



Standard Test Method for The Thermal Stability Of Chemicals By Differential Scanning Calorimetry¹

This standard is issued under the fixed designation E 537; 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 (ε) indicates an editorial change since the last revision or reappraisal.

INTRODUCTION

Committee E-27 is currently engaged in developing methods to determine the hazard potential of chemicals. An estimate of this potential may usually be obtained by the use of program CHETAH 7.0 to compute the maximum energy of reaction of the chemical or mixture of chemicals.²

The expression “hazard potential” as used by this committee is defined as the degree of susceptibility of material to ignition or release of energy under varying environmental conditions.

The primary purpose of this test method is to detect enthalpic changes and to approximate the temperature of initiation and enthalpies (heats) of these events. Differential scanning calorimetry offers the advantage of using very small specimens on the order of a few milligrams.

1. Scope

1.1 This test method describes the ascertainment of the presence of enthalpic changes in a test specimen, using minimum quantities of material, approximates the temperature at which these enthalpic changes occur and determines their enthalpies (heats) using differential scanning calorimetry or pressure differential scanning calorimetry.

1.2 This test method may be performed on solids, liquids, or slurries.

1.3 This test method may be performed in an inert or a reactive atmosphere with an absolute pressure range from 100 Pa through 7 MPa and over a temperature range from 300 to 800 K (27 to 527 °C).

1.4 SI values are the standard.

1.5 There is no ISO standard equivalent to this test method.

1.6 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety concerns 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.* Specific safety precautions are given in Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*³

E 473 Terminology Relating to Thermal Analysis and Rheology

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

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

E 968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters

E 1445 Terminology Relating to Hazard Potential of Chemicals

E 1860 Test Method for Elapsed Time Calibration of Thermal Analyzers

3. Terminology

3.1 *Definitions:*

3.1.1 Specific technical terms used in this standard are defined in Terminologies **E 473** and **E 1445**.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *DSC curve*—a record of a differential scanning calorimeter where the change in heat flow (Δq) is plotted on the ordinate and temperature or time is plotted on the abscissa (see **Figs. 1 and 2** and Terminology **E 473**).

¹ This test method is under the jurisdiction of ASTM Committee E27 on Hazard Potential of Chemicals and is the direct responsibility of Subcommittee E27.02 on Thermal Stability and Condensed Phases.

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² A complete assessment of the hazard potential of chemicals must take into account a number of realistic factors not considered in this test method or the CHETAH program.

³ 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.

