



Designation: E537 – 20

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 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 K to 800 K (27 °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 5.3, 7.2.2.1, 7.2.2.2, and 11.4.

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

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

E1445 Terminology Relating to Hazard Potential of Chemicals

E1860 Test Method for Elapsed Time Calibration of Thermal Analyzers

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.

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**).

3.2.2 *onset temperature (T_o), n*—the temperature at which a deflection from the established heat flow baseline is first observed.

3.2.2.1 *Discussion*—This is also known as the first-deviation-from-baseline.

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

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 simultaneously heated at a controlled rate of 2 K/min to 20 K/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_s), 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 1—The choice of pressure may sometimes be estimated by the pressure of the application to which the material is exposed.

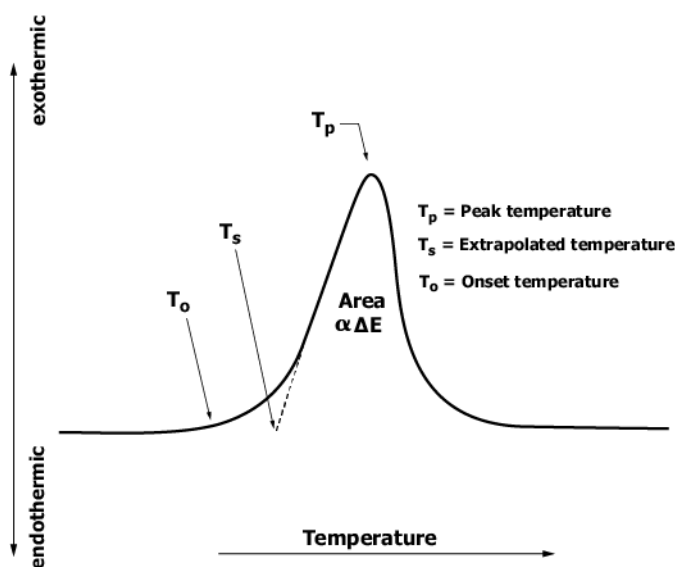


FIG. 1 Typical *DSC* Curve with Exotherm

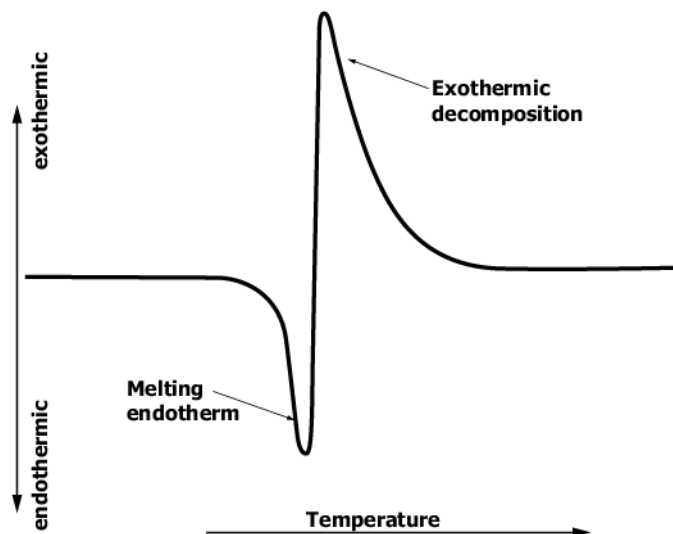


FIG. 2 DSC Curve Illustrating a Melting Process Immediately Followed by an Exothermic Decomposition

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 test method,

7.2.1.2 *Temperature sensor*, to provide an indication of the specimen/furnace temperature to ± 0.1 K,

7.2.1.3 *Differential sensor*, to detect a temperature or heat flow difference between the specimen and reference equivalent to 0.1 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 2—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 3—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 K/min to 20 K/min constant to ± 0.1 K/min, and

NOTE 4—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 A *data collection device*, to provide a means of acquiring, storing, and displaying measured or calculated signals, or both. The minimum output signals required for differential scanning calorimetry are, heat flow, temperature, and time.

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 MPa to 1.27 MPa (0 psig 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 MPa and 1.3 MPa (0 psig 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: