Designation: E2070 – 13

Standard Test Method 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 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 to 900 K (nominally 30 to 630°C). This test method is 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 test method is similar but not equivalent to ISO DIS 11357, Part 5, and provides more information than the ISO standard.

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

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 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

E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

E968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters

E1142 Terminology Relating to Thermophysical Properties

E1445 Terminology Relating to Hazard Potential of Chemicals

E1858 Test Method for Determining Oxidation Induction Time of Hydrocarbons by Differential Scanning Calorimetry

E1860 Test Method for Elapsed Time Calibration of Thermal Analyzers

E1970 Practice for Statistical Treatment of Thermoanalytical Data

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[1] This test method is 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] 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.

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

2.2 *ISO Standard:*[3]

ISO DIS 11357 Part 5: Determination of Temperature and/or Time of Reaction and Reaction Kinetics

3. Terminology

3.1 Specific technical terms used in this test method 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:

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

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:

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

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

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

where:

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

NOTE 1—There are a large number of conversion function expressions for [*f*(α)].[4] Those described here are the most common but are not the only functions suitable for this test method. 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.

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

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

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 ɱ 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:

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

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:

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

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:

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

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:

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

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 = $-E/R$
x = $1/T$
c = m
y = $\ln[1 - \alpha]$

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[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[4] Sbirrazzuoli, N., Brunel, D., and Elegant, L., *Journal of Thermal Analysis*, Vol 38, 1992, pp. 1509–1524.

[5] Sestak, J., and Berggren, G., *Thermochimica Acta*, Vol 3, 1971, p. 1.

[6] Gorbachiev, V.M., *Journal of Thermal Analysis*, Vol 18, 1980, pp. 193–197.

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:

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

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 $d\alpha/dt = dH/dt \ / \ (H)$ to yield:

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

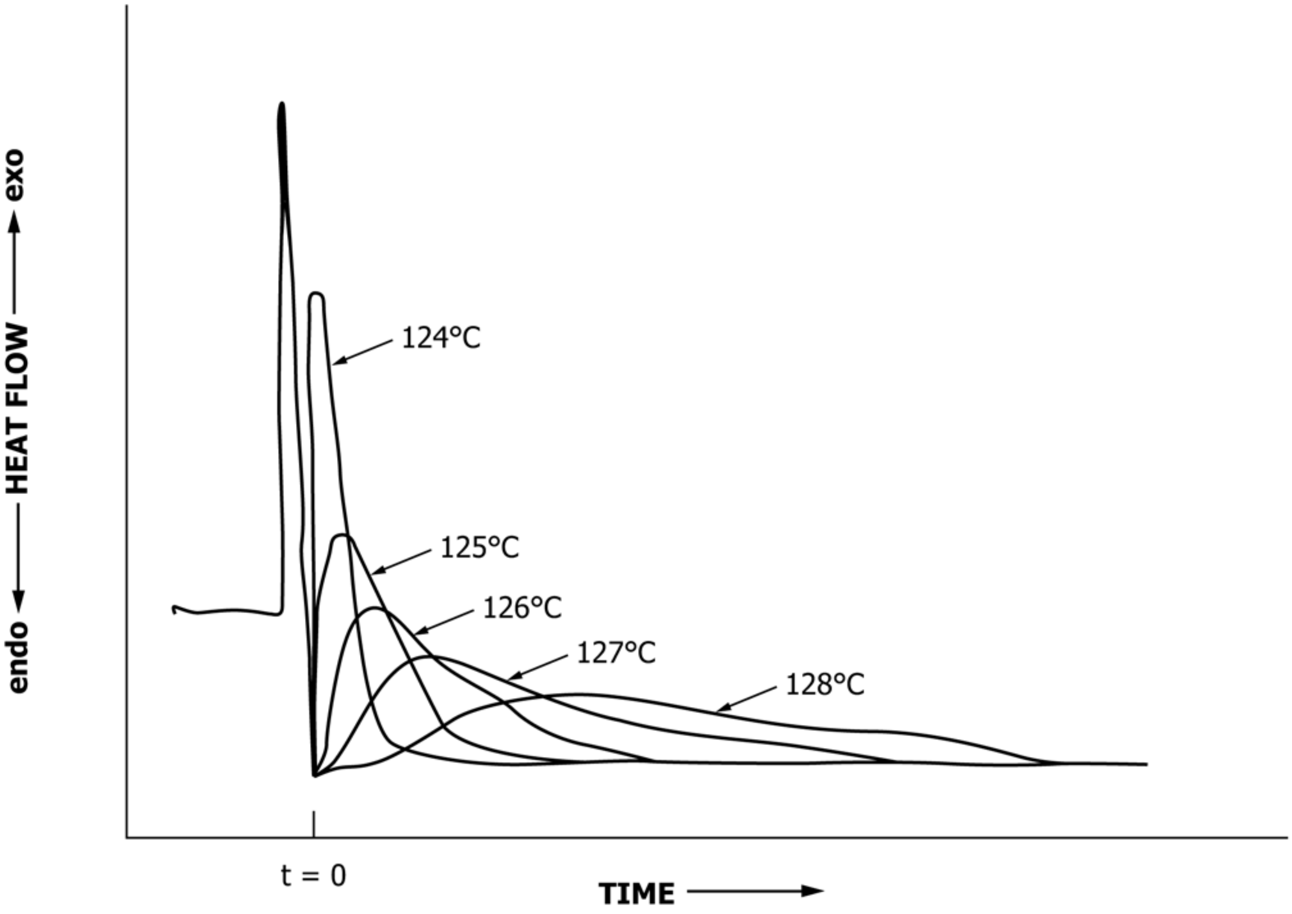
where:

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 $d\alpha/dt$, α, $(1 - \alpha)$ and T to solve Eq 6, Eq 7, Eq 9, and Eq 10.



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

5.12 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 provides *dH/dt* and *T* to solve Eq 12

5.13 A variety of time-to-event experiments such as oxidation induction time methods (Practice D3350 and Test Methods D3895, D4565, D5483, D6186, and E1858) and reaction induction time methods (Test Method E2046) provide values for Δt and T to solve equation Eq 11.

