



Designation: E537 – 24

Standard Test Method for Thermal Stability of Chemicals by Differential Scanning Calorimetry¹

This standard is issued under the fixed designation E537; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

INTRODUCTION

Committee E27 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 (version 11.0 in 2023) 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.

NOTE 1—Caution should be used if trying to use pressure differential scanning calorimetry to understand the thermal stability of a liquid or a solid (if it melts during the test or produces gas or liquid products), because the headspace volume to sample size is relatively large, so that the vaporization effect could significantly skew the results. Typically, the pressure differential scanning calorimeter would be limited to situations where a pressurized reactive headspace is required (that is, reactivity of a liquid or solid sample with a gas, more detail in [Appendix X1](#)). Sealed high-pressure sample containers are still recommended for the evaluation of intrinsic thermal stability of liquid or solid samples, even within a pressure DSC instrument.

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

1.3 This test method may be performed in a sealed high-pressure sample container with an inert or a reactive headspace

atmosphere with an absolute pressure range from 100 Pa through 30 MPa and over a temperature range from 273 K to 800 K (0 °C to 527 °C).

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4.1 *Exceptions*—Inch-pound units are provided as a courtesy to the user in [X1.3.3](#), [X1.4.1](#), and [X1.4.2](#).

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific safety precautions are given in [Section 8](#).

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:³

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 www.astm.org/contact. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

D6186 Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC)

E473 Terminology Relating to Thermal Analysis and Rheology

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

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

E968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters (Withdrawn 2023)⁴

E1445 Terminology Relating to Hazard Potential of Chemicals

E1858 Test Methods for Determining Oxidation Induction Time of Hydrocarbons by Differential Scanning Calorimetry

E1860 Test Method for Elapsed Time Calibration of Thermal Analyzers

E2009 Test Methods for Oxidation Onset Temperature of Hydrocarbons by Differential Scanning Calorimetry

E2744 Test Method for Pressure Calibration of Thermal Analyzers

3. Terminology

3.1 Definitions:

3.1.1 Specific technical terms used in this standard are defined in Terminologies **E473** and **E1445**, including *calorimeter*, *differential scanning calorimetry*, *extrapolated onset value*, *first-deviation-from-baseline*, *peak*, *reaction*, and *thermal stability*.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *DSC curve*, *n*—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 **E473**).

3.2.1.1 *first scan*—DSC curve of the first ramping from start temperature to end temperature. It records the thermal activity of the original sample.

3.2.1.2 *rescan*—DSC curve of the second ramping from the start temperature to the end temperature with the same tested sample after the cool-down following the first scan. It records the thermal activity of the sample having been heated in the first scan or decomposition products of the original sample.⁵ Typically, it provides a good reference for baseline.

3.2.2 *onset temperature* (T_o), *n*—the temperature at which a deflection from the established heat flow baseline is first observed (left limit in **Figs. 1 and 2**).

3.2.2.1 *Discussion*—This is also known as the first deviation from the baseline or the left limit of the peak integration. For thermal stability evaluation, this onset temperature is recommended to use.

3.2.3 *extrapolated onset temperature* (T_x)—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 (onset in **Figs. 1 and 2**).

3.2.4 *peak temperature* (T_p), *n*—the temperature corresponding to the maximum heat flow deflection of the DSC curve (peak in **Figs. 1 and 2**).

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. Also measured are the absolute temperature (T) of the sample or reference or the average temperature of both and elapsed time.

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 heated simultaneously at a controlled rate of 2 K/min to 20 K/min (10 K/min is recommended for a general thermal stability evaluation purpose) with an appropriate headspace 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_x), peak temperature (T_p), end temperature (T_e), and the integrated peak area (enthalpy change, dH) 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 (or a screening test) for detecting the thermal hazards of a chemical substance or a mixture where the thermal stability is poorly understood (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 If sample mass loss (the mass difference before and after DSC analysis divided by the tested sample mass before DSC analysis) is greater than 10 %, a leak likely has happened and the data is compromised. Sample leaking typically causes an artificial endotherm or cancels exothermic activities which could lead to an unsafe thermal stability evaluation.⁵ Therefore, it is highly recommended to discard such data and repeat the analysis.

⁴ The last approved version of this historical standard is referenced on www.astm.org.

⁵ Sheng, M., Valco, D., Tucker, C., Cayo, E., Lopez, T., *Organic Process Research & Development*, Vol 23(10), 2019, pp. 2200–2209.

