



Designation: E 793 – 01

# Standard Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry<sup>1</sup>

This standard is issued under the fixed designation E 793; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

## 1. Scope

1.1 This test method covers the determination of the enthalpy (heat) of fusion (melting) and crystallization by differential scanning calorimetry (DSC).

1.2 This test method is applicable to solid samples in granular form or in any fabricated shape from which an appropriate specimen can be cut, or to liquid samples that crystallize within the range of the instrument. Note, however, that the results may be affected by the form and mass of the specimen, as well as by other experimental conditions.

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

1.4 This test method is generally applicable to thermally stable materials with well defined endothermic or exothermic behavior.

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

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

1.7 *This standard does not purport to address all of the safety concerns, 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 794 Test Method for Melting Temperatures and Crystallization Temperatures by Thermal Analysis<sup>2</sup>

E 968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters<sup>2</sup>

<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.

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.

## 4. Summary of Test Method

4.1 This test method involves heating (or cooling) a test specimen at a controlled rate in a controlled environment through the temperature region of fusion or crystallization. The heat flow associated with fusion, an endothermic process (and crystallization, an exothermic process), is recorded and integrated over time. Absolute values for the enthalpy of fusion (and enthalpy of crystallization) or relative values for comparative purposes can thus be obtained.

NOTE 1—Melting (or crystallization) temperatures are sometimes determined in conjunction with measurements of the enthalpy of fusion or crystallization. These temperature values may be obtained by Test Method E 794.

## 5. Significance and Use

5.1 Differential scanning calorimetry provides a rapid method for the determination of enthalpic changes accompanying first-order transitions of materials.

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

## 6. Apparatus

6.1 *Differential Scanning Calorimeter*, capable of heating or cooling rates up to at least  $10^{\circ}\text{C}/\text{min}$  and of automatically recording the differential heat flow between a specimen and a reference material, both to the required sensitivity and precision. For comparison, the same heating rate shall be used for all calibrations and test runs. Thermal curves are recorded on a time based recorder for peak area measurements. The instruments should have sufficient heat flow sensitivity to provide precision of  $\pm 1\%$ . The instrument shall have a time base precision of  $\pm 1\%$  over the time base range from 0.1 to 2.0 min/cm ( $10.0$  to  $0.5$  cm/min) of chart. Some instrument models allow computer acquisition of heat flow data which may be plotted.

6.2 *Planimeter*, or other method of area measurement with precision of  $\pm 1\%$  or better.

6.3 *Specimen Capsule*, material composed of aluminum or other material of high thermal conductivity.

6.4 *Nitrogen*, or other inert gas supply for purging purposes.

6.5 *Balance*, with capacity greater than 100 mg, capable of weighing to the nearest 0.01 mg, or better.

## 7. Hazards and Interferences

7.1 Since milligram quantities of specimens are used, it is essential that samples are homogeneous.

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

7.3 Samples that release volatiles upon heating will change mass and invalidate the test.

7.4 In the use of commercial instrumentation, the operator should read the manufacturer's instruction manual to be aware of potential hazards of operation, such as burn hazards from hot surfaces.

## 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 other 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, and any mass loss resulting from this treatment, should be noted in the report.

## 9. Calibration

9.1 Using the same heating rate, purge gas, and flow rate to be used for specimens, calibrate the heat flow axis of the instrument, using the procedure in Practice E 968.

## 10. Procedure

10.1 Weigh 1 to 15 mg of specimen to an accuracy of  $\pm 0.1\%$  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. Weighing to less accuracy than one part per thousand may limit the accuracy of the enthalpy determination.

10.2 Seal or crimp the specimen capsule with a lid under ambient conditions. Minimize the free space between the specimen and the lid. For specimens sensitive to oxidation, hermetic sealing under an inert atmosphere may be desirable.

10.3 Load the specimen into the instrument chamber. Purge the chamber with dry nitrogen (or other inert gas) at a 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.

10.4 For graphical analysis on a recorder output, select the appropriate heat flow axis and time axis sensitivities to yield an

area of 30 to 60 cm<sup>2</sup> under the fusion endotherm (or crystallization exotherm). For digital data storage, select a sufficient rate of data collection to minimize interpolation error. Typical rates are one point/s for polymers and 5 points/s for simple organic or inorganic materials.

NOTE 2—Preliminary analysis on a similar specimen may be required to provide this information.

10.5 The specimen may be heated rapidly to 50°C below the expected melting temperature and allowed 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.

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

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

10.8 Cool the specimen at 10°C/min through the exotherm until baseline is reestablished below the crystallization exotherm. Other cooling rates may be used but must be noted in the report. To allow the system to achieve steady state, provide at least 3 min of scanning time 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.

10.9 Reweigh the specimen after completion of scanning and discard. Discard the data if mass losses exceed 1% of the original mass or if there is evidence of reaction with the specimen capsule.

10.10 A duplicate determination shall be made on a different specimen and the mean value for enthalpy of fusion (or crystallization) reported.

10.11 If a comparative method is to be used, for example, using a planimeter, then weighed specimen of an appropriate reference material shall be analyzed using identical scanning and recorder conditions. Refer to Practice E 968.

## 11. Calculation

11.1 Construct a baseline on the differential heat flow thermal curve by connecting the two points at which the melting endotherm (or freezing exotherm) deviates from the relatively straight baseline (see Fig. 1 and Fig. 2).

11.2 Measure the area under the fusion endotherm (or crystallization exotherm). If a manual graphical method is used, measure the area three times and use the average for calculation. If electronic or computer means of area integration are used, the area need be determined only once.

11.3 Calculate, retaining all meaningful decimal places, the enthalpy of fusion (or enthalpy of crystallization). The following equation pertains to the calculation of enthalpy of a material relative to that of a reference standard using the relative peak areas as measured by planimeter.

$$H = (ABT/W)(H_s W_s / A_s T_s B_s) \quad (1)$$