6. Significance and Use

6.1 This test method is useful for research and development, quality assurance, regulatory compliance and specification acceptance purposes.

6.2 The determination of the order of a chemical reaction or transformation at specific temperatures or time conditions is beyond the scope of this test method.

6.3 The activation energy results obtained by this test method may be compared with those obtained from Test Method E698 for *n*th order and accelerating reactions. Activation energy, pre-exponential factor, and reaction order results by this test method may be compared to those for Test Method E2041 for *n*th order reactions.

7. Interferences

7.1 The approach is applicable only to exothermic reactions.

NOTE 3—Endothermic reactions are controlled by the rate of the heat transfer of the apparatus and not by the kinetics of the reaction and may not be evaluated by this test method.

7.2 This test method is intended for a reaction mechanism that does not change during the transition. This test method assumes a single reaction mechanism when the shape of the thermal curve is smooth (as in Fig. 2 and Fig. 3) and does not exhibit shoulders, multiple peaks or discontinuation steps.

7.3 Test method precision is enhanced with the selection of the appropriate conversion function [$f(\alpha)$] that minimizes the number of experimental parameters determined. The shape of the thermal curve, as described in Section 11, may confirm the selection of the *n*th order or accelerating models.

7.4 Typical *n*th order reactions include those in which all but one of the participating species are in excess.

7.5 Typical accelerating reactions include thermoset cure, crystallization and pyrotechnic reactions.

7.6 For *n*th order kinetic reactions, this test method anticipates that the value of *n* is small, non-zero integers, such as 1 or 2. This test method should be used carefully when values of *n* are greater than 2 or are not a simple fraction, such as ½ = 0.5.

7.7 Accelerating kinetic reactions anticipate that *m* and *n* are fractions between 0 and 2 and that their sum ($m + n$) is less than 3.

