Designation: E1231 – 19

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) National Fire Protection Association (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 *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.*

1.8 *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]

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

[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.

Diffusivity by Modulated Temperature Differential Scanning Calorimetry
E2041 Test Method for Estimating Kinetic Parameters by Differential Scanning Calorimeter Using the Borchardt and Daniels Method
E2070 Test Methods 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, n*—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, n*—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, n*—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, n*—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, n*—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, n*—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, n*—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, n*—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, n*—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.

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

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**).[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 (**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.

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

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 (**1, 3**):

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

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 (**4**):

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

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 (**1, 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]) (**5**):

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

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.

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:

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

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

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

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

8.13.3

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

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

[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 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}