Designation: E1231 – 15

Standard Practice for
Calculation of Hazard Potential Figures of Merit for Thermally Unstable Materials[1]

This standard is issued under the fixed designation E1231; 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.

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
C518 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 Kinetic Parameters 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.

Current edition approved Nov. 1, 2015. Published January 2016. Originally approved in 1988. Last previous edition approved in 2010 as E1231 – 10. DOI: 10.1520/E1231-15.

[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

E2716 Test Method for Determining Specific Heat Capacity by Sinusoidal Modulated Temperature Differential Scanning Calorimetry

E2890 Test Method for Kinetic Parameters for Thermally Unstable Materials by Differential Scanning Calorimetry Using the Kissinger Method

2.2 *Other Standards:*

NFPA 704 Identification of the Hazards of Materials for Emergency Response, 2012[3]

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, E2070, or E2890. The specific heat capacity may be obtained from Test Methods E1269 or E2716. 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 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.

---

[3] Available from National Fire Protection Association (NFPA), 1 Batterymarch Park, Quincy, MA 02269, http://www.nfpa.org.

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**).[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**)):

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

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**)):

$$TMR = C_p\, R\, T_1^2 / E\, q \qquad (2)$$

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**)):

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

where:

a = critical half-thickness, cm;
λ = thermal conductivity, W/(cm K);
T_o = environment temperature, K;
ρ = density or concentration, g/cm^3; 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**)):

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

where:

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

8.5 Adiabatic decomposition temperature rise T_d is defined by:

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

where:

T_d = adiabatic decomposition temperature rise, K.

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

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

where:

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

8.7 Shock sensitivity *SS* is defined by (**7**):

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

where:

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

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

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

---

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

[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.

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

8.10 *Methods of Obtaining Parameters:*

8.10.1 The activation energy E and frequency factor Z may be obtained by Test Methods E698, E2041, or E2070. Other methods may be used but shall be reported.

NOTE 3—In Test Methods E698 and E2041, the activation energy and pre-exponential are mathematically related and must be determined from the same experimental study.

8.10.2 The enthalpy (heat) of reaction H may be obtained by Test Methods E793 or E537. Other methods may be used but shall be reported.

8.10.3 Room temperature specific heat capacity, C_p, may be obtained by Test Method E1269.

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

8.10.5 Concentration or density of material ρ is the amount of reactive material per unit volume. The value of 1.28 g/cm^3 may be assumed for many organic materials.

8.10.6 The form factor δ 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.

8.10.7 Thermal conductivity λ may be obtained by Test Methods E1952, C177, or C518 or by estimation from literature values of model compounds. A value of 0.00040 W cm^{-1} K^{-1} may be assumed for many organic solid materials.

NOTE 4—The actual thermal conductivity of a material is quite dependent upon the form of the material–powder, fiber, solid, etc. The value may be as much as a factor of 10 lower than literature values depending upon packing.

8.10.8 The shortest half-thickness d is the distance from the center of the container to the outside in its shortest dimension.

8.10.9 Onset temperature, T_{onset}, shall be obtained by Test Method E537 or similar DSC methods.

8.10.10 The initial heat flow (q) at temperature T_1 may be obtained from Test Method E2070.

8.11 The values for time-to-thermal-runaway, time-to-maximum-rate, critical thickness, adiabatic decomposition temperature rise, explosion potential, shock sensitivity, and instability power density are calculated by substitution of parameters into Eq 1, Eq 2, Eq 4, Eq 5, Eq 6, and Eq 7, respectively. The value for instability rating is obtained from Table 1.

TABLE 1 NPFA 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}

8.12 The determination of critical temperature (such as Eq 4) requires an iterative determination. A value for critical temperature, T_c, is first assumed based upon one of the low heating rate curves used to obtain the activation energy from Test Method E698. This first estimation for critical temperature is substituted within the right side of Eq 4 and a new value for T_c is calculated. This new value is resubmitted to Eq 4 as T_c and a third estimation calculated. This process is repeated until the value calculated for T_c converges (that is the recalculated value differs from the previous calculation by less than 1 K).