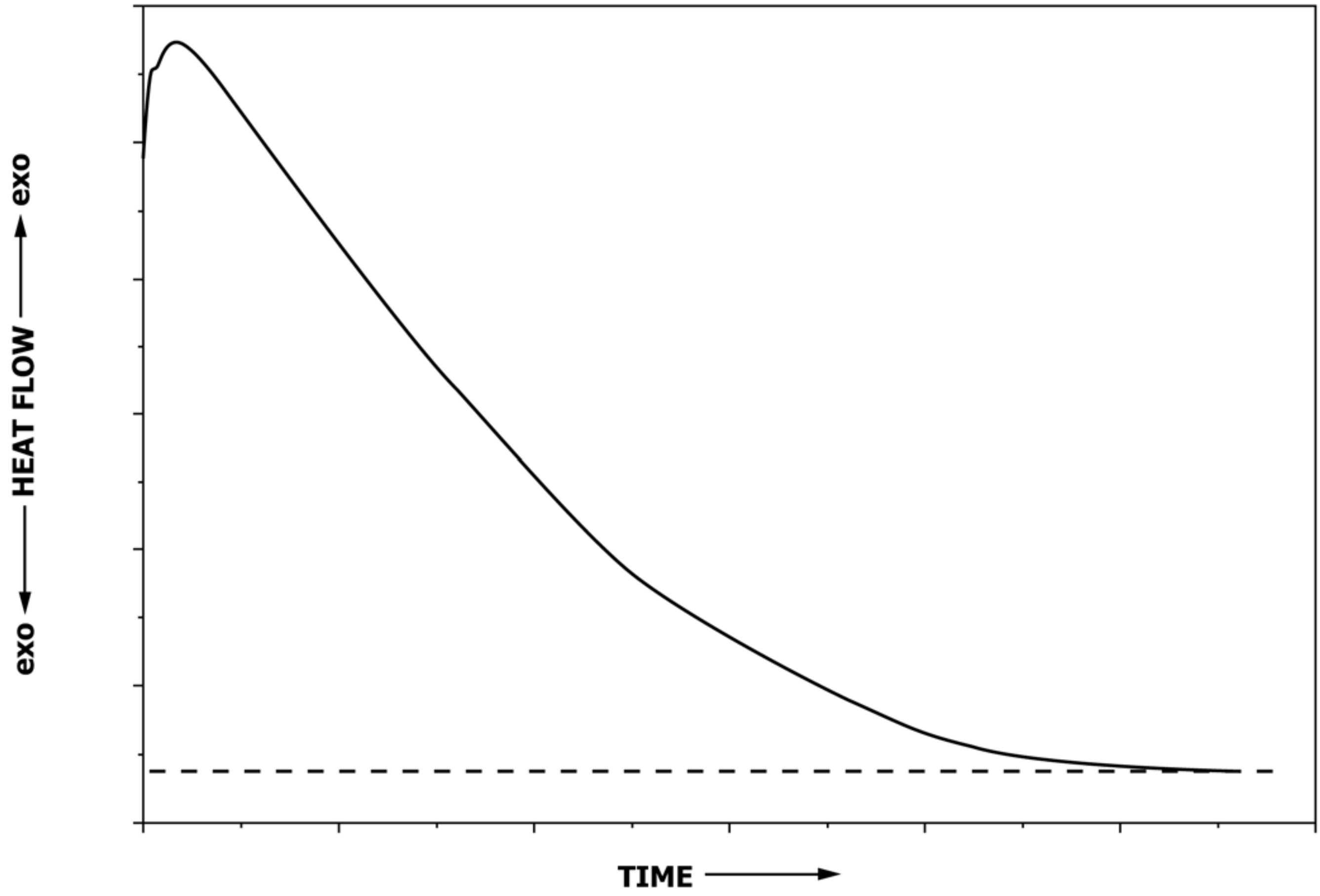


FIG. 2 Heat Flow Curve for an *n*th Order Reaction

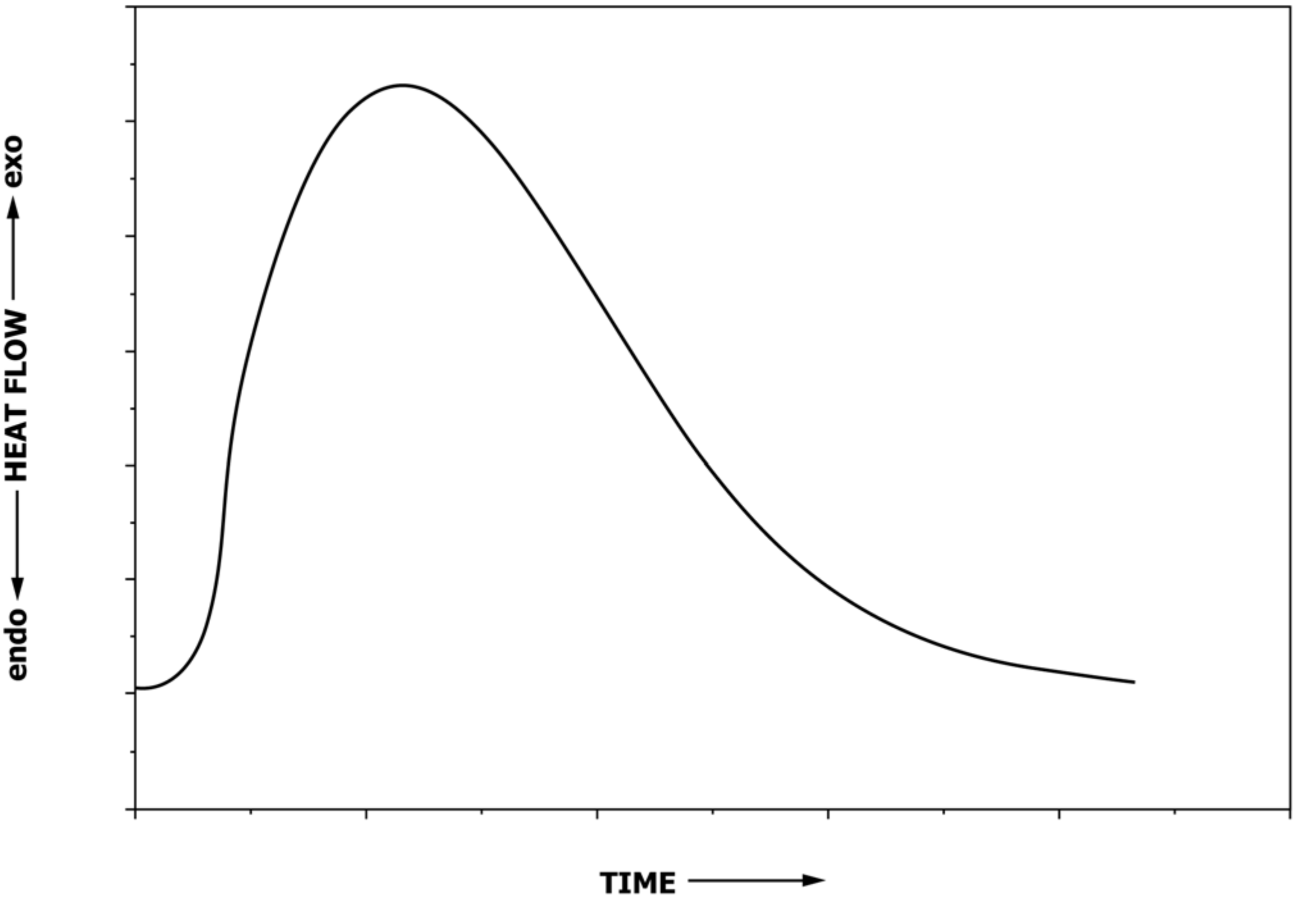


FIG. 3 Heat Flow Curve for an Accelerating Reaction

7.8 Accelerating kinetic reactions anticipate that p is an integer often with a value of ≤4.

7.9 Since this test method uses milligram quantities it is essential that the test specimens are homogeneous and representative of the larger samples from which they are taken.

7.10 Test specimens may release toxic and corrosive effluents that may be harmful to personnel or apparatus. Operation with a venting or exhaust system is recommended.

8. Hazards

8.1 Special precautions shall be taken to protect personnel and equipment when the apparatus in use requires the insertion of specimens into a heated furnace. These special precautions include adequate shielding and ventilation of equipment and face and hand protections for users (see Note 6).

9. Apparatus

9.1 A differential scanning calorimeter (DSC) that provides the minimum calorimetric capability for this test method includes:

9.1.1 *A DSC Test Chamber,* composed of:

9.1.1.1 *A Furnace(s),* that provides uniform controlled heating of a specimen and reference to constant temperature at a constant rate between 300 and 900 K.

9.1.1.2 *A Temperature Sensor,* that indicates the specimen/furnace temperature to ±0.01 K.

9.1.1.3 *A Differential Sensor,* that detects heat flow differences between the specimen and reference equivalent to 1 µW.

9.1.1.4 A means of sustaining a purge gas rate of 10 to 50 ± 5 mL/minute in the test chamber.

NOTE 4—Typically inert purge gases that inhibit sample oxidation are 99.9+ % pure nitrogen, helium or argon. Dry gases are recommended for all experiments unless the effect of moisture is part of the study.

9.1.2 *A Temperature Controller,* capable of executing a specific temperature program by operating the furnace(s) between 300 and 900 K at a rate of temperature change of up to 100 K min^{-1} constant to ±0.1 K min^{-1} or at an isothermal temperature constant to ±0.1 K.

9.1.3 *A Data Collection Device,* to provide a means of acquiring, storing, and displaying measured or calculated signals, or both. The minimum output signals required for DSC are heat flow, temperature and time.

9.2 *Containers* (pans, crucibles, vials, etc. and lids) that are inert to the specimen and reference materials of suitable structural shape and integrity to contain the specimen and reference.

9.3 *A Balance,* to weigh specimens or containers, or both, to ±10 µg with a capacity of at least 100 mg.

9.4 *Calculation,* capability to perform multiple linear regression analysis for four or more unknowns.

