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Standard Test Methods for Kinetic Parameters by Differential Scanning Calorimetry Using Isothermal Methods¹

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1. Scope*

1.1 Test Methods A, B, and C determine kinetic parameters for activation energy, pre-exponential factor and reaction order using differential scanning calorimetry (DSC) from a series of isothermal experiments over a small (≈ 10 K) temperature range. Test Method A is applicable to low n th order reactions. Test Methods B and C are applicable to accelerating reactions such as thermoset curing or pyrotechnic reactions and crystallization transformations in the temperature range from 300 K to 900 K (nominally 30 °C to 630 °C). These test methods are applicable only to these types of exothermic reactions when the thermal curves do not exhibit shoulders, double peaks, discontinuities or shifts in baseline.

1.2 Test Methods D and E also determines the activation energy of a set of time-to-event and isothermal temperature data generated by this or other procedures

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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.* Specific precautionary statements are given in Section 8.

1.5 *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.*

¹ These test methods are under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Calorimetry and Mass Loss.

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2. Referenced Documents

2.1 *ASTM Standards:*²

- D3350 Specification for Polyethylene Plastics Pipe and Fittings Materials
- D3895 Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry
- D4565 Test Methods for Physical and Environmental Performance Properties of Insulations and Jackets for Telecommunications Wire and Cable
- D5483 Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry
- D6186 Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC)
- E473 Terminology Relating to Thermal Analysis and Rheology
- E537 Test Method for 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
- E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers
- E968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters (Withdrawn 2023)³
- E1142 Terminology Relating to Thermophysical Properties
- E1445 Terminology Relating to Hazard Potential of Chemicals
- E1858 Test Methods for Determining Oxidation Induction Time of Hydrocarbons by Differential Scanning Calorimetry

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.

³ The last approved version of this historical standard is referenced on www.astm.org.

*A Summary of Changes section appears at the end of this standard

E1860 Test Method for Elapsed Time Calibration of Thermal Analyzers

E1970 Practice for Statistical Treatment of Thermoanalytical Data

E2041 Test Method for Estimating Kinetic Parameters by Differential Scanning Calorimeter Using the Borchardt and Daniels Method

E2046 Test Method for Reaction Induction Time by Thermal Analysis

3. Terminology

3.1 Specific technical terms used in these test methods are defined in Terminologies **E473**, **E1142**, and **E1445**, including the terms *calorimeter*, *Celsius*, *crystallization*, *differential scanning calorimetry*, *general rate law*, *isothermal*, *peak*, and *reaction*.

4. Summary of Test Method

4.1 A test specimen is held at a constant temperature in a differential scanning calorimeter throughout an exothermic reaction. The rate of heat evolution, developed by the reaction, is proportional to the rate of reaction. Integration of the heat flow as a function of time yields the total heat of reaction.

4.2 An accelerating (Sestak-Berggren or Avrami models), n th order data, or model free treatment^{4,5,6} is used to derive the kinetic parameters of activation energy, pre-exponential factor and reaction order from the heat flow and total heat of reaction information obtained in 4.1. (See Basis for Methodology, Section 5.)

5. Basis of Methodology

5.1 Reactions of practical consideration are exothermic in nature; that is, they give off heat as the reaction progresses. Furthermore, the rate of heat evolution is proportional to the rate of the reaction. Differential scanning calorimetry measures heat flow as a dependent experimental parameter as a function of time under isothermal experimental conditions. DSC is useful for the measurement of the total heat of a reaction and the rate of the reaction as a function of time and temperature.

5.2 Reactions may be modeled with a number of suitable equations of the form of:

$$d\alpha/dt = k(T)f(\alpha) \quad (1)$$

where:

$d\alpha/dt$ = reaction rate (s^{-1}),

α = fraction reacted (dimensionless),

$k(T)$ = specific rate constant at temperature T (s^{-1}),

$f(\alpha)$ = conversion function. Commonly used functions include:

$$f_1(\alpha) = (1 - \alpha)^n \quad (2)$$

$$f_2(\alpha) = \alpha^m (1 - \alpha)^n \quad (3)$$

$$f_3(\alpha) = p(1 - \alpha)[-1 - n(1 - \alpha)]^{(p-1)/p} \quad (4)$$

where:

n , m , and p = partial reaction order terms.

NOTE 1—There are a large number of conversion function expressions for $[f(\alpha)]$.⁴ Those described here are the most common but are not the only functions suitable for these test methods. Eq 1 is known as the general rate equation while Eq 3 is the accelerating (or Sestak-Berggren) equation.^{5,6}

Eq 4 is the accelerating Avrami equation. Eq 2 is used for n th order reactions while Eq 3 or Eq 4 are used for accelerating reaction, such as thermoset cure and crystallization transformations.