8.13 Example calculations are as follows:

8.13.1 Assuming:

E = 132 kJ/mol^{-1},
Z = 2.00×10^9/s^{-1},
H = 2.40 kJ/g^{-1},
λ = 0.00040 W cm^{-1} K^{-1},
ρ = 1.280 g/cm^{-3},
δ = 2.0 (for cylinder),
C_p = 1.80 J/g^{-1} K^{-1},
R = 8.314 J/K^{-1} mol^{-1},
T = 330 K,
T_o = 300 K,
T_{onset} = 500 K,
D = 30 cm,
q = 0.20 W/g, and
T_i = 400 K.

8.13.2 Then:

$$t_c = \left[\frac{1.8\ \text{J}/(\text{g K}) \times 8.314\ \text{J}/(\text{K mol}) \times (330\ \text{K})^2}{132\,000\ \text{J/mol} \times 6.3 \times 10^{16}/\text{yr} \times 2400\ \text{J/g}}\right] \tag{9}$$

$$\times \exp\left[\frac{132\,000\ \text{J/mol}}{8.314\ \text{J}/(\text{K mol}) \times 330\ \text{K}}\right]$$

$$t_c = 8.166 \times 10^{-20}\ \text{years} \times \exp(48.11)$$

$$= 8.166 \times 10^{-20}\ \text{years} \times 7.845 \times 10^{20}$$

$$t_c = 64\ \text{years}$$

8.13.3

$$TMR = \left[\frac{1.8\,0\text{J}/(\text{g K}) \times 8.314\ \text{J}/(\text{K mol}) \times (400\ \text{K})^2}{132\,000\ \text{J/mol} \times 0.20\ \text{W/g} \times 1\ \text{J/W s}}\right] = 91\ s \tag{10}$$

NOTE 5—This *TMR* value indicates a hazardous condition (that is, short time) unacceptable for most processes

8.13.4 And:

$$a = \left[\frac{2.0 \times 0.00040\ \text{W}/(\text{cm K}) \times 8.314\ \text{J}/(\text{K mol}) \times (300\ \text{K})^2}{2400\ \text{J/g} \times 2.0 \times 10^9/\text{s} \times 132\,000\ \text{J/mol} \times 1.28\ \text{g/cm}^3}\right. \tag{11}$$

$$\left.\exp\left[\frac{132\,000\ \text{J/mol}}{\{(8.314\ \text{J/K mol})(300\ \text{K})\}}\right]\right]^{\frac{1}{2}}$$

$$a = [7.38 \times 10^{-16}\ \text{cm}^2 \times \exp(52.9)]^{\frac{1}{2}}$$

$$a = [6.95 \times 10^{+7}]^{\frac{1}{2}} = 8.3 \times 10^3\ \text{cm}$$

8.13.5 Assume:

$$T_c' = 560\ \mathrm{K} \tag{12}$$

$$T_c'' = \left[\frac{8.314\ \mathrm{J/K\ mol}}{132\,000\ \mathrm{J/mol}} \right.$$

$$\times \ln\left(\frac{(30\ \mathrm{cm})^2 \times 1.28\ \mathrm{g/cm}^3 \times 2400\ \mathrm{J/g}}{(560\ \mathrm{K})^2 \times 0.00040\ \mathrm{W/(cm\ K)}} \right.$$

$$\left. \left. \times \frac{2.0 \times 10^9/\mathrm{s} \times 132\,000\ \mathrm{J/mol}}{2.0 \times 8.314\ \mathrm{J/(K\ mol)}} \right) \right]^{-1}$$

$$T_c'' = \left[\frac{1}{15\,877\ \mathrm{K}} \times \ln(3.50 \times 10^{17}) \right]^{-1} = \left[\frac{40.40}{15\,877\ \mathrm{K}} \right]^{-1}$$

$$T_c'' = 393\ \mathrm{K}$$

A second interation produces:

$$T_c''' = 386\ \mathrm{K} \tag{13}$$

$$T_c'''' = 386\ \mathrm{K}$$

8.13.6

$$T_d = (2.40\ \mathrm{kJ\ g^{-1}} \times 1000\ \mathrm{J\ kJ^{-1}})/(1.80\ \mathrm{J\ g^{-1}\ K^{-1}}) = 1333\ \mathrm{K} \tag{14}$$