10. Calibration

10.1 Perform set up and calibration procedures according to the instrument operator's manual.

10.2 Calibrate the DSC temperature signal over the range of the reaction at a heating rate of 1 K min^{-1} using Test Method E967.

10.3 Calibrate the DSC heat flow signal using Practice E968.

10.4 Confirm that the elapsed time conformity of the thermal analyzer clock is better than 0.1 % using Test Method E1860.

11. Procedure (Determination of Reaction Type)

11.1 Differing forms of the rate equation are used for *n*th order and accelerating reactions. This section describes a useful test procedure for identifying the reaction type applicable to the material under test.

11.2 Weigh 4 to 7 mg of the test specimen into a tarred sample container and hermetically seal the container. Do NOT load the test specimen into the apparatus. Load an equivalent empty specimen container as the reference into the apparatus. Close the DSC sample chamber and prepare the apparatus for an experimental run.

11.3 Select an isothermal test temperature corresponding to 10 % of the peak area from a scouting run performed by Test Method E537. Equilibrate the apparatus at this test temperature for at least two minutes.

11.4 Initiate the experiment recording heat flow as a function of time.

11.5 Open the DSC sample chamber and load the test specimen into the apparatus. Immediately close the sample chamber. Record the thermal curve for 20 min or until the exothermic event is complete (that is, the rate of heat flow approaches zero). (**Warning—**Burn hazard. The sample chamber, heat shields and covers present a burn hazard to the operator. Exercise great care in this operation. Protective safety equipment shall be used to ensure the safety of the operator (See Note 6).)

11.6 Prepare a display of the heat flow on the Y-axis and time on the X-axis.

11.7 Observe the shape of the resultant thermal curve. An nth order reaction is likely when the heat flow curve reaches a maximum within seconds of being placed in the DSC then slowly decays as shown in Fig. 2. A heat flow curve that builds to a maximum (after tens of seconds) and then decays, as shown in Fig. 3, is likely to be an accelerating reaction.

11.8 If the reaction is *n*th order, then use Procedure A. If the reaction is accelerating, then use either Procedures B or C.

12. Procedure (Test Method A for *n*th Order Reactions)

12.1 Weight 4 to 7 mg of test specimen into a tared sample container. Hermetically seal the container. Record the total weight of the specimen and the container to ±10 µg.

12.2 Place the test specimen and similar empty reference container in the apparatus. Close the DSC sample chamber.

12.3 Use a heating rate of 20 K/min or greater to raise the furnace temperature quickly from ambient temperature to the experimental isothermal temperature and that produces no more than 1 K overshoot at the experimental temperature. Start the clock and collect the isothermal test data of heat flow and time when the specimen test temperature reaches ±1 K of the isothermal test temperature.

NOTE 5—A dynamic test, such as Test Method E537 may be used to determine the experimental isothermal test temperature. Isothermal test temperatures typically are selected to be those between 1 and 10 % of the total reaction by Test Method E537.

NOTE 6—In some apparatus, it may not be possible to achieve less than 1 K overshoot. In such a case, load the specimen and reference into the furnace preheated to the isothermal test temperature. This practice is contrary to good laboratory practice and is discouraged for safety reasons. If practiced, protective safety equipment shall be used to ensure the safety of the operator from thermal burns and from premature rupture of the specimen container.

12.4 Record the specimen temperature as, *T*, 5 min into the experiment.

12.5 Terminate the isothermal experiment when the reaction exotherm is complete, that is, when the thermal curve is horizontal to the time axis.

12.6 Cool the test specimen to ambient temperature at any convenient rate. The thermal curve need not be recorded. Reweight the specimen and container. Record and report any change in mass greater than 0.1 mg from that measured in 12.1.

12.7 Repeat 12.1 – 12.6 with freshly prepared test specimens at (at least) three additional isothermal test temperatures. Select the experimental temperatures so that total isothermal test times to complete the exotherm reaction are between 15 and 100 min.

12.8 Using the thermal curves from 12.1 – 12.7, calculate activation energy (E) , natural logarithm of the pre-exponetial factor ($\ln[Z]$) and reaction order (n) according to the procedure described in Section 13.

13. Calculation (Test Method A for *n*th Order Reactions)

13.1 Prepare a display for each isotheral thermal curve obtained in 12.1 – 12.7, with heat flow on the Y-axis and time on the X-axis. Construct a linear baseline from a point on the baseline immediately before the reaction exotherm to a point on the baseline immediately after the reaction exotherm for each thermal curve.

NOTE 7—An *n*th order reaction may require extrapolation of the baseline at the end of the experiment forward in time as shown in Fig. 2.

13.2 Integrate the total peak areas bounded by the peaks themselves and the constructed baselines to obtain the heat of reaction (ΔH) in mJ for each thermal curve.

NOTE 8—It is important that the reaction go to completion. This may be observed by an unchanging baseline under expanded scale conditions following the reaction exotherm.

NOTE 9—In *n*th order reactions, an appreciable fraction of the reaction may take place before temperature equilibrium of the test specimen is achieved. In such cases, the value of ΔH may be taken from a linearly temperature programmed experiment such as Test Method E537.

13.3 Identify the times that correspond to approximately 10 to 90 % of the peak areas obtained in 13.2.

13.4 Select a time interval that provides a minimum of ten equally spaced time values between the time limits determined in 13.3.

13.5 For each of the time intervals in 13.4, record the rate of reaction (*dH*/*dt*) in mW, the heat of reaction completed (ΔH_c) in mJ and the heat of reaction remaining (ΔH_r) in mJ as illustrated in Fig. 4.

NOTE 10—mW = mJ/s

NOTE 11—It is convenient to prepare a table of these values for each thermal curve along with the respective isothermal test temperature from 12.4 for the experiment.

13.6 For each fraction area obtained in 13.5, determine the fraction remaining (1 – α) and the fractional rate of reaction (*d*α/*dt*) using Eq 13 and Eq 14:

$$(1 - \alpha) = \Delta H_r / \Delta H \tag{13}$$

$$d\alpha/dt = (dH/dt)/\Delta H \tag{14}$$

NOTE 12—Retain all available significant figures for the calculations and round to the final results to the number of significant figures described in Section 22.

