Designation: E793 – 06 (Reapproved 2012)

Standard Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry[1]

This standard is issued under the fixed designation E793; 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 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°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 standard. No other units of measurement are included in this standard.

1.7 The enthalpy of melting and crystallization portion of ISO 11357-3 is equivalent to this standard.

1.8 *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:*[2]

E473 Terminology Relating to Thermal Analysis and Rheology

E794 Test Method for Melting And Crystallization Temperatures By Thermal Analysis

E968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters

E1142 Terminology Relating to Thermophysical Properties

E1860 Test Method for Elapsed Time Calibration of Thermal Analyzers

2.2 *ISO Standard:*[3]

ISO 11357–3 Plastics – Differential Scanning Calorimetry (DSC) – Part 3: Temperature and Enthalpy of Melting and Crystallization

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 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

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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.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

crystallization. These temperature values may be obtained by Test Method E794.

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 *DSC,* The essential instrumentation required to provide the minimum differential scanning calorimetric capability for this method includes:

6.1.1 DSC Test Chamber composed of:

6.1.1.1 a *furnace(s)*, to provide uniform controlled heating and cooling of a specimen and reference to a constant temperature or at a constant rate from –120 to 600°C.

6.1.1.2 A *temperature sensor*, to provide an indication of the specimen temperature to ±0.1°C.

6.1.1.3 *Differential sensors*, to detect a heat flow difference between specimen and reference with a range of at least ±100 mW and a sensitivity of ±5 mW.

6.1.1.4 A means of sustaining a test chamber environment of an inert purge gas as at rate of 10 to 50 ± 5 mL/min.

NOTE 2—Typically, 99.99+% pure nitrogen, argon or helium is used 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.

6.1.2 A *temperature controller*, capable of executing a specific temperature program by operating the furnaces(s) between selected temperature limits at a rate of temperature change of up to at least 20°C/min constant to ±0.1°C/min. or at an isothermal temperature constant to ±0.1°C.

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

6.2 *Specimen 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.

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

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

NOTE 3—Balances readable to 0.01 mg are suitable for use with test specimens on the order of 10 mg in mass. A balance readable to 0.001 mg is required for test specimens on the order of 1 mg in mass. to achieve the precision described in this standard.

6.5 Auxiliary instrumentation considered useful or necessary for conducting this method includes:

6.5.1 *Data Analysis* capability of integrating the heat flow signal as a function of time to produce enthalpy information in units of mJ to a precision of ±1 %.

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

6.5.3 A cooling capability to hasten cool down from elevated temperatures, to provide constant cooling rates, or to sustain an isothermal subambient temperature.

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 operations 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 E968.

9.2 Calibrate the elapsed time signal of the differential scanning calorimeter using Test Method E1860.

10. Procedure

10.1 Weigh 1 to 15 mg of specimen to an accuracy of ±0.1 % into a clean, dry specimen capsule.

NOTE 4—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. 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.

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

NOTE 5—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 baseline is reestablished above the melting endotherm.

NOTE 6—Other heating rates may be used but shall be noted in the report. Results may depend on heating rate and equilibration times.

NOTE 7—To allow the system to achieve steady state, provide at least 3 min of scanning time both before and after the peak.

10.6 Hold the specimen at this temperature for 2 min.

NOTE 8—Other periods may be used, but shall be noted in the report

10.7 Cool the specimen at 10°C/min through the exotherm

NOTE 9—Other cooling rates may be used but must be noted in the report.

NOTE 10—To allow the system to achieve steady state, provide at least 3 min of scanning time both before and after the peak.

NOTE 11—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 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.

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 Integrate the area under the fusion endotherm (or crystallization exotherm) as a function of time.

11.3 Calculate, retaining all meaningful decimal places, the enthalpy of fusion (or enthalpy of crystallization) (H_o) using Eq 1.

$$H = E\, H_o / W \tag{1}$$

where:

H = enthalpy of fusion (or crystallization) of the sample in J/g,

W = mass of the specimen, mg,

E = Calibration constant from Practice E968,

H_o = observed enthalpy of fusion (or crystallization), mJ

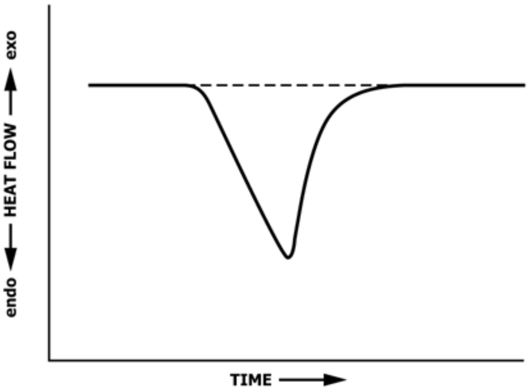

FIG. 1 Melting Endotherm (DSC)

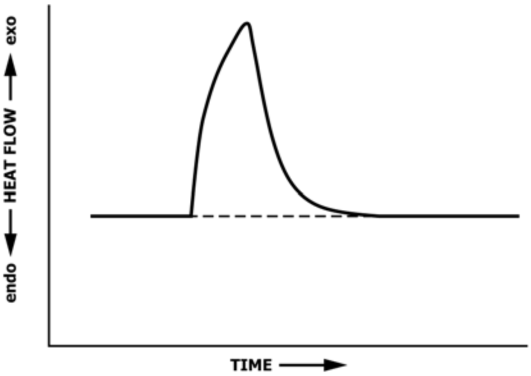

FIG. 2 Crystallization Exotherm (DSC)

12. Report

12.1 Report the following information:

12.1.1 Complete identification and description of the material tested including source and manufacturer code.

12.1.2 Description of the instrument used for test.

12.1.3 Statement of the mass, dimensions, geometry, and material of the specimen capsule, and the heating (cooling) rate used.

12.1.4 Description of the calibration procedure.

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

12.1.6 Enthalpy of fusion (or crystallization) in J/g.

12.1.7 The specific dated edition of the method used.

13. Precision and Bias[4]

13.1 The precision of this test method was determined in an interlaboratory investigation in which 18 laboratories participated using six instrument models. Polymeric, organic, and inorganic materials were included for measuring both enthalpy of fusion and crystallization.

13.2 The following criteria should be used for judging the acceptability of enthalpy of fusion or crystallization results:

13.2.1 *Repeatability* (Single Analyst)—The coefficient of variation of results (each the average of duplicates), for enthalpy of fusion or crystallization, obtained by the same analyst or instrument on different days, is estimated to be 2.8 % with 88 degrees of freedom. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 7.8 %.

13.2.2 *Reproducibility of Polymers* (Multilaboratory)—The coefficient of variation of results (each the average of duplicates) for enthalpy of fusion or crystallization for polymers (that is, materials melting or crystallizing over a broad temperature range), obtained by analysts in different laboratories, is estimated to be 8.0 % at 30 degrees of freedom. Two such results should be considered suspect (95 % confidence level) if they differ by more than 23 %.

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1001.

13.2.3 *Reproducibility of Pure Materials* (Multilaboratory)—The coefficient of variation of results (each the average of duplicates) for enthalpy of fusion or crystallization for organic and inorganic materials (that is, materials melting or crystallizing over a narrow temperature range), obtained by analysts in different laboratories, is estimated to be 3.0 % at 58 degrees of freedom. Two such results should be considered suspect (95 % confidence level) if they differ by more than 8.6 %.

13.3 An estimation of the accuracy of the enthalpy of fusion measurement was obtained by comparing the overall mean value obtained during the interlaboratory testing with values reported in the literature.

Material	Heat of Fusion (J/g)	
	Interlaboratory Test	Literature
Lead[A]	22.2 ± 0.8	23.16 ± 0.30
Adipic acid[B]	252 ± 9	238.5 ± 2.4

[A] Hultgren, R.R., et al, *Selected Values of Thermodynamic Properties of the Elements*, John Wiley & Sons, Inc., New York, NY, 1973.

[B] Cingolani, A., et al., *Journal of Thermal Analysis, Vol 6,* 1974, p. 87.

Based on this comparison, the accuracy of the enthalpy of fusion measurement is estimated to be ±5.5 %.

13.4 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.

13.5 Precision results for melting tin, and for melting and crystallization of polypropylene. For the melting of polypropylene, an uncertainty in how to define the peak start resulted in a large apparent imprecision.

13.5.1 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.

13.5.2 Repeatability, r, for ΔH, the melting enthalpy of tin was 0.92 J/g. (1.5 %)

13.5.3 Repeatability, r, for ΔH, the melting (peak) enthalpy of polypropylene was 9.3 J/g. (10.3 %)

13.5.4 Repeatability, r, for ΔH, the crystallization enthalpy of polypropylene was 3.1 J/g. (3.4 %)

13.5.5 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.

13.5.5.1 Reproducibility, R, for ΔH, the melting enthalpy of tin was 1.22 J/g. (2.0 %)

13.5.5.2 Reproducibility, R, for ΔH, the melting (peak) enthalpy of polypropylene was 20.1 J/g. (22.5 %)

13.5.5.3 Reproducibility, R, for ΔH, the crystallization enthalpy of polypropylene was 6.7 J/g. (7.3 %)

13.6 *Bias:*

13.6.1 An estimate bias is obtained by comparing the mean melting value of tin compared to the known melting point using literature values. That is, bias = (mean value) – (known value). The average from this ILT was found to be 60.27 J/g. The literature value (NIST certified value) for 99.9995% pure tin is 60.22 J/g. This ILT average and the literature value are the same within the ILT precision; hence, the bias is not significant.

14. Keywords

14.1 crystallization; differential scanning calorimeter; DSC; energy; enthalpy; fusion; heat; melting