8.13.7

$$EP = \log[2.40\ \mathrm{kJ\ g^{-1}} \times 1000\ \mathrm{J\ kJ^{-1}}] \tag{15}$$

$$-0.38 \log[500\ \mathrm{K} - 298\ \mathrm{K}] - 2.29$$

$$= 3.38 - 0.38 \times 2.31 - 2.29$$

$$= 0.21$$

8.13.8

$$SS = \log[2.40\ \mathrm{kJ\ g^{-1}} \times 1000\ \mathrm{J\ kJ^{-1}}] \tag{16}$$

$$-0.72 \log[500\ \mathrm{K} - 298\ \mathrm{K}] - 1.60$$

$$= 3.38 - 0.72 \times 2.31 - 1.60$$

$$= 0.12$$

8.13.9

$$IPD = 2.40\ \mathrm{kJ\ g^{-1}} \times 1000\ \mathrm{J\ kJ^{-1}} \times 2.00 \times 10^9\ \mathrm{s^{-1}} \tag{17}$$

$$\times 1.28\ \mathrm{g\ cm^{-3}} \times \mathrm{cm^3\ mL^{-1}} \times \mathrm{W\ s\ J^{-1}}$$

$$\times \exp[-\ 132\ \mathrm{kJ\ mol^{-1}}\ \times\ 1000\ \mathrm{J\ kJ^{-1}}$$

$$/\ (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}} \times 523\ \mathrm{K})]$$

$$= 6.144 \times 10^{12}\ \mathrm{W\ mL^{-1}} \times \exp[-30.357]$$

$$= 6.144 \times 10^{12}\ \mathrm{W\ mL^{-1}} \times 6.548 \times 10^{-14}$$

$$= 0.40\ \mathrm{W\ mL^{-1}}$$

8.13.10 The instability rating, *IR*, is determined from Table 1. The *IR* value is 1 for *IPD* = 0.40 W mL^{-1}.

8.14 Estimation of uncertainty in values for time-to-thermal-runaway, critical half thickness, critical temperature, adiabatic decomposition temperature rise, explosion potential, shock sensitivity, and instantaneous power density are defined in 10.1.1 – 10.1.8, respectively.

9. Report

9.1 The report shall include the following:

9.1.1 Identification of the sample by name or composition, stating the source, past history, form (that is, solid or liquid), and weight of the sample taken together with its purity and method of assessing purity.

9.1.2 The values for all parameters used in the calculation, their sources whether experimentally determined, obtained from handbooks, or estimated, and their uncertainties.

9.1.3 The calculated values for time-to-thermal-runaway, critical temperature, critical thickness, adiabatic decomposition temperature rise, explosion potential, shock sensitivity, instantaneous power density, and their respective uncertainties along with NFPA instability power rating.

10. Precision and Bias

10.1 The relative error of the individual figures of merit may be estimated by the propagation of errors method (**9**).

10.1.1 The relative error of the calculated time-to-thermal-runaway value may be estimated by:

$$\frac{\Delta t_c}{t_c} = \left[\left(\frac{\Delta C_p}{C_p} \right)^2 + \left(\frac{\Delta Z}{Z} \right)^2 + \left(\frac{\Delta H}{H} \right)^2 + \left(\frac{1}{RT} - \frac{1}{E} \right)^2 (\Delta E)^2 \right]^{\frac{1}{2}} \tag{18}$$

where:

Δt_c = estimation of error in the calculation of time-to-thermal-runaway, s,

ΔC_p = estimation of error in the specific heat capacity value, J/(g K),

$\Delta\ E$ = estimation of error in the activation energy value, J/mole,

ΔZ = estimation of error in the pre-exponential factor, s^{-1}, and

ΔH = estimation of error in the enthalpy (heat) of reaction value, J/g.

NOTE 6—Since the pre-exponential factor *Z* is determined from the activation energy *E* and a function of the reaction rate, the error in *Z* (that is, Δ*Z*) is dependent upon the error in *E* (that is, Δ*E*) and temperature, *T*.

$$\frac{\Delta Z}{Z} = \exp\left[\frac{\Delta E}{R} \left(\frac{1}{T'} - \frac{1}{T''} \right) \right]\ 1 \tag{19}$$

where:

T' = the temperature in the center of the experimental range over which *E* and *Z* have been determined and

T'' = the temperature at which the data is being used (that is, $\cong T_c$, T_o, or *T*).