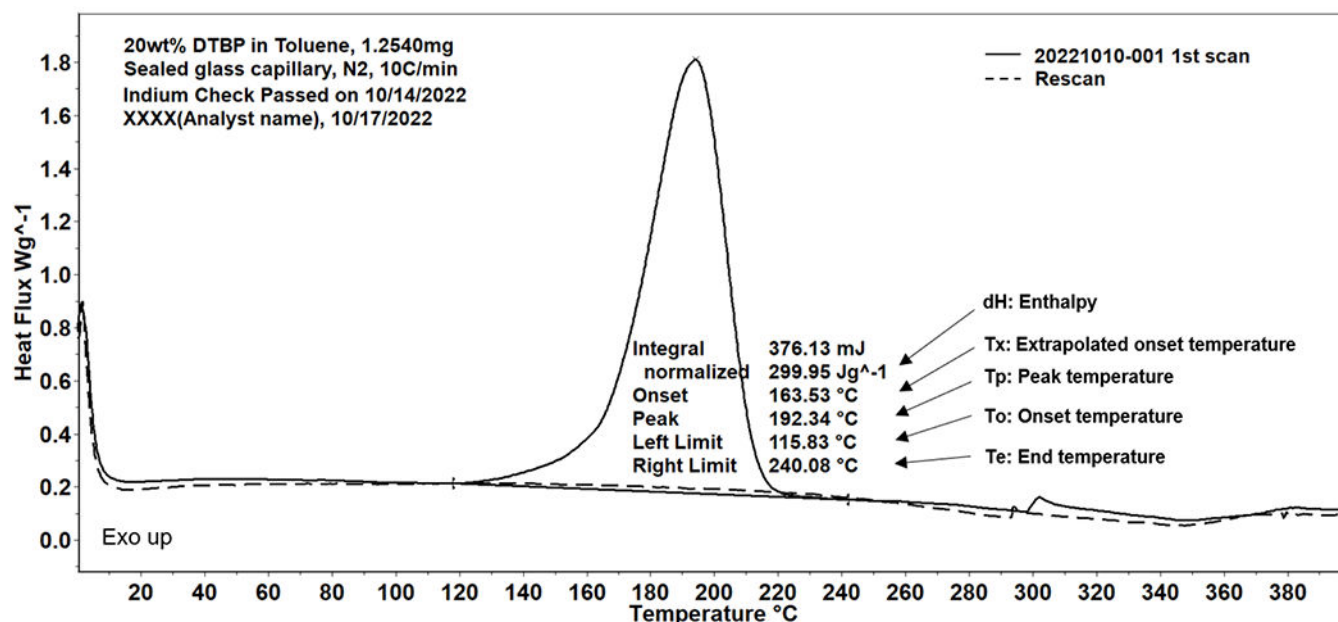


FIG. 1 Typical DSC Curve with Exotherm; Tested Sample: 20 % by Weight Di-tert-butyl peroxide (DTBP) in Toluene; Solid Curve – The First Scan; Dash Curve – The Rescan of the Same Sample

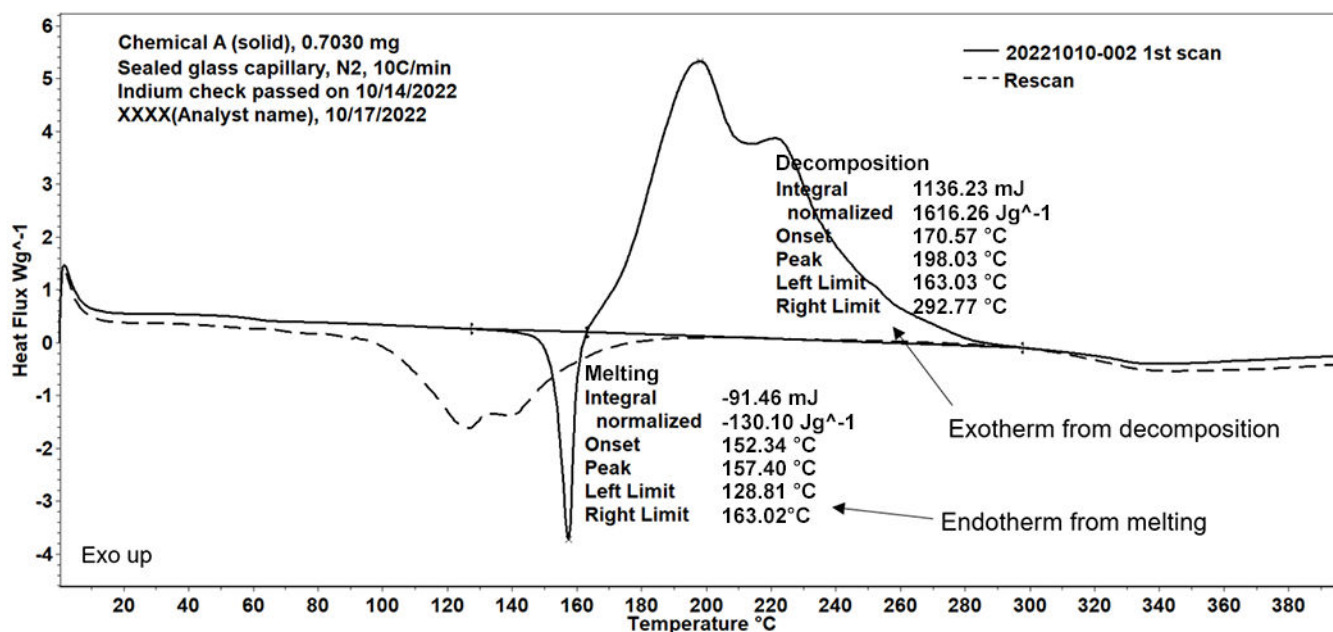


FIG. 2 DSC Curve Illustrating a Melting Process Immediately Followed by an Exotherm

5.4 When solid substances which will melt in the temperature range of a DSC analysis or liquids are being studied, it is important to perform the DSC analysis within a sealed high-pressure DSC sample container (able to hold at least 7 MPa or two times the vapor pressure at the highest temperature). Such sealed high-pressure containers could minimize the endothermic effect of vaporization. For example, 20 % by weight DTBP in toluene sample has been studied within a pinhole aluminum pan and a sealed aluminum pan in a temperature range from 0 °C to 400 °C. Both analyses had a sample mass loss of over 99 %. The pinhole aluminum pan one (Fig. 3) demonstrates a

single endotherm peak due to the vaporization around the boiling point (boiling point: 111 for DTBP, 110.6 for toluene), while the sealed aluminum pan one (Fig. 4) shows rupture activities. Neither of them provides the exotherm information, as seen in Fig. 1.⁵

5.5 The headspace gas in the sealed high-pressure DSC sample container may impact thermal stability evaluation. A reactive headspace gas may introduce an exothermic peak (for example, oxidation peak when using air) compared to an inert headspace gas, especially for organic samples.⁵ For example,