Designation: E 794 – 06

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

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 (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 SI units are the 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]

E 473 Terminology Relating to Thermal Analysis and Rheology

E 793 Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry

E 967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

E 1142 Terminology Relating to Thermophysical Properties

3. Terminology

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

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 (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:

7.1.1.1 *Test Chamber* composed of:

[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 Test Methods and Recommended Practices.

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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.

(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 E 967.

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

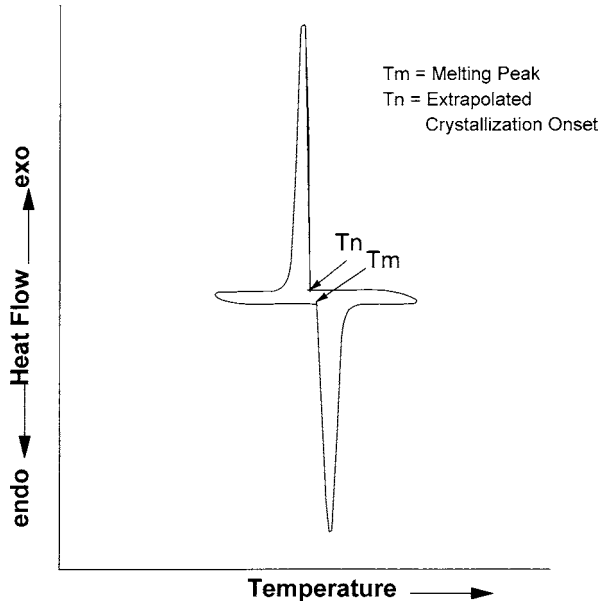

FIG. 1 Fusion and Crystallization Temperatures for Pure Crystalline Material