10.1.2 The relative error of the calculated time-to-maximum-rate value may be estimated by:

$$\frac{\Delta TMR}{TMR} = \left[\left(\frac{\Delta C_p}{C_p} \right)^2 + 2\left(\frac{\Delta T_1}{T_1} \right) + \left(\frac{\Delta E}{E} \right)^2 2 + \left(\frac{\Delta q}{q} \right)^2 \right]^{\frac{1}{2}} \tag{20}$$

10.1.3 The relative error of the calculated critical half thickness value may be estimated by (see Note 6):

$$\frac{\Delta a}{a} = \frac{1}{2} \left[\left(\frac{\Delta \lambda}{\lambda} \right)^2 + \left(\frac{\Delta H}{H} \right)^2 \right. \tag{21}$$

$$\left. + \left(\frac{\Delta Z}{Z} \right)^2 + \left(\frac{\Delta \rho}{\rho} \right)^2 + \left(\frac{1}{RT_o} - \frac{1}{E} \right)^2 (\Delta E)^2 \right]^{\frac{1}{2}}$$

where:

Δa = estimation of error in the calculation of critical semi-thickness, cm,

$\Delta\lambda$ = estimation of error in thermal conductivity value, W/(cm K), and

$\Delta\rho$ = estimation of error in the density or concentration value, g/cm^3.

10.1.4 The relative error of the calculated critical temperature value may be estimated by (see Note 6):

$$\frac{\Delta T_c}{T_c} = \frac{RT_c}{(2RT_c - E)}\left[\left(\frac{\Delta\rho}{\rho}\right)^2 + \left(\frac{\Delta H}{H}\right)^2 + \left(\frac{\Delta Z}{Z}\right)^2 + \left(\frac{\Delta\lambda}{\lambda}\right)^2 + \left(1 - \frac{E}{RT_c}\right)^2\left(\frac{\Delta E}{E}\right)^2\right]^{\frac{1}{2}} \quad (22)$$

10.1.5 The relative error of the calculated adiabatic decomposition temperature rise may be estimated by:

$$\frac{\Delta T_d}{T_d} = \left[\left(\frac{\Delta H}{H}\right)^2 + \left(\frac{\Delta C_p}{C_p}\right)^2\right]^{\frac{1}{2}} \quad (23)$$

where:

ΔT_d = estimation of error in adiabatic decomposition temperature rise value, K, and

10.1.6 The relative error of the calculated explosion potential may be estimated by:

$$\frac{\Delta EP}{EP} = \frac{1}{EP}\left[\left(\frac{0.38\,\Delta T_{onset}}{T_{onset} - 298\text{ K}}\right)^2 + \left(\frac{\Delta H}{H}\right)^2\right]^{1/2} \quad (24)$$

where:

ΔEP = estimation of error in the calculation of explosion potential, and

ΔT_{onset} = estimation of error in onset temperature, K.

10.1.7 The relative error of the calculated shock sensitivity value may be estimated by:

$$\frac{\Delta SS}{SS} = \frac{1}{SS}\left[\left(\frac{0.72\,\Delta T_{onset}}{T_{onset} - 298\text{ K}}\right)^2 + \left(\frac{\Delta H}{H}\right)^2\right]^{1/2} \quad (25)$$

where:

ΔSS = estimation of error in shock sensitivity.

10.1.8 The relative error of the calculated instantaneous power density may be estimated by:

$$\frac{\Delta IPD}{IPD} = \left[\left(\frac{\Delta H}{H}\right)^2 + \left(\frac{\Delta Z}{Z}\right)^2 + \left(\frac{\Delta\rho}{\rho}\right)^2 + \left(\frac{\Delta E}{RT}\right)^2\right]^{1/2} \quad (26)$$

where:

ΔIPD = estimation of error in instantaneous power density, W mL^{-1}.

