



Designation: E 1231 – 01<sup>e1</sup>

## Standard Practice for Calculation of Hazard Potential Figures-of-Merit for Thermally Unstable Materials<sup>1</sup>

This standard is issued under the fixed designation E 1231; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>e1</sup> NOTE—Equation 6 was corrected editorially in February 2004

### 1. Scope

1.1 This practice covers the calculation of hazard potential figures-of-merit for exothermic reactions, including:

- (1) Time-to-thermal-runaway,
- (2) Critical half thickness,
- (3) Critical temperature,
- (4) Adiabatic decomposition temperature rise
- (5) Explosion potential,
- (6) Shock sensitivity,
- (7) Instantaneous power density, and
- (8) NFPA instability rating.

1.2 The kinetic parameters needed in this calculation may be obtained from differential scanning calorimetry (DSC) curves by methods described in other documents.

1.3 This technique is the best applicable to simple, single reactions whose behavior can be described by the Arrhenius equation and the general rate law. For reactions which do not meet these conditions, this technique may, with caution, serve as an approximation.

1.4 The calculations and results of this practice might be used to estimate the relative degree of hazard for experimental and research quantities of thermally unstable materials for which little experience and few data are available. Comparable calculations and results performed with data developed for well characterized materials in identical equipment, environment, and geometry are key to the ability to estimate relative hazard.

1.5 The figures-of-merit calculated as described in this practice are intended to be used only as a guide for the estimation of the relative thermal hazard potential of a system (materials, container, and surroundings). They are not intended to predict actual thermokinetic performance. The calculated errors for these parameters are an intimate part of this practice and must be provided to stress this. It is strongly recommended that those using the data provided by this practice seek the consultation of qualified personnel for proper interpretation.

1.6 The SI units are standard.

1.7 There is no ISO standard equivalent to this practice.

1.8 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

### 2. Referenced Documents

2.1 *ASTM Standards:*

**C 177** Test Method for Steady-State Heat Flux Measurements and Thermal Transmission Properties by Means of the Guarded Hot Plate Apparatus<sup>2</sup>

**C 518** Test Method for Steady-State Heat Flux Measurements and Thermal Transmission Properties by Means of the Heat Flow Meter Apparatus<sup>2</sup>

**D 4351** Test Method for Measuring the Thermal Conductivity of Plastics by the Evaporation-Calorimetric Method<sup>3</sup>

**E 473** Terminology Relating to Thermal Analysis<sup>4</sup>

**E 537** Test Method for Assessing the Thermal Stability of Chemicals by Methods of Differential Thermal Analysis<sup>4</sup>

**E 698** Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials<sup>4</sup>

**E 793** Test Method for Heats of Fusion and Crystallization by Differential Scanning Calorimetry<sup>4</sup>

**E 1269** Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry<sup>4</sup>

**E 1952** Test Method for Determining Thermal Conductivity and Thermal Diffusivity by Modulated Temperature Differential Scanning Calorimetry<sup>4</sup>

**E 2041** Method for Estimating Kinetic Parameters by Differential Scanning Calorimetry Using the Borchardt and Daniels Method<sup>4</sup>

**E 2070** Test Method for Kinetic Parameters by Differential Scanning Calorimetry Using Isothermal Methods<sup>4</sup>

2.2 *Other Standards:*

Publication 704, Identification of the Hazards of Materials

<sup>1</sup> This practice 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.

Current edition approved Feb. 10, 2001. Published April 2001. Originally published as E 1231 – 88. Last previous edition E 1231 – 96a.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 04.06.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 08.03.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.02.

for Emergency Response, 1996<sup>5</sup>

### 3. Terminology

#### 3.1 Definitions:

3.1.1 The definitions relating to thermal analysis appearing in Terminology E 473 shall be considered applicable to this practice.

#### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *time-to-thermal-runaway*,  $t_c$ —an estimation of the time required for an exothermic reaction, in an adiabatic container, (that is, no heat gain or loss to the environment), to reach the point of thermal runaway, expressed by Eq 1.

3.2.2 *critical half thickness*,  $a$ —an estimation of the half thickness of a sample in an *unstirred container*, in which the heat losses to the environment are less than the retained heat. This buildup of internal temperature leads to a thermal-runaway reaction, expressed by Eq 2.

3.2.2.1 *Discussion*—This description assumes perfect heat removal at the reaction boundary. This condition is not met if the reaction takes place in an insulated container such as when several containers are stacked together or when a container is boxed for shipment. These figures-of-merit underestimate the hazard as a result of this underestimation of thermal conductivity.

