



~~Designation: E 537-02~~ Designation: E 537 - 07

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 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 Department of Defense.

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 ~~covers~~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 Practice~~ 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 ~~Hazardous~~Hazard Potential of Chemicals

E 1860 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 Annual Book of ASTM Standards, Vol 14.02.

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 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).

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),

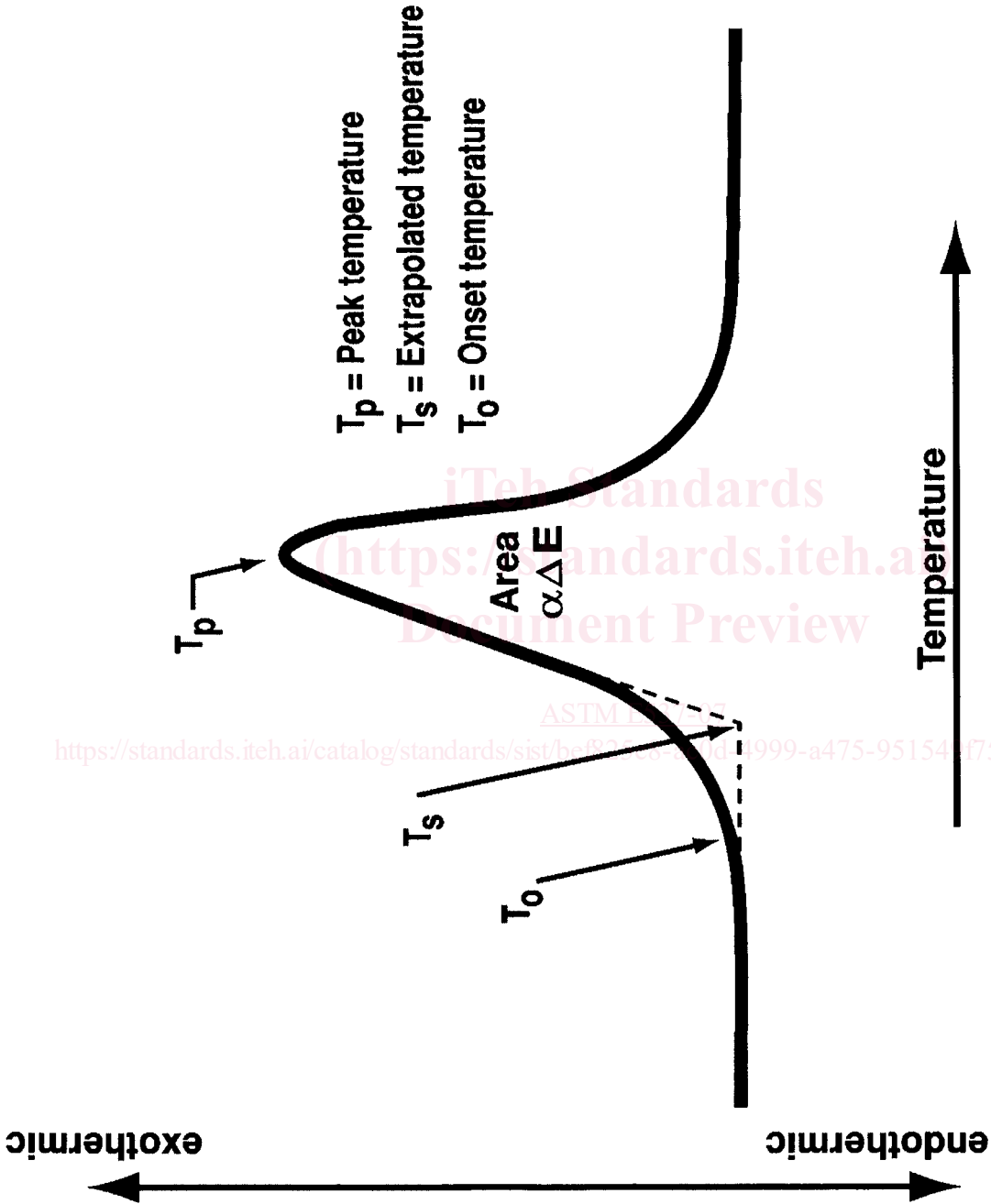


FIG. 1 Typical DSC Curve with Exotherm

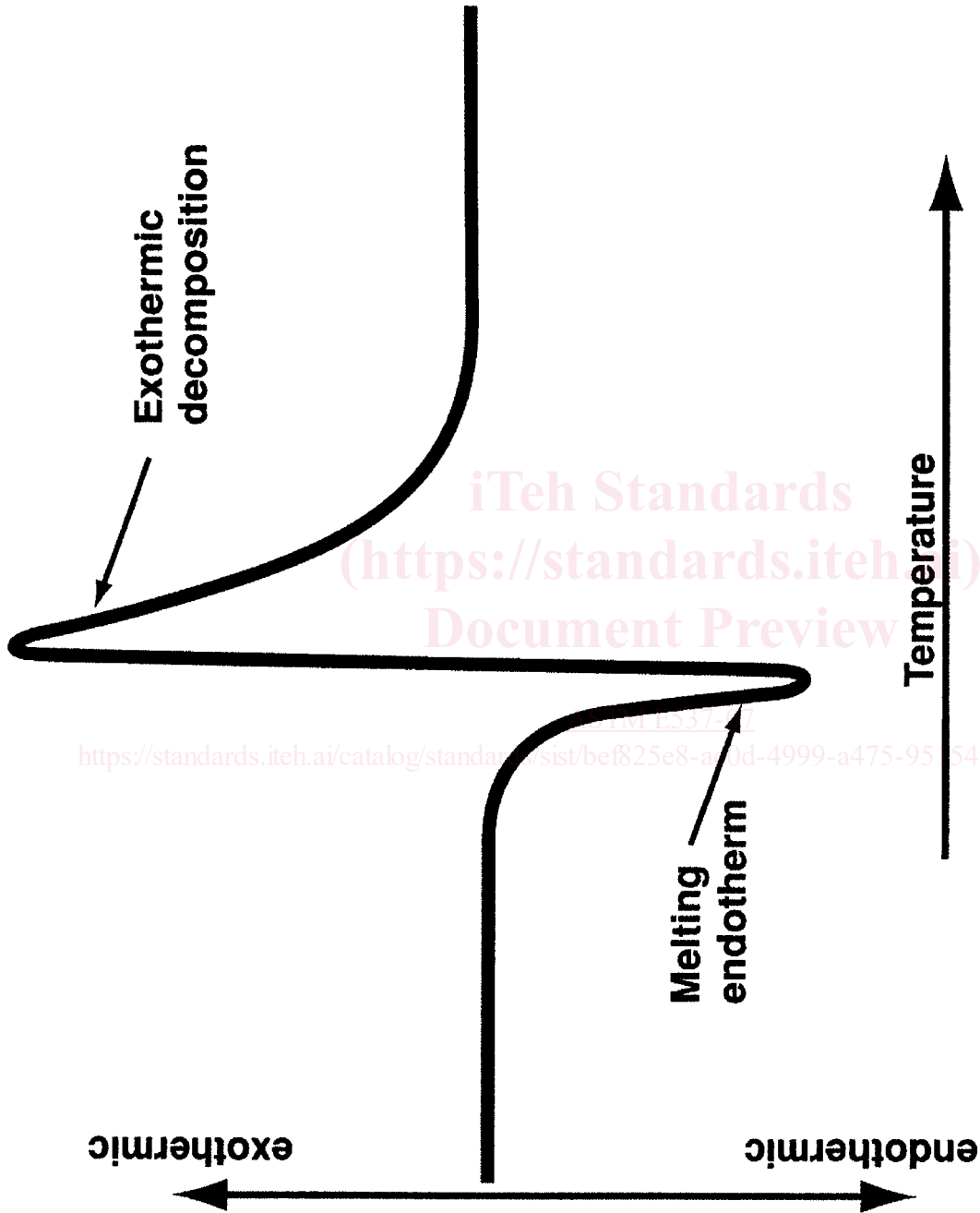


FIG. 2 DSC Curve Illustrating a Melting Process Immediately Followed by an Exothermic Decomposition