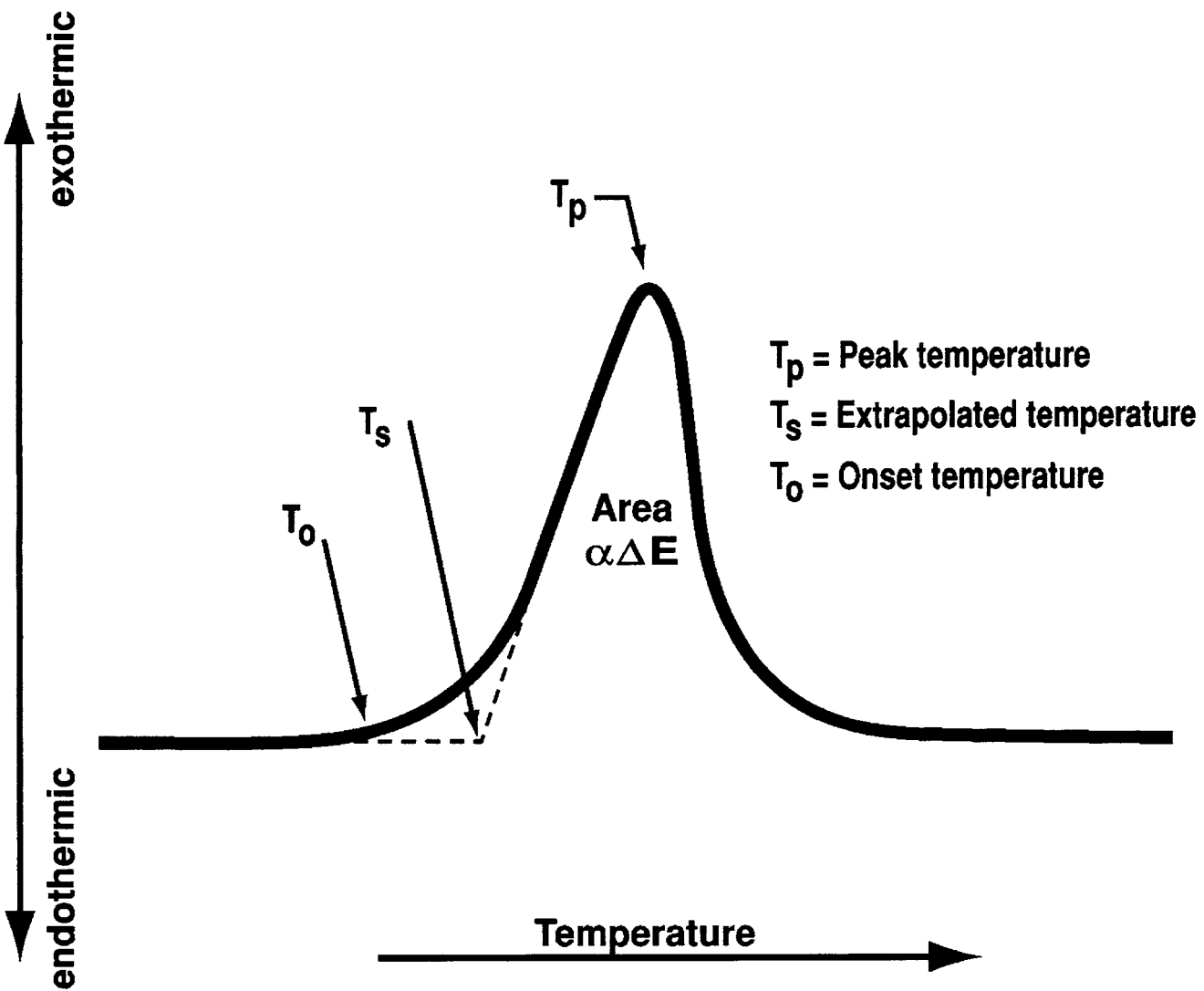


FIG. 1 Typical DSC Curve with Exotherm

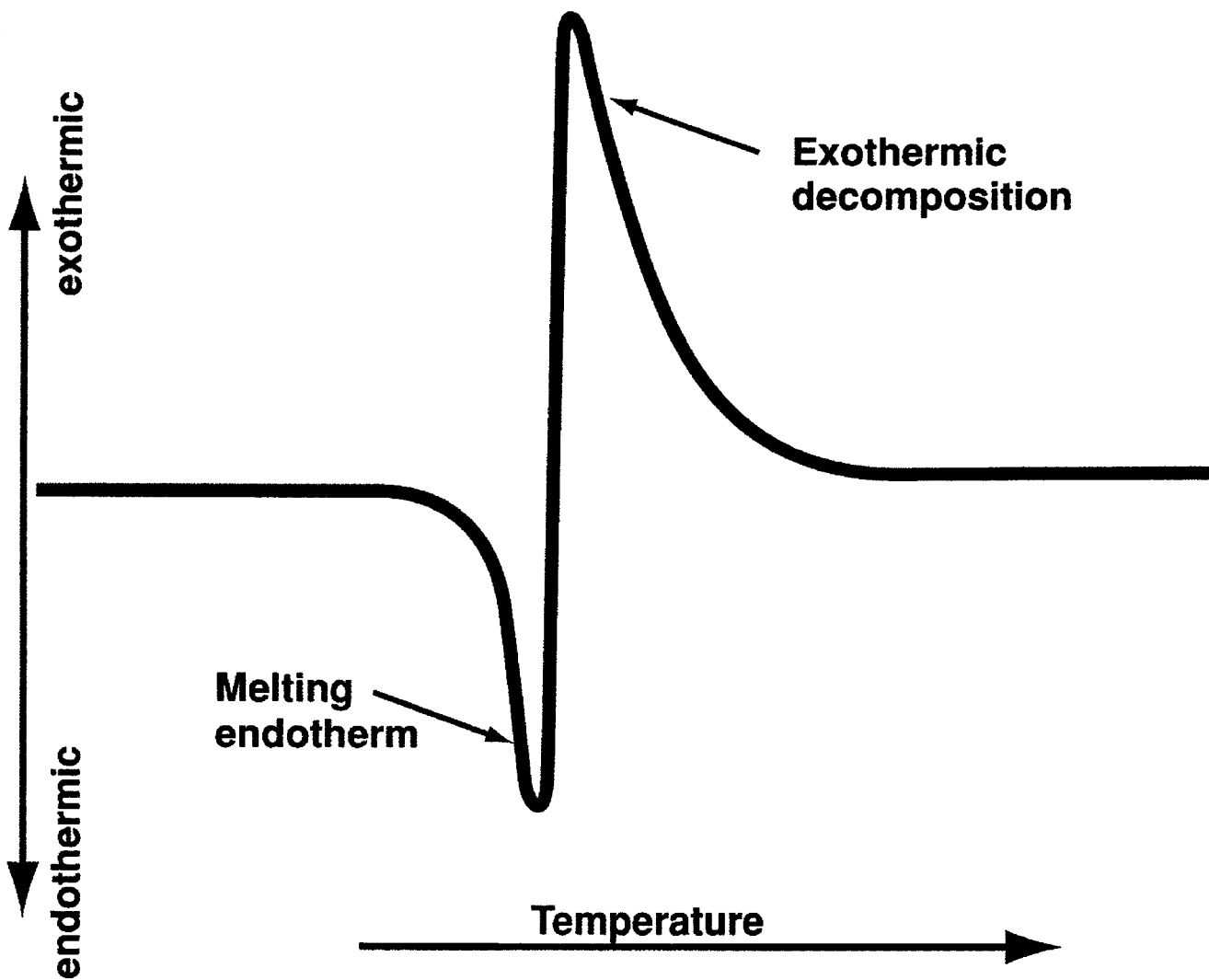


FIG. 2 DSC Curve Illustrating a Melting Process Immediately Followed by an Exothermic Decomposition

3.2.2 *peak*—that portion of a thermal curve that is attributable to the occurrence of a single process. It is normally characterized by a deviation from the established baseline, a maximum deflection, and a reestablishment of a baseline not necessarily identical to that before the peak (see Fig. 1).

NOTE 1—There will be instances when upon scanning in temperature an endotherm will be observed that is immediately followed by or is in conjunction with an exotherm as shown in Fig. 2. These types of competing reactions make it difficult and at times impossible to locate the true peak and onset temperatures.

3.2.3 *peak temperature* (T_p)—the temperature corresponding to the maximum deflection of the DSC curve.

3.2.4 *onset temperature* (T_o)—the temperature at which a deflection from the established baseline is first observed.

3.2.5 *extrapolated onset temperature* (T_e)—empirically, the temperature found by extrapolating the baseline (prior to the peak) and the tangent at the inflection point on the leading side of the peak to their intersection (see Fig. 1).

3.2.6 *reaction*—any transformation of material accompanied by a change of enthalpy that may be endothermic or exothermic.

3.2.7 *thermal stability*—the absence of a reaction (for the purposes of this test method only, see 3.2.6).

4. Summary of Test Method

4.1 In DSC, a measurement is made of the heat flow (Δq) associated with the observed change of enthalpy. Provisions are made to measure the absolute temperature (T) of the sample or reference or the average temperature of both.

4.2 A sample of the material to be examined and of a thermally inert reference material are placed in separate holders.

4.3 The sample and reference materials are simultaneously heated at a controlled rate of 2 to 20 °C/min under an equilibrated atmosphere. A record of Δq on the ordinate is made as a function of temperature (T) on the abscissa.

4.4 When the sample undergoes a transition involving a change of enthalpy, that change is indicated by a departure from the initially established baseline of the heat flow record.

4.5 The onset temperature (T_o), extrapolated onset temperature (T_e), and the integrated peak area (enthalpy) are determined and reported.