10.1.9 Definitions of the symbols not included in 10.1.1 – 10.1.8 appear in Section 8.

10.2 Sample calculations for estimation of precision are given below using the values given in 8.13.1:

10.2.1 Assuming:

ΔE = 2.8 kJ/mol lmC $\Delta E/E$ = 0.021

ΔZ = 0.060 × 10^9/s lmC $\Delta\ Z/Z$ = 0.0300

ΔH = 0.029 kJ/g lmC $\Delta H/H$ = 0.0121

$\Delta\lambda$ = 0.0133 mW/(cm·K) lmC $\Delta\lambda/\lambda$ = 0.0300

$\Delta\rho$ = 0.0013 g/cm^3 lmC $\Delta\rho/\rho$ = 0.00102

ΔC_p = 0.036 J/(g·K) lmC $\Delta C_p/C_p$ = 0.020

ΔT_{onset} = 3.0 K lmC $\Delta T_{onset}/\Delta\ T_{onset}$ = 0.006

Δq = 0.003 W/g $\Delta q/q$ = 0.0150

ΔT_1 = 1.0 K $\Delta T_1/T_1$ 0.0025

10.2.2 Then:

$$\frac{\Delta t_c}{t_c} = [(0.0200)^2 + (0.0300)^2 + (0.0121)^2 + (2.8\text{ kJ/mol})^2 \quad (27)$$

$$\times\left(\frac{1}{(8.314\ \ \text{J / (K mol)}\ \times\ 330\ \ \text{K}} \times \frac{10^3\text{ J}}{\text{kJ}} - \frac{1}{132\text{ kJ/mol}}\right)^2\Bigg]^{\frac{1}{2}}$$

$$= [(0.0200)^2\ +\ (0.0300)^2\ +\ (0.0121)^2$$

$$+\ (2.8)^2\ \times\ (0.3643 - 0.0076)^2]^{\frac{1}{2}}$$

or expressed as a percent:

$$\frac{\Delta t_c}{t_c} = 100\,\% \quad (28)$$

NOTE 7—The major contribution to the imprecision of the time-to-thermal-runaway estimation is the imprecision in the activation energy measurement *E*. Thus, activation energy measurements of the highest attainable precision should be used.

10.2.3

$$\frac{\Delta TMR}{TMR} = [(0.0200)^2 + 2\times(0.0025)^2 + (0.021)^2 + (0.0150)^2]^{\frac{1}{2}} = 0.03284 \quad (29)$$

or expressed as a percent:

$$\frac{\Delta TMR}{TMR} = 3.3\,\% \quad (30)$$

10.2.4 And:

$$\frac{\Delta a}{a} = \frac{1}{2}[(0.300)^2 + (0.0121)^2 + (0.300)^2 + (0.00102)^2 \quad (31)$$

$$+(2.8\text{ kJ/mol})^2\left(\frac{1}{8.314\text{ J/(K mol)}\times 300\text{ K}} \times \frac{10^3\text{ J}}{\text{kJ}}\right.$$

$$\left. - \frac{1}{132\text{ kJ/mol}}\right)^2\Bigg]^{\frac{1}{2}}$$

$$= \frac{1}{2}[(0.0300)^2\ +\ (0.0121)^2$$

$$+\ (0.0300)^2\ +\ (0.00102)^2\ +\ (2.8)^2\ \times\ (0.4009 - 0.0076)^2]^{\frac{1}{2}}$$

or expressed as percent

$$\frac{\Delta a}{a} = 55\,\% \quad (32)$$

10.2.5 And:

$$\frac{E}{RT_c} = \left[\frac{132\text{ kJ/mol}\times 1000\text{ J/kJ}}{8.314\text{ J/(K mol)}\times 386\text{ K}}\right] = 41.13 \quad (33)$$

$$\frac{\Delta T_c}{T_c} = \frac{8.314\ \mathrm{J/(K\ mol)} \times (386\ \mathrm{K})}{2 \times 8.314\ \mathrm{J/(K\ mol)} \times (386\ \mathrm{K}) - 132\ \mathrm{kJ/mol} \times 1000\ \mathrm{J/kJ}} \quad (34)$$

$$\times[(0.00102)^2 + (0.0121)^2 \quad (35)$$

$$+(0.0300)^2+(0.0300)^2+(1-41.13)^2$$

$$\times(0.021)^2]^{\frac{1}{2}} = \frac{3326}{6418-132\,000}[0.6621]^{\frac{1}{2}} \quad (36)$$

or expressed as percent:

$$\frac{\Delta T_c}{T_c} = 84\,\% \quad (37)$$

10.2.6 And:

$$\frac{\Delta T_d}{T_d} = [(0.012)^2+(0.0200)^2]^{\frac{1}{2}} \quad (38)$$

or expressed as percent:

$$\frac{\Delta T_d}{T_d} = 2.3\,\% \quad (39)$$

10.2.7 And:

$$\frac{\Delta EP}{EP} = \frac{1}{0.21}\left[\left(\frac{0.38 \times 3\ \mathrm{K}}{202\ \mathrm{K}}\right)^2 + (0.0121)^2\right]^{1/2} \quad (40)$$

$$= 4.76[(0.00564)^2+(0.0121)^2]^{1/2}$$

or expressed as percent:

$$\frac{\Delta EP}{EP} = 6.4\,\% \quad (41)$$

10.2.8 And:

$$\frac{\Delta SS}{SS} = \frac{1}{0.12}\left[\left(\frac{0.72 \times 3\ \mathrm{K}}{202\ \mathrm{K}}\right)^2 + (0.0121)^2\right]^{1/2} \quad (42)$$

$$= 8.33[0.0107)^2+(0.0121)^{21/2}$$

or expressed as percent:

$$\frac{\Delta SS}{SS} = 13\,\% \quad (43)$$

10.2.9 And:

$$\frac{\Delta IPD}{IPD} = \left[(0.0121)^2+(0.0300)^2+(0.00102)^2 + \left(\frac{2.8\ \mathrm{kJ\ mol^{-1}} \times 1000\ \mathrm{J\ kJ^{-1}}}{8.314\ \mathrm{J\ mol^{-1}\ K^{-1}} \times 523\ \mathrm{K}}\right)^2\right]^{1/2} \quad (44)$$

$$= [(0.0121)^2+(0.0300)^2+(0.00102)^2+(0.6439)^2]^{1/2}$$

or expressed as percent:

$$\frac{\Delta IPD}{IPD} = 64\,\% \quad (45)$$

10.3 Since the hazard potential figures of merit calculated in this practice have only relative significance, no bias may be estimated.

11. Keywords

11.1 adiabatic decomposition temperature rise; adiabatic temperature rise; critical dimension; critical temperature; differential scanning calorimetry; explosion potential; hazard; instability rating; instantaneous power density; shock sensitivity; thermal analysis; thermal hazard; thermal runway

APPENDIX

(Nonmandatory Information)

X1. GUIDELINES FOR THE USE OF HAZARD POTENTIAL FIGURES OF MERIT

X1.1 Users of the figures of merit generated by this standard may wish to compare results with other materials or to make qualitative safety comparison from one material to another. This appendix provides guidelines for evaluating these figures of merit (and other) values.

X1.2 In the evaluation of relative safety risk, the user shall use a wide variety of measurements. No one measurement provides all of the information needed.

X1.3 The figures of merit generated by this standard are primarily used to identify those materials that merit a more thorough examination of relative risk.

X1.4 Onset Temperature

X1.4.1 In general, low risk is indicated when the operating temperature of a process is more than 100°C lower than the nearest detectable exotherm observed in a DSC experiment (onset temperature by Test Method E537), the reaction is question is considered to be of low risk (**10, 11**).

X1.4.2 Certain conditions such as large quantities of material, poor heat transfer, etc., may result in increased risk.

X1.5 Enthalpy of Reaction

X1.5.1 Exothermic enthalpies of reaction are considered to be more hazardous than endothermic reactions.

X1.5.2 In general, the potential hazard of a reaction increases with increasing exothermic nature of the reaction.

X1.5.3 Exothermic enthalpies of reaction in excess of 800 J/g are considered hazardous (**12**).

X1.6 Explosion Potential

X1.6.1 Positive values of explosion potential are considered highly hazardous.

X1.6.2 The greater the positive numerical value for explosion potential, the greater the hazard.

X1.6.3 Negative values of explosion potential are considered low hazard.

X1.7 Shock Sensitivity (7) (See 3.2.7)

X1.7.1 Positive values of shock sensitivity are considered highly hazardous.

X1.7.2 The greater the positive numerical value for shock sensitivity, the greater the hazard potential.

X1.7.3 Negative values of shock sensitivity are considered low hazard potential.