NOTE 13—For ten time intervals as described in 13.4, the values for (1 – α) should range between 0.9 and 0.1.

13.7 Calculate the natural logarithm for the rate of the reaction (ln[*d*α/*dt*]), where *d*α/*dt* has the units of s^{-1}, for each value determined in 13.5 and 13.6.

13.8 Calculate the value of ln[1 – α] for each value determined in 13.6.

13.9 Prepare a display with ln[*d*α/*dt*] on the Y-axis and ln[1 – α] on the X-axis.

NOTE 14—This display should be approximately linear. If it is not, then this test method is not applicable.

13.10 Using linear regression techniques (Practice E1970), determine the slope (*m*) and intercept (*b*) of the straight line displayed in 13.9 along with their respective standard deviations *s*(*m*) and *s*(*b*).

13.11 Calculate the value of reaction order *n* and ln[*k*(*T*)] using Eq 15 and Eq 16:

$$n = m \tag{15}$$

$$\ln[k(T)] = b \tag{16}$$

13.12 Prepare a display of ln[*k*(*T*)] from 13.11 on the Y-axis and 1/*T* from 12.4 on the X-axis (see Note 14).

13.13 Using linear regression technique (Practice E1970), determine the slope (*m*) and intercept (*b*) of the straight line in 13.12 along with their respective standard deviations *s*(*m*) and *s*(*b*).

13.14 Using the values of *m*, *b*, *s*(*m*), and *s*(*b*) from 13.13, determine the activation energy (*E*) and natural logarithm of the pre-exponential factor (ln[*Z*]) and their respect standard deviations *s*(*E*) and *s*(ln[*Z*]) using Eq 17-20:

$$E = -mR \tag{17}$$

$$\ln[Z] = b \tag{18}$$

$$s(E) = s(m)R \tag{19}$$

$$s(\ln[Z]) = s(b)R \tag{20}$$

where:

R = 8.314510 J/(K mol).

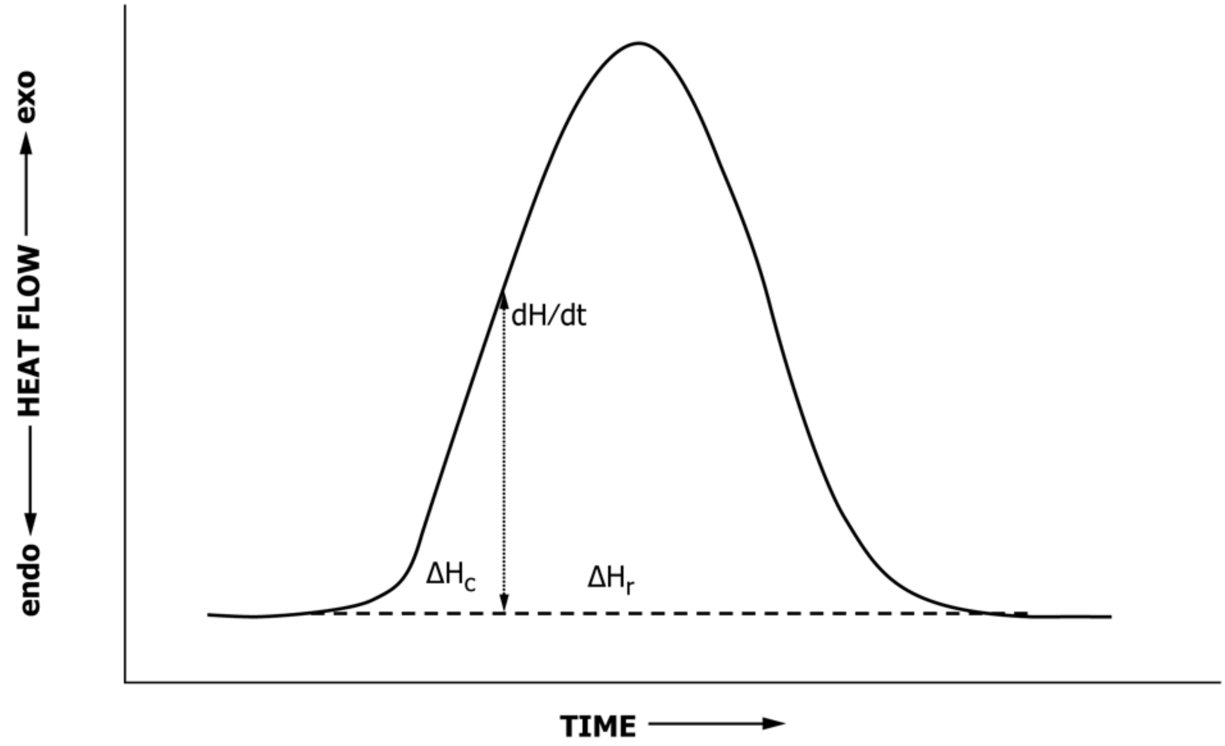


FIG. 4 Partial Area

13.15 Determine the mean value of n (Practice E1970) and its standard deviation $s(n)$ from 13.11.

13.16 Report Test Method A along with the values from 13.14 and 13.15 for $E \pm s(E)$, $\ln[Z] \pm s(\ln[Z])$, and $n \pm s(n)$.

14. Procedure (Test Method B for Sestak Berggren Accelerating Reactions)

14.1 Weigh 4 to 7 ± 1 mg of test specimen in a tared sample container. Hermetically seal the container. Record the total weight of the specimen and the container to ±10 µg.

14.2 Place the test specimen and a similar empty reference container in the apparatus. Close the DSC sample chamber.

14.3 Use a heating rate of 20 K min^{-1} or greater raise the furnace temperature quickly from ambient temperature to the experimental isothermal temperature to produces no more than 1 K overshoot at the experimental temperature. Start the clock and collect the isothermal test data when the specimen test temperature reaches ±1 K of the isothermal test temperature. (See Note 5 and Note 6.)

14.4 Record the sample temperature as, T, 5 min into the experiment.

14.5 Terminate the isothermal experiment when the reaction exotherm is complete, that is, when the thermal curve is horizontal to the time axis.