5. Significance and Use

5.1 This test method is useful in detecting potentially hazardous reactions including those from volatile chemicals and in estimating the temperatures at which these reactions occur and their enthalpies (heats). This test method is recommended as an early test for detecting the thermal hazards of an uncharacterized chemical substance or mixture (see Section 8).

5.2 The magnitude of the change of enthalpy may not necessarily denote the relative hazard in a particular application. For example, certain exothermic reactions are often accompanied by gas evolution that increases the potential hazard. Alternatively, the extent of energy release for certain exothermic reactions may differ widely with the extent of confinement of volatile products. Thus, the presence of an exotherm and its approximate temperature are the most significant criteria in this test method (see Section 3 and Fig. 1).

5.3 When volatile substances are being studied, it is important to perform this test with a confining pressurized atmosphere so that changes of enthalpy that can occur above normal boiling or sublimation points may be detected. As an example, an absolute pressure of 1.14 MPa (150 psig) will generally elevate the boiling point of a volatile organic substance 100 °C. Under these conditions exothermic decomposition is often observed.

5.4 For some substances the rate of enthalpy change during an exothermic reaction may be small at normal atmospheric pressure, making an assessment of the temperature of instability difficult. Generally a repeated analysis at an elevated pressure will improve the assessment by increasing the rate of change of enthalpy.

NOTE 2—The choice of pressure may sometimes be estimated by the pressure of the application to which the material is exposed.

5.5 The four significant criteria of this test method are: the detection of a change of enthalpy; the approximate temperature at which the event occurs; the estimation of its enthalpy and the observance of effects due to the cell atmosphere and pressure.

6. Limitations

6.1 A host of environmental factors affect the existence, magnitude, and temperature of an exothermic reaction. Some, including heating rate, instrument sensitivity, degree of confinement, and atmosphere reactivity, will affect the detectability of an exothermic reaction using this procedure. Therefore, it is imperative that the qualitative results obtained from the application of this test method be viewed only as an indication of the thermal stability of a chemical.

7. Apparatus

7.1 The equipment used in this test method shall be capable of displaying changes of enthalpy as a function of temperature (T), and shall have the capability of subjecting the sample cell to different atmospheres of equilibrated pressures.

7.2 *Differential Scanning Calorimeter (DSC)*—the essential instrumentation required to provide the minimum differential scanning calorimetric capability for this test method include:

7.2.1 A test chamber composed of:

7.2.1.1 *Furnace(s)*, to provide uniform controlled heating of a specimen and reference to a constant temperature or at a constant rate within the applicable temperature range of this method,

7.2.1.2 *Temperature sensor*, to provide an indication of the specimen/furnace temperature to ± 0.5 K,

7.2.1.3 *Differential sensor*, to detect a temperature or heat flow difference between the specimen and reference equivalent to 0.2 mW,

7.2.1.4 *Means of sustaining a test chamber environment* of inert (for example, nitrogen, helium or argon) or reactive (for example, air) gas at a purge rate of 50 ± 5 mL/min,

NOTE 3—Typically, at least 99 % 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.

NOTE 4—Other purge gas rates may be used but shall be reported.

7.2.1.5 *Temperature controller*, capable of executing a specific temperature program by operating the furnace(s) between selected temperature limits (ambient temperature to 800 K) at a rate of temperature change of from 2 to 20 K/min constant to ± 0.1 K/min, and

NOTE 5—The temperature range of the apparatus and the experiment may be extended to 120 K with the use of appropriate cooling or to 1273 K or greater with suitable apparatus.

7.2.1.6 *Recording device*, either digital or analog, capable of recording and displaying any portion of the differential heat flow on the ordinate as a function of temperature on the abscissa, including the signal noise.

