



Designation: E1231 – 10

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) Time-to-maximum-rate,
- (3) Critical half thickness,
- (4) Critical temperature,
- (5) Adiabatic decomposition temperature rise,
- (6) Explosion potential,
- (7) Shock sensitivity,
- (8) Instantaneous power density, and
- (9) 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 values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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:²

- C177 Test Method for Steady-State Heat Flux Measurements and Thermal Transmission Properties by Means of the Guarded-Hot-Plate Apparatus
- E518 Test Method for Steady-State Thermal Transmission Properties by Means of the Heat Flow Meter Apparatus
- E473 Terminology Relating to Thermal Analysis and Rheology
- E537 Test Method for The Thermal Stability of Chemicals by Differential Scanning Calorimetry
- E698 Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method
- E793 Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry
- E1269 Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry
- E1952 Test Method for Thermal Conductivity and Thermal Diffusivity by Modulated Temperature Differential Scanning Calorimetry
- E2041 Test Method for Estimating Kinetic Parameters by Differential Scanning Calorimeter Using the Borchardt and Daniels Method

¹ 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 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.

E2070 Test Method for Kinetic Parameters by Differential Scanning Calorimetry Using Isothermal Methods

2.2 *Other Standards:*

NFPA 704 Identification of the Hazards of Materials for Emergency Response, 1996³

3. Terminology

3.1 Definitions:

3.1.1 The definitions relating to thermal analysis appearing in Terminology **E473** shall be considered applicable to this practice.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *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 5**. High values represent high hazard potential.

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 3**.

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 4**. This temperature buildup leads to a thermal-runaway reaction. (See **Note 3**.)

3.2.4 *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.

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

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

3.2.6 *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.

3.2.7 *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.

3.2.8 *time-to-maximum-rate, TMR* —an estimate 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 maximum rate of reaction, expressed by **Eq 2**.

3.2.9 *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**.

4. Summary of Practice

4.1 This practice describes the calculation of nine 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), time-to-maximum-rate (*TMR*), 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 (λ), heat of reaction (H), heat flow rate (q) and density or concentration (ρ). The activation energy and pre-exponential factor may be calculated using Test Methods **E698**, **E2041**, or **E2070**. The specific heat capacity may be obtained from Test Method **E1269**. Thermal conductivity may be obtained from Test Methods **C177**, **C518**, or **E1952**. Heat of reaction may be obtained from Test Method **E793**. Heat flow rate may be obtained from Test Method **E2070**, 13.5, where it is called dH/dt . 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 nine 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

³ Available from National Fire Protection Association (NFPA), 1 Batterymarch Park, Quincy, MA 02169-7471, <http://www.nfpa.org>.

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).⁴

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).

6.5 Extrapolation of TMR to temperatures below those actually measured shall be done only with caution due to the potential changes in kinetics (activation energy), the potential for autocatalysis, and the propagation of errors.

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.

NOTE 1—Time-to-thermal-runaway is related to time-to-maximum-rate but assumes a first order reaction.

8.2 Time-to-maximum-rate, TMR, is defined by (see Refs (1) and (3)):

$$C_p R T_1^2 / E q \quad (2)$$

where:

- T_1 = initial temperature, K (that is, the temperature at which TMR is to be estimated), and
- q = mass normalized heat flow rate at (T_1), W/g.

NOTE 2—Time-to-maximum-rate is related to time-to-thermal-runaway but assumes a zeroth order reaction.

8.3 Critical half thickness at environmental temperature T_o is defined by (see Ref (4)):

$$a = \left(\frac{\delta \lambda R T_o^2 e^{E/RT_o}}{H Z E \rho} \right)^{\frac{1}{2}} \quad (3)$$

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

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) (4, 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.

8.4 Critical temperature T_c is defined by (see Refs (1) and (6)):

$$T_c = \left(\frac{R}{E} \ln \left(\frac{d^2 \rho H Z E}{T_c^2 \lambda \delta R} \right) \right)^{-1} \quad (4)$$

where:

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

8.5 Adiabatic decomposition temperature rise T_d is defined by:

$$T_d = \frac{H}{C_p} \quad (5)$$

where:

- T_d = adiabatic decomposition temperature rise, K.

8.6 Explosion potential EP is defined by (7, 8) :

$$EP = \log[H] - 0.38 \log[T_{onset} - 298 \text{ K}] - 2.29 \quad (6)$$

where:

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

8.7 Shock sensitivity SS is defined by (7):

$$SS = \log[H] + 0.72 \log[T_{onset} - 298 \text{ K}] - 1.60 \quad (7)$$

where:

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

8.8 Instantaneous power density at 250 °C is defined by (NFPA 704):⁵

$$IPD = H Z \rho \exp[-E/523 \text{ K } R] \quad (8)$$

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

8.10 *Methods of Obtaining Parameters:*

⁵ Reprinted with permission from NFPA 704–1996, “Identification of the Hazards of Materials for Emergency Response,” copyright © 1996, National Fire Protection Association, Quincy, MA. This reprinted material is not the complete and official position of the NFPA on the referenced subject which is represented only by the standard in its entirety.

TABLE 1 NFPA Instability Rating

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