5.3 For a reaction conducted at temperature (T), the accelerating rate Eq 3 and the rate equation Eq 1 may be cast in their logarithmic form.

$$d\alpha/dt = k(T) \alpha^m (1 - \alpha)^n \quad (5)$$

$$\ln[da/dt] = \ln[k(T)] + m \ln[\alpha] + n \ln[1 - \alpha] \quad (6)$$

This equation has the form $z = a + bx + cy$ and may be solved using multiple linear regression analysis where $x = \ln[\alpha]$, $y = \ln[1 - \alpha]$, $z = \ln[da/dt]$, $a = \ln[k(T)]$, $b = m$ and $c = n$.

NOTE 2—The rate equation (Eq 3) reduces to the simpler general rate equation (Eq 2) when the value of reaction order parameter m equals zero thereby reducing the number of kinetic parameters to be determined.

5.4 For reactions conducted at temperature (T), the accelerating rate equation of Eq 4 may be cast as:

$$\ln[-\ln(1 - \alpha)] = p \ln[k(T)] + p \ln[t] \quad (7)$$

This equation has the form of $y = mx + b$ and may be solved by linear regression where $x = \ln[t]$, $y = \ln[-\ln(1 - \alpha)]$, with $p = m$, $b = p \ln[k(T)]$, and $t = \text{time}$.

5.5 The Arrhenius equation describes how the reaction rate changes as a function of temperature:

$$k(T) = Z e^{-E/RT} \quad (8)$$

where:

Z = pre-exponential factor (s^{-1}),

E = activation energy ($J \text{ mol}^{-1}$),

T = absolute temperature (K),

R = gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and

e = natural logarithm base = 2.7182818.

5.6 Eq 8 cast in its logarithmic form is:

$$\ln[k(T)] = \ln[Z] - E/RT \quad (9)$$

Eq 9 has the form of a straight line, $y = mx + b$, where a plot of the logarithm of the reaction rate constant ($\ln[k(T)]$) versus the reciprocal of absolute temperature ($1/T$) is linear with the slope equal to $-E/R$ and an intercept equal to $\ln[Z]$.

5.7 As an alternative to Eq 6 and Eq 7, the rate and Arrhenius equations combined and cast in logarithmic form is:

$$\ln[da/dt] = \ln[Z] - E/RT + m \ln[\alpha] + n \ln[1 - \alpha] \quad (10)$$

Eq 10 has the form, $z = a + bx + cy + dw$, and may be solved using multiple linear regression analysis.

where:

$z = \ln[da/dt]$

$a = \ln[Z]$

$b = -E/R$

⁴ Sbirrazzuoli, N., Brunel, D., and Elegant, L., "Differential Kinetic Equation Analysis" *Journal of Thermal Analysis*, Vol 38, 1992, pp. 1509–1524.

⁵ Sestak, J., and Berggren, G., "Study of the Kinetics of the Mechanism of Solid-State Reactions at Increasing Temperatures" *Thermochimica Acta*, Vol 3, 1971, pp. 1–12.

⁶ Gorbachiev, V.M., "Some Aspects of Sestak's Generalized Kinetic Equation in Thermal Analysis" *Journal of Thermal Analysis*, Vol 18, 1980, pp. 193–197.

$x = 1/T$
 $c = m$
 $y = \ln[\alpha]$
 $d = n$, and
 $w = \ln[1 - \alpha]$.

5.8 If activation energy values only are of interest, Eq 11 may be solved under conditions of constant conversion to yield:

$$\ln[\Delta t] = E/RT + b \quad (11)$$

where:

Δt = lapsed time (s), at constant conversion and at isothermal temperature, T , and
 b = constant.

Eq 11 has the form of a straight line, $y = mx + b$, where a plot of the logarithm of the lapsed time under a series of differing isothermal conditions versus the reciprocal of absolute temperature ($1/T$) is linear with a slope equal to E/R .

5.9 If activation energy values only are of interest, Eq 11 may be solved under conditions of constant conversion and the equality $da/dt = dH/dt / (H)$ to yield:

$$\ln[dH/dt] = -E/RT + b = m/T + b \quad (12)$$

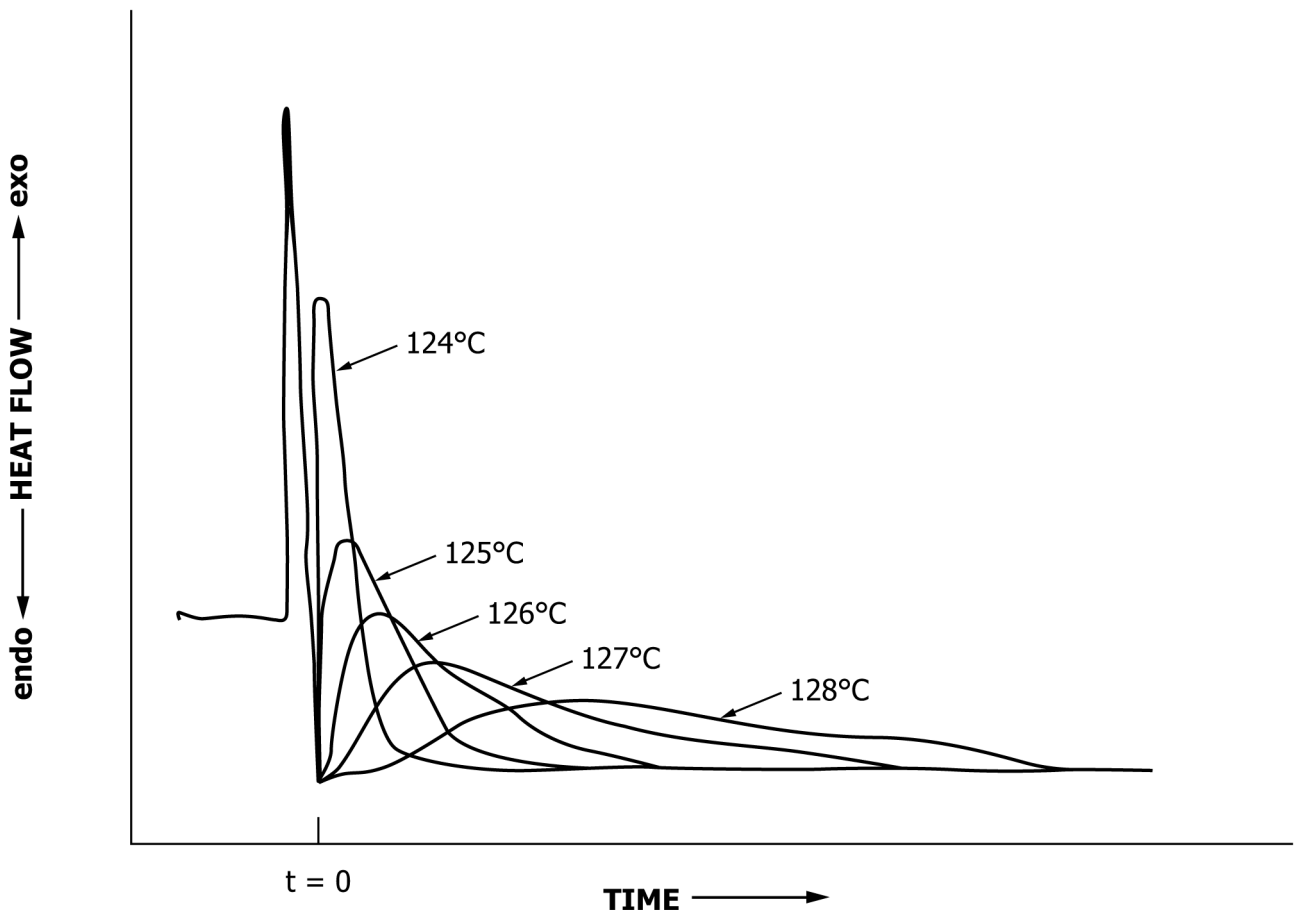
where:

H = total heat of reaction (mJ),
 dH/dt = instantaneous heat flow (mW),
 b = constant, and
 m = slope (K).

Eq 12 has the form of a straight-line $y = mx + b$, where a plot of the logarithm of the heat flow ($\ln[dH/dt]$) at the peak of the exotherm under a series of differing isothermal temperature conditions versus the reciprocal of the absolute temperature ($1/T$) is linear with a slope equal to E/R .

5.10 A series of isothermal experiments by Test Method A, B, and C described in Section 11 at four or more temperatures, determines the kinetic parameters of activation energy, pre-exponential factor and reaction order. Alternatively, the time to a condition of constant conversion for a series of experiments at four or more temperatures obtained by this or alternative Test Method D, described in Section 12, may be used to determine activation energy only.

5.11 A series of not less than four isothermal DSC experiments, covering a temperature range of approximately 10 K and a time less than 100 min (such as those shown in Fig. 1) provides values for da/dt , α , $(1 - \alpha)$ and T to solve Eq 6, Eq



NOTE 1—This figure is for a crystallization application in which the reaction rate increases with decreasing temperature. Chemical reactions show an increase in reaction rate with increasing temperature.

FIG. 1 Heat Flow Curves at a Series of Isothermal Temperatures