7.2.2 If experiments are to be carried out under pressure conditions:

7.2.2.1 *Pressure vessel*, or similar means of sealing the test chamber at any applied pressure within 0.10 to 1.27 MPa (0 to 170 psig) pressure limits required by this test method,

7.2.2.2 *Pressurized gas source*, capable of sustaining a regulated gas pressure in the test chamber between 0.10 and 1.27 MPa (0 and 170 psig),

7.2.2.3 *Pressure transducer*, or similar device to measure the pressure inside the test chamber to ± 5 % including any temperature dependence of the transducer,

7.2.2.4 *Pressure regulator*, or similar device to adjust the applied pressure in the test chamber to ± 5 % of the desired value,

7.2.2.5 *Ballast*, or similar means to maintain the applied pressure in the test chamber constant to ± 5 %,

7.2.2.6 *Valves*, to control pressurizing gas in the test chamber or to isolate components of the pressure system, or both.

7.2.3 If subambient temperatures are desired:

7.2.3.1 *Cooling system*, to hasten cool down from elevated temperatures and to sustain an isothermal subambient temperature.

7.3 *Containers*, (pans, crucibles, vials, etc.) which are inert to the specimen and reference materials and which are of suitable structural shape and integrity to contain the specimen and reference in accordance with the specific requirements of this method.

7.4 *Balance*, with a capacity of 100 mg or greater to weigh specimens or containers, or both, to a sensitivity of ± 10 μ g.

8. Safety Precautions

8.1 The use of this test method as an initial test for material whose potential hazards are unknown requires that precautions be taken during the sample preparation and testing.

8.2 Where particle size reduction by grinding is necessary, the user of the test method should presume that the material is sensitive to stimuli such as friction and electrostatic discharge. Accordingly, appropriate test shall be conducted on those materials prior to grinding. Use of suitable protective equipment is always recommended when preparing materials of unknown hazard. If a Material Safety Data Sheet is available, it shall be acquired and studied prior to handling unknown materials.

8.3 The use of this test method may require operation at elevated temperatures and pressures. All precautions associated with such temperatures and pressures should be observed.

8.4 Toxic or corrosive effluents, or both, may be released when heating the material and could be harmful to the personnel or the apparatus. Use of an exhaust system to remove such effluents is recommended.

9. Calibration

9.1 Perform any calibration procedures recommended by the apparatus manufacturer as described in the Operator's manual.

9.2 Calibrate the temperature signal within ± 2 °C using Practice E 967.

9.3 Calibrate the heat flow signal within ± 1 % using Test Method E 968.

9.4 Calibrate the time signal within ± 0.5 % using Test Method E 1860.

10. Sample and Reference Materials

10.1 The selection of an adequate sample size will depend upon the availability of the material, the degree of dilution required, the sensitivity of the instrument, the magnitude of the change of enthalpy, and the heating rate. Additionally, sample size must be compatible with the potential for a sudden large energy release. This test method should, therefore, be carried out on as small a quantity of material as possible, typically 1 to 50 mg.

10.2 Samples should be representative of the material being studied including particle size and purity.

10.3 The reference material must not undergo any thermal transformation over the temperature range under study. Typical reference materials include calcined aluminum oxide, glass beads, silicone oil, or an empty container.

11. Recommended Conditions of Tests

11.1 *Specimen Size*—A 5-mg specimen is generally considered adequate. Decrease the specimen size if the response is greater than 8 mW.

NOTE 6—For materials whose characteristics are unknown, it is safest to start with a specimen size of no more than 1 mg, and then increase the size if the exothermic response is insufficiently large.

11.2 *Heating Rate*—A rate of 10 to 20 °C/min is considered normal. If an endothermic response is immediately followed by an exotherm (see Note 1 and Fig. 2), then lower heating rates of 2 to 6 °C/min are recommended.

NOTE 7—The onset temperature, extrapolated onset temperature, and peak temperature are affected by heating rate. Only results obtained at the same heating rate shall be compared.

11.3 *Temperature Range*—The temperature typically ranges from 300 to 800 K (27 to 527 °C).

11.4 *Pressure Range*—An equilibrated absolute pressure of 1.14 MPa (150 psig) is adequate for most elevated pressure tests.

NOTE 8—The applied pressure should be selected based upon the characteristics of the material. If the material to be tested has a high vapor pressure, it may evaporate before the end temperature is reached. To minimize evaporation, the applied pressure shall exceed the vapor pressure of the material at the maximum test temperature. The amount by which the applied pressure shall exceed the vapor pressure of the material depends upon the test apparatus, size of the pinhole (12.2), heating rate

and other factors. In some cases, it may be desirable to set the applied pressure to be the maximum pressure anticipated under production conditions.

