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Standard Guide for Assessing Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry[1]

This standard is issued under the fixed designation E1981; 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.

INTRODUCTION

This guide is one of several standards being developed by ASTM Committee E27 for determining the physicochemical hazards of chemicals and chemical mixtures. This guide should be used in conjunction with other test methods, as a complete assessment of the hazard potential of chemicals must take into account a number of realistic factors not necessarily considered in this guide. 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.

It is the intent of this guide to include any calorimetric device consistent with the principles of adiabatic calorimetry. Device-specific information and specifications are located in appendices to the guide. Any reference to specific devices in the guide are for purposes of illustration or clarity only.

1. Scope

1.1 This guide covers suggested procedures for the operation of a calorimetric device designed to obtain temperature and pressure data as a function of time for systems undergoing a physicochemical change under nearly adiabatic conditions.

1.2 This guide outlines the calculation of thermodynamic parameters from the time, temperature, and pressure data recorded by a calorimetric device.

1.3 The assessment outlined in this guide may be used over a pressure range from full vacuum to the rated pressure of the reaction container and pressure transducer. The temperature range of the calorimeter typically varies from ambient to 500 °C, but also may be user specified (see 6.6).

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

1.5 *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 outlined in Section 7.

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:*[2]

E476 Test Method for Thermal Instability of Confined Condensed Phase Systems (Confinement Test) (Withdrawn 2008)[3]

E487 Test Methods for Constant-Temperature Stability of Chemical Materials

E537 Test Method for Thermal Stability of Chemicals by Differential Scanning Calorimetry

E680 Test Method for Drop Weight Impact Sensitivity of Solid-Phase Hazardous Materials

E698 Test Method for Kinetic Parameters for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method

E1231 Practice for Calculation of Hazard Potential Figures of Merit for Thermally Unstable Materials

[1] This guide 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] 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] The last approved version of this historical standard is referenced on www.astm.org.

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *adiabatic calorimeter, n*—an instrument capable of making calorimetric measurements while maintaining a minimal heat loss or gain between the sample and its environment, which is verifiable by the capability to continuously measure the temperature differential between the sample and its surroundings.

3.1.2 *autocatalytic reaction, n*—a chemical reaction in which a product or reaction intermediate functions as a catalyst.

3.1.3 *drift, n*—a gradual unintended increase or decrease in the system (sample container and surroundings) temperature due to limitations in the system calibration, or to changes which occur in the system after calibration.

3.1.4 *final temperature (T_{final}), n*—the observed system temperature at the end of an exotherm, generally at the temperature where the self-heat rate of the reaction has decreased below the operator-defined slope sensitivity threshold.

3.1.5 *heat of reaction (ΔH), n*—the net calculated heat (energy) liberated during an exothermic reaction.

3.1.6 *ideal adiabatic temperature rise (ΔT_{ad}), n*—the temperature rise which would be observed in an exothermic reaction if all of the heat liberated were used to increase the temperature of only the sample. It is conveniently calculated as the product of the observed adiabatic temperature rise, ΔT_{obs}, and the thermal inertia factor, φ.

3.1.7 *observed adiabatic temperature rise (ΔT_{obs}), n*—the observed temperature rise in the system during an exotherm; mathematically, it is equal to the temperature difference between the final temperature and the onset temperature of an exotherm.

3.1.8 *onset temperature (T_{start}), n*—the observed system temperature at the start of an exotherm where the self-heating rate first exceeds the operator-defined slope sensitivity threshold, usually 0.02 °C/min; the onset temperature is not a fundamental property of a substance, but is apparatus-dependent, based upon the inherent sensitivity of the calorimetric system.

3.1.9 *self-heating, adj*—any exothermic process which increases the temperature of the system by the self absorption of the liberated heat.

3.1.10 *thermal inertia factor (φ), n*—a correction factor applied to time and temperature differences observed in exothermic reactions in the system (sample and container) under test, which accounts for the sensible heat absorbed by the sample container that otherwise would lead to erroneously low heats of reaction and adiabatic temperature rise, as well as to erroneously high time to maximum rates (TMR's) (see 3.1.12). See also 10.1 for a mathematical formula definition of the thermal inertia factor.

3.1.11 *thermal runaway reaction, n*—a chemical reaction in which the heat generation rate in a system exceeds the heat removal rate of that system.

3.1.12 *time-to-maximum rate (TMR), n*—the amount of time that is needed for a reaction to reach its maximum self-heating rate or pressure rate in a thermal runaway reaction, normally referenced from the time corresponding to the onset temperature, but may also be referenced from any time-temperature point to the time at which the maximum self-heating or pressure rate occurs. The experimentally observed TMR is normally divided by the thermal inertia factor (see 3.1.10) to obtain a more conservative assessment of TMR. (TMR divided by the thermal inertia factor is often referred to as the "φ-corrected" TMR).

4. Summary of Guide

4.1 A sample is placed in a reaction container and positioned in the calorimeter (see Fig. 1).

4.2 The sample container is heated to a user-specified initial temperature and allowed to come to equilibrium, whereupon a search for evidence of an exothermic reaction is undertaken. An exotherm is considered to have occurred when the user-specified rate of temperature rise is first exceeded. If no exotherm is detected, the system temperature is raised a specified increment and the system allowed to equilibrate again. This heat-wait-search cycle is repeated until either an exotherm is detected or the upper temperature limit of the test is reached. If an exotherm is detected, the surroundings are kept at the same temperature as the reaction container, allowing the system to be maintained without heat loss as the temperature of the system increases due to the heat evolved during the exotherm.

4.3 Time, temperature, and pressure data are recorded at specified temperature intervals as a function of time. Additional user-selected parameters may also be recorded or stored.

4.4 The recorded data are used to calculate the time rates of changes of pressure and temperature. These data may also be used to calculate a time-to-maximum rate (as defined in 3.1.12) and to obtain kinetic parameters **(1-4)**[4] for simple, non-autocatalytic exothermic reactions using the equations specified in the vendors' manual (subject to the limitations of 6.5). These data may also be adjusted for the sample- and container-specific heats to calculate an adiabatic temperature rise and heat of reaction.

5. Significance and Use

5.1 The data from this guide seldom, if ever, directly simulate thermal and pressure events in the processing, storage, and shipping of chemicals. However, the data obtained from this guide may be used, with suitable precautions, to predict the thermal and pressure hazards associated with processing, storage, and shipping of a chemical or mixture of chemicals after appropriate scaling of the data. This has been addressed in the literature **(1-4)** but is beyond the scope of this guide.

5.2 This guide is suitable, under the proper conditions, for the investigation of the effects of catalyst, inhibitors, initiators,

[4] The boldface numbers in parentheses refer to a list of references at the end of this standard.