X1.8 Adiabatic Decomposition Temperature Rise (11)

X1.8.1 There is an increase in hazard with increasing adiabatic temperature rise.

X1.8.2 Hazard often results due to the pressure created when the adiabatic temperature rise exceeds the boiling temperature of the reaction solvent.

X1.8.3 In the absence of volatilization, the hazard may be evaluated using Table X1.1.

TABLE X1.1 Hazard Potential Associated with Adiabatic Decomposition Temperature Rise (Without Volatilization) (13)

Hazard	Temperature Rise, K
High	>200
Medium	50 to 200
Low	<50

X1.9 Instantaneous Power Density and NFPA Instability Rating

X1.9.1 NFPA Stability Rating, derived from the instantaneous power density, is presented in Table 1.

X1.10 Time-to-Thermal-Runaway and Time-to-Maximum-Rate

X1.10.1 Time-to-thermal-runaway is related to time-to-maximum-rate but assumes first order reaction.

X1.10.2 The hazard increases when time-to-thermal-runaway and time-to-maximum-rate decrease.

X1.10.3 Hazard may be evaluated using Table X1.2.

X1.11 Critical Half Thickness

X1.11.1 The hazard increases as the critical half thickness decreases.

X1.11.2 Hazard is indicated when the shortest distance from any point internal to the container surface exceeds the critical half thickness value.

TABLE X1.2 Hazard Potential for Runaway Time

Hazard	Runaway Time, hr
High	<8
Medium	8 to 24
Low	>24

REFERENCES

(1) Wilberforce, J. K., "Comparison of Methods of Determination of Adiabatic Times to Maximum Rate of Exothermic Reactions," *Journal of Thermal Analysis*, Vol 25, 1982, pp. 593–596.

(2) Smith, L. C., "An Approximate Solution of the Adiabatic Explosion Problem," *Thermochimica Acta*, Vol 13, 1975, pp. 1–6.

(3) Townsend, D. I., and Tou, J. C., "Thermal Hazard Evaluation by an Accelerating Rate Calorimeter," *Thermochimica Acta*, Vol 37, 1980, pp. 1–30.

(4) Duswalt, A. A., "The Practice of obtaining Kinetic Data by Differential Scanning Calorimetry," *Thermochimica Acta*, Vol 8, 1974, p. 57.

(5) Parks, J. R., "Critical Criteria for Various Configurations of a Self-Heating Chemical as Functions of Activation Energy and Temperature of Assembly," *Journal of Chemical Physics*, Vol 34, No. 1, 1961, p. 46–50.

(6) Rogers, R. N., "Thermochemistry of Explosives," *Thermochimica Acta*, Vol 11, 1975, pp. 131–139.

(7) Yoshida, T., Yoshizawa, F., Itoh, M., Matsunaga, T., Watanabe, M., and Tamura, M., "Prediction of Fire and Explosion Hazards of reactive Chemicals (I). Estimating of Explosive Properties of Self-Reactive Chemicals from SC-DSC Data," *Koguo Kayaku*, Vol 48, No. 5, 1987, pp. 311–316.

(8) Yoshida, T., Wada, Y., and Foster, N., *Safety of Reactive Chemicals and Pyrotechnics*, Elsevier, New York, 1995, pp. 22–24 .

(9) Perrin, C. L., *Mathematics for Chemists*, Section 6.9, Wiley-Interscience, New York, NY.

(10) Hofelich, T. C., and Thomas, R. C., "The Uses/Misuse of the 100 Degree Rule in the Interpretation of Thermal Hazard Tests," *International Symposium on Runaway Reactions*, American Institute of Chemical Engineers, New York, 1989, pp. 74–85,

(11) Cammenga, H. K., and Epple, M., "Basic Principles of Thermoanalytical Techniques and Their Application in Preparation Chemistry," *Angewandte Chemie*, International Edition English, Vol 34, No. 11, 1995, pp. 1171–1187.

(12) United Nations, *Recommendations on the Transport of Dangerous Goods – Manual of Tests and Criteria*, New York, 2009, pp. 29–49.

(13) Stoessel, F., "What Is Your Thermal Risk?," *Chemical Engineering Progress*, Vol 89, No. 10, 1993, pp. 68–75.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/