12. Procedure

12.1 Weigh and record the mass of the empty specimen container. Into this tared specimen container, weigh the test specimen to within $\pm 10 \mu\text{g}$ and record this weight as n in mg

NOTE 9—For volatile materials it is often of interest to examine thermal stability at temperatures beyond the normal boiling or sublimation point. Additionally, samples suspected of being potentially energetic may exhibit nondescript exothermic activity at ambient pressure. In either situation a repeat analysis in an atmosphere of elevated pressure using either sealed sample containers or a pressurized measuring cell is recommended.

12.2 For equipment that includes a pressurizable measuring cell, seal and adjust the measuring cell atmosphere to the desired equilibrium pressure.

NOTE 10—When sealed containers are used, they should be provided with a 50 to 100 μm diameter vent (pinhole) to ensure that the internal pressure is in equilibrium with the applied pressure. A vent hole may also permit the loss of material, and more importantly, the loss of heat that will nullify the determination of enthalpy.

12.3 For equipment that cannot maintain an elevated pressure within its measuring cell, place the sample and reference materials in hermetically sealed containers with an appropriate atmosphere.

NOTE 11—Hermetically sealed containers will self-pressurize with measuring temperature due to increased partial pressures and gas evolution. For most specimens, this internal pressure will not be known but is typically less than 300 kPa. Enthalpies measured with sealed containers may be different from those with vented containers due to differences in the heat of vaporization.

12.4 Heat the measuring cell at a controlled rate of 2 to 20 $^{\circ}\text{C}/\text{min}$ and record the DSC curve. Continue heating until the highest temperature of interest is recorded or until the sample is destroyed or is lost by volatilization. For most organic compounds the normal temperature range is from 20 to 500 $^{\circ}\text{C}$.

NOTE 12—Other heating rates may be used but shall be reported.

NOTE 13—Any increase in heating rate may accentuate the recorder

response for the ordinate but will also increase the measured onset temperature of an exothermic reaction.

12.5 Record the onset temperature (T_o), extrapolated onset temperature (T_c) and peak temperature (T_p) for any reaction(s) observed (see Fig. 1).

12.6 Restore the measuring cell to ambient temperature and pressure upon completion of the analysis.

NOTE 14—It may be informative to repeat the analysis at a slower heating rate (2 to 10 $^{\circ}\text{C}/\text{min}$) when a complex change of enthalpy is encountered (see Fig. 2 and Note 1)

12.7 Reweigh the specimen container. Compare the container weight with n determined in 12.1. Report any change in container weight observed.

12.8 Calculate the enthalpy of the exothermic reaction by the procedures described in 14.

13. Calculations

13.1 Construct a baseline on the differential heat flow curve from a point on the baseline before the reaction exotherm to a point on the baseline after the reaction (see Fig. 3).

13.2 Integrate the area under the reaction exotherm as a function of time.

13.3 Calculate, retaining all the meaningful decimal places, the enthalpy of the reaction. $\Delta H = A/m$

where:

ΔH = enthalpy of reaction, J g⁻¹,

m = mass of the test specimen, mg, and

A = area of the reaction exotherm, mJ

14. Report

14.1 Report the following information:

14.1.1 Sample and reference by name, composition, combination thereof, or formula, or any sample preparation or pretreatment, or both.

