Designation: E2070 – 23

Standard Test Methods for Kinetic Parameters by Differential Scanning Calorimetry Using Isothermal Methods[1]

This standard is issued under the fixed designation E2070; 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 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.*

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

[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.

Current edition approved Oct. 1, 2023. Published October 2023. Originally approved in 2000. Last previous edition approved in 2018 as E2070 – 13 (2018). DOI: 10.1520/E2070-23.

[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:

$$d\alpha/dt = k(T)\, f(\alpha) \tag{1}$$

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:

$$f_1(\alpha) = (1-\alpha)^n \tag{2}$$

$$f_2(\alpha) = \alpha^m\,(1-\alpha)^n \tag{3}$$

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

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.

$$d\alpha/dt = k(T)\,\alpha^m\,(1-\alpha)^n \tag{5}$$

$$\ln[d\alpha/dt] = \ln[k(T)] + m\ln[\alpha] + n\ln[1-\alpha] \tag{6}$$

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

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

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 = time.

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

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

where:

Z = pre-exponential factor (s^{-1}),
E = activation energy (J mol^{-1}),
T = absolute temperature (K),
R = gas constant = (8.314 J mol^{-1} K^{-1}), and
e = natural logarithm base = 2.7182818.

5.6 Eq 8 cast in its logarithmic form is:

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

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:

$$\ln[d\alpha/dt] = \ln[Z] - E/RT + m\ln[\alpha] + n\ln[1-\alpha] \tag{10}$$

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

where:

z = $\ln[d\alpha/dt]$
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.