3.2.3 *critical temperature*,  $T_c$ —an estimation of the lowest temperature of an *unstirred container* at which the heat losses to the environment are less than the retained heat leading to a buildup of internal temperature expressed by Eq 3. This temperature buildup leads to a thermal-runaway reaction. (See Note 1.)

3.2.4 *adiabatic decomposition temperature rise*,  $T_d$ —an estimation of the computed temperature which a specimen would attain if all of the enthalpy (heat) of decomposition reaction were to be absorbed by the sample itself, expressed by Eq 4. High values represent high hazard potential.

3.2.5 *explosion potential*,  $EP$ —an index value, the magnitude and sign of which may be used to estimate the potential for a rapid energy release that may result in an explosion. Positive values indicate likelihood. Negative values indicate unlikelihood. The reliability of this go-no-go indication is provided by the magnitude of the numerical value. The greater the magnitude, the more reliable the go-no-go indication.

3.2.6 *shock sensitivity*,  $SS$ —an estimation of the sensitivity of a material to shock induced reaction relative to *m*-dinitrobenzene reference material. A positive value indicates greater sensitivity; a negative value less sensitivity. The reliability of this go-no-go indication is provided by the magnitude of the numerical value. The greater the magnitude, the more reliable the go-no-go indication.

3.2.7 *instantaneous power density*,  $IPD$ —the amount of energy per unit time per unit volume initially released by an exothermic reaction.

3.2.7.1 *Discussion*—This practice calculates the  $IPD$  at 250°C (482°F, 523 K).

3.2.8 *NFPA instability rating*,  $IR$ —an index value for ranking, on a scale of 0 to 4, the instantaneous power density of materials. The greater the value, the more unstable the material.

### 4. Summary of Practice

4.1 This practice describes the calculation of eight figures-of-merit used to estimate the relative thermal hazard potential of thermally unstable materials. These figures-of-merit include time-to-thermal-runaway ( $t_c$ ), critical half thickness ( $a$ ), critical temperature ( $T_c$ ), adiabatic decomposition temperature rise ( $T_d$ ), explosion potential ( $EP$ ), shock sensitivity ( $SS$ ), instantaneous power density ( $IPD$ ), and instability rating ( $IR$ ). These calculations are based upon the determined or assumed values for activation energy ( $E$ ), pre-exponential factor ( $Z$ ), specific heat capacity ( $C_p$ ), thermal conductivity ( $\lambda$ ), heat of reaction ( $H$ ), and density or concentration ( $\rho$ ). The activation energy and pre-exponential factor may be calculated using Test Method E 698, Method E 2041, or Test Method E 2070. The specific heat capacity may be obtained from Test Method E 1269. Thermal conductivity may be obtained from Test Methods C 177, C 518, D 4351, or E 1952. Heat of reaction may be obtained from Test Method E 793. Values for concentration or density may be estimated from known values of model materials or through actual measurement. In addition, certain assumptions, such as initial temperature and container geometries, must be supplied.

### 5. Significance and Use

5.1 This practice provides eight figures-of-merit which may be used to estimate the relative thermal hazard potential of thermally unstable materials. Since numerous assumptions must be made in order to obtain these figures-of-merit, care must be exercised to avoid too rigorous interpretation (or even misapplication) of the results.

5.2 This practice may be used for comparative purposes, specification acceptance, and research. It should not be used to predict actual performance.

### 6. Interferences

6.1 Since the calculations described in this practice are based upon assumptions and physical measurements which may not always be precise, care must be used in the interpretation of the results. These results should be taken as relative figures-of-merit and not as absolute values.

6.2 The values for time-to-thermal-runaway, critical half thickness, and critical temperature are exponentially dependent upon the value of activation energy. This means that small imprecisions in activation energy may produce large imprecisions in the calculated figures-of-merit. Therefore, activation energy of the highest precision available should be used (**1**).<sup>6</sup>

6.3 Many energetic materials show complex decompositions with important induction processes. Many materials are used or shipped as an inhibited or stabilized composition, ensuring an induction process. In such cases, time-to-thermal-runaway will be determined largely by the induction process

<sup>5</sup> Available from the National Fire Protection Association, Quincy, MA.

<sup>6</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

while critical temperature will be determined by the maximum-rate process. These two processes typically have very different kinetic parameters and follow different rate-law expressions.

6.4 It is believed that critical temperature, using the same size and shape container, provides the best estimate of relative thermal hazard potential for different materials (see Section 10).