14.1.2 Apparatus and sample containers,

14.1.3 Composition and pressure of the sample atmosphere,

14.1.4 Heating rate and temperature range, and

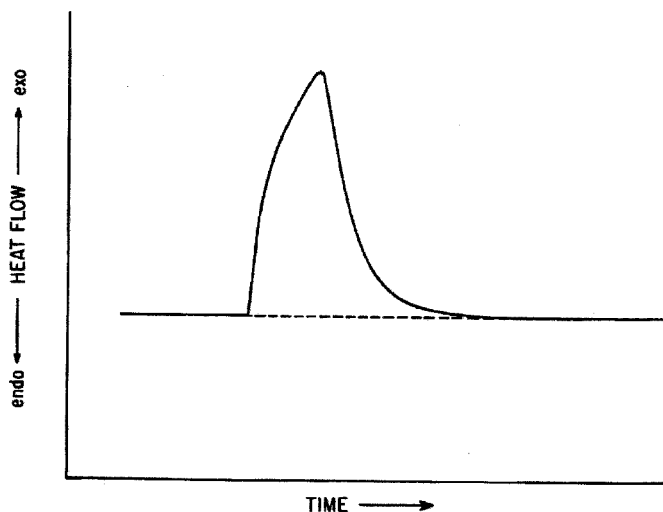


FIG. 3 Integration of Exotherm

14.1.5 Determine the onset, extrapolated onset, and peak temperatures of all reactions recorded from the DSC curve. Report any processes (such as melting) which may interfere with the determination of one or more of these parameters.

14.2 When a thermal analysis is repeated using a different atmospheric composition or pressure or a different heating rate, note any significant changes in the DSC curves resulting from the different experimental conditions. Report the enthalpy of reaction, and specimen percent weight loss.

14.3 The specific dated version of this test method used.

15. Precision and Bias

15.1 An interlaboratory study (ILS) was conducted in 2000 involving participation by six (6) laboratories using apparatus from three (3) manufacturers five (5) instrument models. Each laboratory characterized trityl azide (also known as azidotriphenylmethane) in quintuplicate. The results were evaluated using Practice E 691. The study is on file at ASTM Headquarters.⁴

15.2 *Precision*—Within laboratory variability may be described using the repeatability value (*r*) obtained by multiplying the repeatability standard deviation by 2.8. The repeatability value estimates the 95 % confidence limit. That is, two within laboratory results should be considered suspect if they differ by more than the repeatability value (*r*).

15.2.1 The repeatability relative standard deviation for reaction is enthalpy is 3. 5%.

15.2.2 The repeatability standard deviation for extrapolated onset temperature is 0.52 °C.

15.2.3 The repeatability standard deviation for the onset temperature is 3.4 °C.

15.3 Between laboratory variability may be estimated using the reproducibility value (*R*) obtained by multiplying the

reproducibility standard deviation by 2.8. The reproducibility value estimates the 95 % confidence limit. That is, two between laboratory results should be considered suspect if they differ by more than the reproducibility value (*R*).

15.3.1 The reproducibility relative standard deviation for reaction enthalpy is 4.7 %

15.3.2 The reproducibility standard deviation for extrapolated onset temperature is 3.4 °C

15.3.3 The reproducibility standard deviation for the onset temperature is 10 °C.

15.4 *Bias*—Bias is the difference between a test result and an accepted reference value. There is no accepted reference value for reaction enthalpy, onset temperature, or extrapolated onset temperature for trityl azide. Therefore, no bias information can be provided.

15.4.1 The mean values for the reaction enthalpy, onset temperature and extrapolated onset temperature of trityl azide were observed to be: $\Delta H = 722.8 \text{ kJ g}^{-1}$, $T_o = 158.7 \text{ °C}$, $T_e = 196.5 \text{ °C}$.

15.4.2 Intralaboratory testing on one material (t-butylperoxybenzoate) in a single laboratory provides the following information:

15.4.2.1 The mean value for the extrapolated onset temperature is 118.1 °C at 10 °C min⁻¹ heating rate. It ranges from 109.7 to 122.0 °C for heating rates between 4 and 14 °C min⁻¹.

15.4.2.2 The mean value for the enthalpy of reaction by DSC is $987 \pm 83 \text{ J g}^{-1}$. This values compare with values in the literature of $709 \pm 23 \text{ J g}^{-1}$ for thermal decomposition in organic solvents measured by microcalorimetry⁵

16. Keywords

16.1 Differential scanning calorimetry; hazard potential; thermal analysis; thermal hazard; thermal stability

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E27–1003.

⁵ Villenave, J.J., Filliatre, C., Mallard, B., *Thermochimica Acta*, Vol.39, pp 215–226 (1980).

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