14.6 Cool the apparatus to ambient room temperature at any convenient rate and reweigh the specimen and container. The thermal curve need not be recorded. Record and report any mass change greater than 0.1 mg from that measured in 14.1.

14.7 Repeat 14.1 – 14.6 with freshly prepared test specimens (at least) three additional isothermal test temperatures. Select experimental temperatures so that total isothermal test times to record the exothermic transition are between 15 and 100 minutes.

14.8 Using the thermal curves from 14.1 – 14.7, calculate partial reaction order parameters (n and m), activation energy, and pre-exponential factor (Z) according to the procedure described in Section 15.

15. Calculation (Test Method B for Accelerating Sestak-Berggren Reactions)

15.1 Prepare a display for each isothermal curve obtained in 14.1 – 14.7 with heat flow on the Y-axis and time on the X-axis for each thermal curve. Construct a linear baseline from a point on the baseline immediately before the reaction exotherm to a point on the baseline immediately after the reaction exotherm for each thermal curve.

15.2 Integrate the total peak areas bounded by the peaks themselves and the constructed baselines to obtain the total heat of reaction (ΔH) in mJ for each thermal curve. (See Note 8.)

15.3 Identify the times that correspond to approximately 10 to 90 % of the peak areas obtained in 15.2.

15.4 Select a time interval that corresponds to a minimum of ten equally time spaced values between the time limits determined in 15.3.

15.5 For each of the intervals in 15.4, record the rate of reaction (dH/dt) in mW, the heat of reaction completed (ΔH_c) in mJ and the heat of reaction remaining (ΔH_f) in mJ as illustrated in Fig. 4. (See Note 10 and Note 11.)

NOTE 15—It is convenient to prepare a table of these values along with the isothermal test temperature in 14.4.

15.6 For each fractional area obtained in 15.5, determine the fraction converted (α), the fraction remaining (1 – α) and the fraction rate of reaction ($d\alpha/dt$) using Eq 13, Eq 14, and Eq 21. (See Note 12.)

$$\alpha = \Delta H_c / \Delta H \quad (21)$$

NOTE 16—For the ten time intervals as described in 15.4, α, values should range between 0.1 to 0.9 and the values for (1 – α) should range between 0.9 and 0.1.

15.7 Calculate the natural logarithm of the rate of reaction ($\ln[d\alpha/dt]$) where $d\alpha/dt$ in units of s^{-1} for each value determined in 15.5 and 15.6.

15.8 Calculate the value for $\ln[\alpha]$ for each value determined in 15.6.

15.9 Calculate the value for $\ln[1 - \alpha]$ for each value determined in 15.5 and 15.6.

15.10 Letting $w = \ln[d\alpha/dt]$, $x = \ln[\alpha]$, and $z = \ln[1 - \alpha]$ solve Eq 22 using multiple linear regression technique for a, b, and c.

$$w = a + bx + cy \quad (22)$$

15.11 Calculate the values for $\ln[k(T)]$ along reaction orders $\not{m}$ and n using Eq 23, Eq 24, and Eq 25.

$$\ln[k\ (T)] = a \quad (23)$$

$$\not{m} = b \quad (24)$$

$$n = c \quad (25)$$

15.12 Calculate the reciprocal of absolute temperature ($1/T$) for each isothermal experiment used in 14.4.

15.13 Prepare a display of $\ln[k(T)]$ from the values from 15.11 on the Y-axis and $1/T$ on the X-axis. (See Note 14.)

15.14 Using a linear regression technique (Practice E1970) determine the slope (m) and intercept (b) of the straight line from 15.13 along with their respective standard deviations $s(m)$ and $s(b)$.

15.15 Calculate the activation energy (E), the natural logarithm of the pre-exponential factor ($\ln[Z]$) and their respective standard deviations $s(E)$ and $s(\ln[Z])$ using Eq 17-20.

15.16 Determine the mean value (Practice E1970) of $\not{m}$ and n along with their respective standard deviations $s(\not{m})$ and $s(n)$.

15.17 Report Test Method B along with the values from steps 15.15 and 15.16 of $E \pm s(E)$, $\ln[Z] \pm s(\ln[Z])$, $\not{m} \pm s(\not{m})$, and $n \pm s(n)$.

16. Procedure (Test Method C for Accelerating Avrami Reactions)

16.1 Weight 4 to 7 mg of test specimen into a tared sample container. Hermetically seal the container. Record the total weight of the specimen and the container to ±10 µg.

16.2 Place the test specimen and similar empty reference container in the apparatus. Close the DSC sample chamber.

16.3 Use a heating rate of 20 K/min or greater to raise the furnace temperature quickly from ambient temperature to the experimental isothermal temperature and that produces no more than 1 K overshoot at the experimental temperature. Start the clock and collect the isothermal test data of heat flow and time when the specimen test temperature reaches ±1 K of the isothermal test temperature. (See Note 5 and Note 6.)

16.4 Record the specimen temperature as, *T*, 5 min into the experiment.

16.5 Terminate the isothermal experiment when the reaction exotherm is complete, that is, when the thermal curve is horizontal to the time axis.

16.6 Cool the test specimen to ambient temperature at any convenient rate. The thermal curve need not be recorded. Reweigh the specimen and container. Record and report any change in mass greater than 0.1 mg from that measured in 16.1.

16.7 Repeat 16.1 – 16.6 with freshly prepared test specimens at (at least) three additional isothermal test temperatures. Select the experimental temperatures so that isothermal test times to complete the exotherm reaction are between 15 and 100 min.

16.8 Using the thermal curves from 16.1 – 16.716.1, calculate activation energy (*E*), natural logarithm of the preexponetial factor (ln[*Z*]) and reaction order (*n*) according to the procedure described in Section 17.

17. Calculation (Test Method C for Accelerating Avrami Reaction)

17.1 Prepare a display for each isothermal experiment obtained in 16.1 – 16.7 with heat flow on the Y-axis and time on the X-axis. Construct a linear baseline form a point on the baseline immediately before the reaction exotherm to a point on the baseline immediately after the reaction for each thermal curve.