## 7. Apparatus

7.1 No special apparatus is required for this calculation.

## 8. Calculation

8.1 Time-to-thermal-runaway from sample initial temperature  $T$  is defined by (see Ref (2)):

$$t_c = \frac{C_p R T^2 e^{E/RT}}{E Z H} \quad (1)$$

where:

- $t_c$  = time-to-thermal-runaway, s,
- $C_p$  = specific heat capacity, J/(g K),
- $R$  = gas constant = 8.314 J/(K mol),
- $E$  = activation energy, J/mol,
- $Z$  = pre-exponential factor, s<sup>-1</sup>,
- $H$  = enthalpy (heat) of reaction, J/g, and
- $T$  = initial temperature, K.

8.2 Critical half thickness at environmental temperature  $T_o$  is defined by (see Ref (3)):

$$a = \left( \frac{\delta \lambda R T_o^2 e^{E/RT_o}}{H Z E \rho} \right)^{\frac{1}{2}} \quad (2)$$

where:

- $a$  = critical half-thickness, cm,
- $\lambda$  = thermal conductivity, W/(cm K),
- $T_o$  = environment temperature, K,
- $\rho$  = density or concentration, g/cm<sup>3</sup>, and
- $\delta$  = form factor (dimensionless) (3, 5):

- 0.88 for infinite slab,
- 2.00 for infinite cylinder,
- 2.53 for a cube,
- 2.78 for a square cylinder, and
- 3.32 for sphere.

8.3 Critical temperature  $T_c$  is defined by (see Refs (1) and (4)):

$$T_c = \left( \frac{R}{E} \ln \left( \frac{d^2 \rho H Z E}{T_c^2 \lambda \delta R} \right) \right)^{-1} \quad (3)$$

where:

- $T_c$  = critical temperature, K, and
- $d$  = shortest semi-thickness, cm.

8.4 Adiabatic decomposition temperature rise  $T_d$  is defined by:

$$T_d = \frac{H}{C_p} \quad (4)$$

where:

- $T_d$  = adiabatic decomposition temperature rise, K.

8.5 Explosion potential  $EP$  is defined by (Refs 7 and 8):

$$EP = \log[H] - 0.38 \log[T_{onset} - 298 \text{ K}] - 2.29 \quad (5)$$

where:

- $EP$  = explosion potential, and
- $T_{onset}$  = onset temperature by DSC, K.

8.6 Shock sensitivity  $SS$  is defined by (Ref 7):

$$SS = \log[H] - 0.72 \log[T_{onset} - 298 \text{ K}] - 1.60 \quad (6)$$

where:

- $SS$  = shock sensitivity relative to *m*-dinitrobenzene.

8.7 Instantaneous power density at 250°C is defined by (NFPA 704):<sup>7</sup>

$$IPD = H Z \rho \exp[-E/523 \text{ K R}] \quad (7)$$

8.8 Instability rating is defined by Table 1 (NFPA 704).

TABLE 1 NFPA Instability Rating

Instability Rating	Instantaneous Power Density at 523 K
4	1000 W mL <sup>-1</sup> or greater
3	at or greater than 100 W mL <sup>-1</sup> and below 1000 W mL <sup>-1</sup>
2	at or greater than 10 W mL <sup>-1</sup> and below 100 W mL <sup>-1</sup>
1	at or greater than 0.01 W mL <sup>-1</sup> and below 10 W mL <sup>-1</sup>
0	below 0.01 W mL <sup>-1</sup>

### 8.9 Methods of Obtaining Parameters:

8.9.1 The activation energy  $E$  and frequency factory  $Z$  may be obtained by Test Method E 698, Method E 2041, or Test Method E 2070. Other methods may be used but shall be reported.

NOTE 1—In Test Method E 698, Method E 2041, or Test Method E 2070, the activation energy and pre-exponential are mathematically related and must be determined from the same experimental study.

8.9.2 The enthalpy (heat) of reaction  $H$  may be obtained by Test Method E 793 or E 537. Other methods may be used but shall be reported.

8.9.3 Room temperature specific heat capacity,  $C_p$ , may be obtained by Test Method E 1269.

8.9.4 Environment temperature  $T_o$  is taken to be the temperature of the air space surrounding the unstirred container.

8.9.5 Concentration or density of material  $\rho$  is the amount of reactive material per unit volume. The value of 1.28 g/cm<sup>3</sup> may be assumed for many organic materials.

8.9.6 The form factor  $\delta$  is a dimensionless unit used to correct for the type of geometry for the unstirred container. Five cases are ordinarily used, including:

- (1) 0.88 for an infinite slab—essentially a two dimensional plane,
- (2) 2.00 for a cylinder of infinite height,
- (3) 2.53 for a cube,
- (4) 2.78 for a square cylinder, and
- (5) 3.32 for a sphere.

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