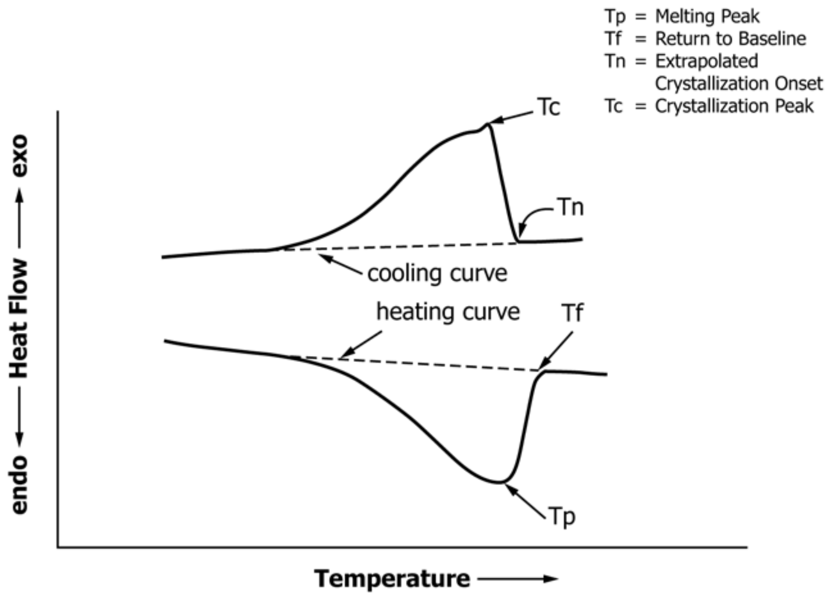

FIG. 2 **Fusion and Crystallization Temperatures for Polymeric Material**

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

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

10.6 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.

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

NOTE 4—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.

10.8 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_ps and T_cs, 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.

NOTE 5—For certain DTA instrumentation, the peak shape obtained from melting a pure, low molecular weight crystalline material (such as a melting point standard) may look quite different from that shown in Fig. 1. If this is the case, report all of the above parameters for any material analyzed. In this case the T_p and T_c values are often taken as the melting and crystallization temperatures, respectively.

NOTE 6—Samples of high purity materials may crystallize with varying amounts of supercooling; therefore, the use of crystallization temperatures should be established prior to use. In general, crystallization temperatures are useful for polymeric, alloy, and impure organic and inorganic chemicals having sufficient nucleation sites for repeatable determinations of crystallization temperatures.

11. Report

11.1 Report the following information:

11.1.1 Complete identification and description of the material tested including source, manufacturer's code, and any thermal or mechanical pretreatment.

11.1.2 Description of instrument (such as manufacturer and model number) used for test.

11.1.3 Statement of the mass, dimensions, geometry, and material of specimen encapsulation, and temperature program.

11.1.4 Description of temperature calibration procedure.

11.1.5 Identification of the specimen environment by gas flow rate, purity, and composition.

11.1.6 Results of the transition measurements using the temperature parameters (T_p, etc.) cited in Figs. 1 and 2. In general, temperature results should be reported to the nearest 0.1°C.

11.1.7 Any side reaction (for example, thermal degradation and oxidation) shall also be reported and the reaction identified, if possible.

11.1.8 The specific dated version of this standard used.

12. Precision and Bias[3]

12.1 The precision and bias were determined by an interlaboratory study in which 17 laboratories participated using five instrument models. The testing was performed on polymer, pure organic, and inorganic materials.

12.2 Based on the results of this study, the following criteria are recommended for judging the acceptability of results:

12.2.1 *Repeatability* (Single Analyst)—The standard deviation of results, obtained by the same analyst on different days, is estimated for the:

12.2.1.1 *Melting Temperature* (M_e)*, Melting Peak Maximum* (T_p)*, Extrapolated Crystallization onset* (T_n)*, and Peak maximum* (T_c) to be 1.1°C at 400 degrees of freedom. Two such results should be considered suspect (95 % confidence level) if they differ by more than 3.1°C.

12.2.2 *Reproducibility*(Multilaboratory)—The standard deviation of results, obtained by analysts in different laboratories, has been estimated for the:

12.2.2.1 *Melting Temperature* (T_m)*, Melting Peak maximum* (T_p)*, Extrapolated Crystallization onset* (T_n)*, and Crystallization Peak maximum* (T_c) to be 2.1°C at 168 degrees of freedom. Two such results should be considered suspect (95 % confidence level) if they differ by more than 5.9°C.

12.3 An estimation of the accuracy of the melting temperature measurement was obtained by comparing the overall mean value obtained during the interlaboratory testing with values reported in the literature.

	Melting Temperatures,°C	
Material	Interlaboratory Test	Literature
Lead[A]	326.4 ± 2.0	327.5 ± 0.03
Adipic acid[B]	151.1 ± 0.7	151.4 ± 0.003

[A] Rossini, F.O., *Pure and Applied Chemistry*, Vol 22, 1972, p. 557.

[B] Colarusso, V.G., et al, *Analytical Chemistry*, Vol 40, 1968, p. 1521.

12.4 A second interlaboratory test (ILT) was carried out in 1997 to determine the extent to which more modern instrumentation and computer calculations have improved the precision and bias over the original ILT. The tests were carried out on two materials, one pure material which melts completely at a single temperature, and one polymer which melts over a temperature range. A total of 10 laboratories using 6 different DSC models from 4 manufacturers participated. The results showed substantial improvement for the onset temperature for a pure material where sample thermal contact is good, but they showed no improvement for the polymer where sample contact variability may effect the peak temperature.

12.5 Precision results for melting tin, and for melting and crystallization of polypropylene.

12.5.1 Within laboratory variability may be described using the repeatability value (r) obtained by multiplying the standard deviation by 2.8. The repeatability value estimates the 95 % confidence limit.

12.5.2 *Repeatability Results:*

12.5.2.1 Repeatability, r, for T_m, the melting temperature of tin was 0.6°C.

12.5.2.2 Repeatability, r, for T_p, the melting (peak) temperature of polypropylene was 2.3°C.

12.5.2.3 Repeatability, r, for T_c, the crystallization (peak) of polypropylene was 1.0°C.

12.5.3 Between laboratory variability may be described using the reproducibility value (R) obtained by multiplying the standard deviation by 2.8. The reproducibility value estimates the 95 % confidence limit.

12.5.4 *Reproducibility Results:*

12.5.4.1 Reproducibility, R, for T_m, the melting temperature of tin was 1.1°C.

12.5.4.2 Reproducibility, R, for T_p, the melting (peak) temperature of polypropylene was 2.7°C.

12.5.4.3 Reproducibility, R, for T_c, the crystallization peak of polypropylene was 4.2°C.

12.6 *Bias:*

12.6.1 An estimate bias is obtained by comparing the mean melting temperature of tin compared to the known melting point using literature values. The average from this ILT was found to be 232.01°C. The literature value (NIST certified value) for 99.9995 % pure tin is 231.95°C. The ILT average and the literature value are the same within the ILT precision; hence, the bias is not significant. NIST materials were not used for this study.

13. Keywords

13.1 crystallization; differential scanning calorimeter; differential thermal analyzer; DSC; DTA; fusion; melting; temperature

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[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1002.