17.2 Integrate the total peak area bounded by the peaks themselves and the constructed baselines in 17.1 to obtain the total heat of reaction (ΔH) in mJ for each thermal curve. (See Note 8.)

17.3 Identify the times that correspond to approximately 10 to 90 % of the peak areas obtained in 17.2.

17.4 Select a time interval that provides a minimum of ten equally time spaced values between the time limits determined in 17.3.

17.5 For each of the time intervals in 17.4, record the heat of the reaction remaining (ΔH_r) in mJ and elapsed time (t) as illustrated in Fig. 4.

NOTE 17—It is convenient to prepare a table of these values along with the respective isothermal test temperature in 16.4.

17.6 For each fractional area obtained in 17.5, determine the fraction remaining ($1 - \alpha$) and the correspond elapsed time (t). (See Eq 13.)

NOTE 18—Retain all available significant figures for the calculation and round the final result to the number of significant figures described in Section 18.

NOTE 19—For ten time intervals as described in 17.4, values for ($1 - \alpha$) should range between 0.9 and 0.1.

17.7 For each elapsed time from 17.5 and fraction remaining from 17.6 determine the natural logarithm of the fraction remaining ($\ln(1 - \alpha)$).

17.8 Determine the natural logarithm for the negative value of each logarithm of the fraction remaining $\ln[-\ln(1 - \alpha)]$.

17.9 Create a display of $\ln[-\ln(1 - \alpha)]$ on the Y-axis versus $\ln[t]$ on the X-axis. (See Note 14.)

17.10 Using linear regression techniques (see Practice E1970), determine the value of the slope (m) and intercept (b) of the straight line display in 17.9.

17.11 Calculate the value of reaction order p and $\ln[k(T)]$ using Eq 26 and Eq 16.

$$p = m \tag{26}$$

17.12 Prepare a display $\ln[k(T)]$ from 17.11 on the Y-axis and 1/T from 16.4 on the X-axis.

17.13 Using linear regression technique (Practice E1970) determine the slope (m) and intercept (b) of the straight line in 17.11 along with their respective standard deviations $s(m)$ and $s(b)$.

17.14 Determine the mean value for reaction order p and its standard deviation $s(p)$ from the table of 17.12.

17.15 Calculate the value of $\ln[Z]$ and its standard deviation ($s(\ln[Z])$ from Eq 20. (See Eq 17-20.)

17.16 Report the values of activation energy and its standard deviation, $s(E)$, $\ln[Z]$ and its standard deviation, $s(\ln[Z])$ and reaction order p and its standard deviation $s(p)$ from 17.14 and 17.15.

17.17 Report $E \pm s(E)$, $\ln[Z] \pm s(\ln[Z])$, and $p \pm s(p)$.

18. Procedure (Test Method D — Time-to-Event)

18.1 Weight 4 to 7 mg of test specimen into a tared sample container. Hermetically seal the container. Record the total weight of the specimen and the container to ±10 µg.

18.2 Place the test specimen and similar empty reference container in the apparatus. Close the DSC sample chamber.

18.3 Use a heating rate of 20 K/min (or greater) to raise the furnace temperature quickly from ambient temperature to the experimental isothermal temperature and that produces no more than 1 K overshoot at the experimental temperature. Start the clock and collect the isothermal test data of heat flow and time when the specimen test temperature reaches ±1 K of the isothermal test temperature. (See Note 5 and Note 6.)

18.4 Record the specimen temperature as, *T*, 5 min into the experiment.

18.5 Terminate the isothermal experiment when the reaction exotherm is complete, that is, when the thermal curve is horizontal to the time axis.

18.6 Cool the test specimen to ambient temperature at any convenient rate. The thermal curve need not be recorded.

Reweight the specimen and container. Record and report any change in mass greater than 0.1 mg from that measured in 18.1.

18.7 Repeat 18.1 – 18.6 with freshly prepared test specimens at (at least) three additional isothermal test temperatures. Select the experimental temperatures so that total isothermal test times to complete the exotherm reaction are between 15 and 100 minutes.

18.8 Calculate activation energy (E), natural logarithm of the pre-exponetial factor (ln[Z]) and reaction order (n) according to the procedure described in Section 19.

19. Calculation (Test Method D — Time-to-Event)

19.1 For each thermal curve obtained in 18.1 – 18.7, determine the lapsed time (Δt) from the initiation of the experiment in 18.3 to the exothermic peak maximum (this lapsed time is the lapsed time required for the test specimen to reach constant conversion).

19.2 Using the lapsed time from 19.1 and temperatures from 18.4, calculate activation energy (E) using calculation Section 19.

19.3 Prepare a display of the values of ln[Δt] from 19.1 on the Y-axis and $1/T$ from 18.4 on the X-axis. (See Note 5 and Note 6.)

19.4 Using linear regression technique (Practice E1970), determine the slope (m) of the straight line in 19.3 along with its standard deviation $s(m)$.

19.5 Using the values from 19.3, determine and report the activation energy (E) and its standard deviation $s(E)$ using Eq 17 and Eq 19.

20. Calculation (Test Method E — Time-To-Event Using Externally Obtained Data)

20.1 Test Method E may be used to determine activation energy from a table of time-to-event (point of constant conversion) and temperature data. The necessary data may use information gathered by other measurements such as Oxidation Induction Time (OIT) Practice D3350 and Test Methods D3895, D4565, D5483, D6186, and E1858 or from Reaction Induction Time (RIT).

20.2 Gather at least four sets of data pairs for time-to-event and corresponding isothermal temperatures, such as those in Section 19.

NOTE 20—It is convenient to prepare a table of these values.

20.3 Calculate the reciprocal of absolute temperature ($1/T$) for each isothermal temperature value in 20.2.

NOTE 21—$1/T$ shall be expressed in units of kK^{-1}.

20.4 Calculate the natural logarithm of the time-to-event (ln[Δt]) for each of the values obtained in 20.2.

NOTE 22—Ensure that the units for all time values are in the same units, preferably seconds.

