



Standard Practice for Calculation of Hazard Potential Figures-of-Merit for Thermally Unstable Materials¹

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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, and
- (4) Adiabatic decomposition temperature rise.

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 *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 Apparatus²
- C 518 Test Method for Steady-State Heat Flux Measurements and Thermal Transmission Properties by Means of the Heat Flow Meter Apparatus²
- D 4351 Test Method for Measuring the Thermal Conductivity of Plastics by the Evaporation-Calorimetric Method³
- E 473 Terminology Relating to Thermal Analysis⁴
- E 698 Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials⁴
- E 793 Test Method for Heats of Fusion and Crystallization by Differential Scanning Calorimetry⁴

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.

NOTE 1—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

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² *Annual Book of ASTM Standards*, Vol 04.06.

³ *Annual Book of ASTM Standards*, Vol 08.03.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

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.

4. Summary of Practice

4.1 This practice describes the calculation of four 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), and adiabatic decomposition temperature rise (T_d). 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 (λ), and density or concentration (ρ). The activation energy and pre-exponential factor may be calculated using Test Method E 698. Values for specific heat, thermal conductivity, and 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 four 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).⁵

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

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⁻¹,
 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,
 λ = thermal conductivity, W/(cm K),
 T_o = environment temperature, K,
 ρ = density or concentration, g/cm³, and
 δ = 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 Methods of Obtaining Parameters:

8.5.1 The activation energy E may be obtained in accordance with Test Method E 698. Other methods may be used but must be indicated in the report.

⁵ The boldface numbers in parentheses refer to the list of references at the end of this standard.