20.5 Prepare a plot of ln[Δt] on the Y-axis versus $1/T$ on the X-axis as shown in Fig. 5.

20.6 Using a linear regression technique (Practice E1970), determine the slope (m) and standard deviation of slope ($s(m)$) for these data. Values of $s(m)$ have the units of kK.

20.7 Calculate the value for activation energy (E) and standard deviation in activation energy ($s(E)$) using Eq 17 and Eq 19:

20.8 Report activation energy and its standard deviation: $E \pm s(E)$.

21. Report

21.1 Report the following information:

21.1.1 Complete identification and description of the material tested, including source, manufacturing codes, etc.;

21.1.2 Description of the calorimeter and software used for the test;

21.1.3 Experimental conditions including test specimen mass, mass loss, heating rate, temperature range of the tests, specimen container, and purge gas type and flow rate;

21.1.4 Description of the software including the version number used for data treatment;

21.1.5 The values and standard deviations for reaction order ($m \pm s(m)$ $n \pm s(n)$, $p \pm s(p)$), activation energy ($E \pm s(E)$),) and logarithm of the frequency factor (ln[Z] $\pm$ s(ln[Z])), or any combination suited for the purpose at hand;

21.1.6 The test method used;

21.1.7 The original thermal curves; and

21.1.8 The dated version of this standard used.

22. Precision and Bias

22.1 An interlaboratory test was conducted in 2003 to determine the precision and bias of Test Method A of E2070 – 00 using phenyltetrazolthiol as a test specimen.[7] The results from a minimum of 13 laboratories, using 5 replicates each (that is, 48 degrees of freedom), are used to provide the information listed below.

22.2 *Precision:*

22.2.1 Within laboratory variability may be described using the repeatability value (**r**) obtained by multiplying the repeatability standard deviation by 2.8. The repeatability value estimates the 95 % confidence limits. That is, two results obtained in the same laboratory should be considered suspect (at the 95 % confidence level) if the differ by more than the repeatability value **r**.

22.2.2 The within laboratory repeatability relative standard deviation for activation energy, logarithm of the pre-exponential factor expressed in min^{-1} (log[Z]), and reaction orders m and n were found to be 3.1, 3.1, 5.2 and 20, % respectively.

22.2.3 Between laboratory variability may be described using the reproducibility value (**R**) obtained by multiplying the reproducibility standard deviation by 2.8. The reproducibility value estimates the 95 % confidence limits. That is, two results obtained in different laboratories, should be considered suspect

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[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1029. Contact ASTM Customer Service at service@astm.org.

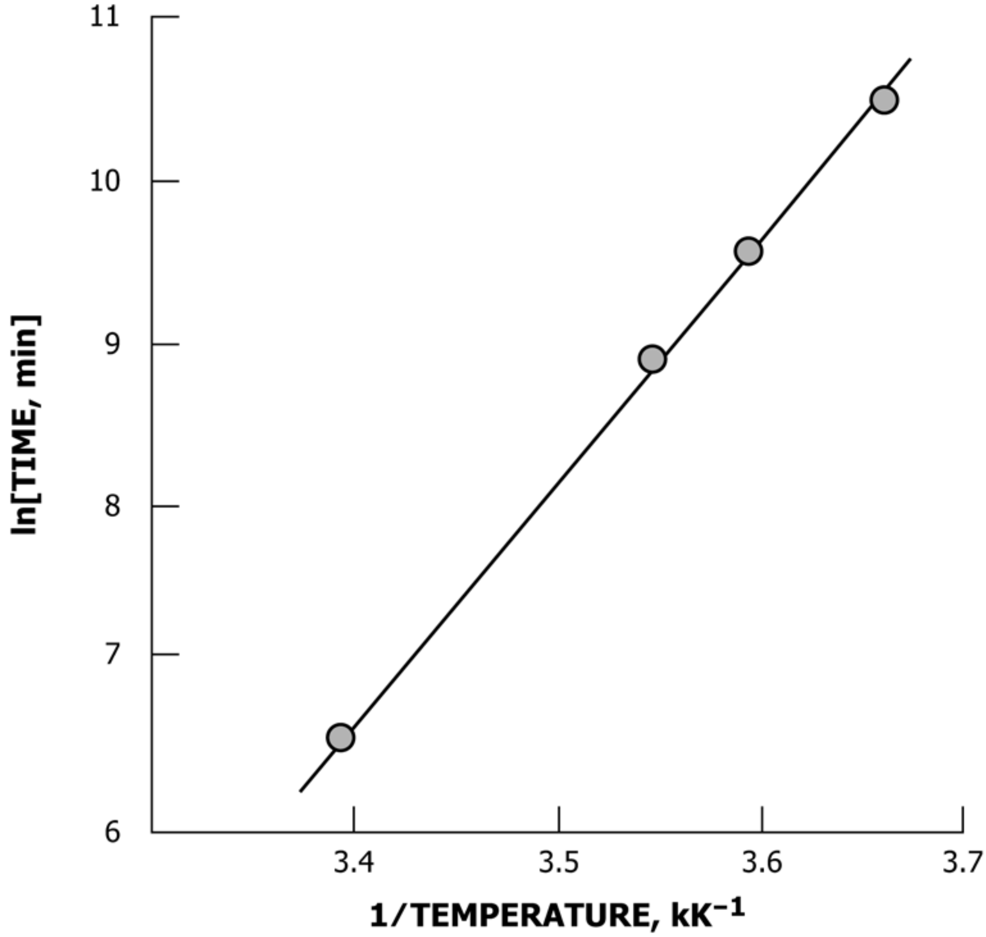

FIG. 5 Plot of ln[*t*] Versus 1/*T*

(at the 95 % confidence level) if they differ by more than the reproducibility value **R**.

22.2.4 The between laboratory reproducibility relative standard deviation for activation energy, logarithm of the pre-exponential factor expressed in min^{-1} (log[*Z*]), and reaction orders *m* and *n* were found to be 12, 11, 9.3 and 21 %, respectively.

22.3 *Bias:*

22.3.1 Bias is the difference between the value obtained and that of a reference material. There are no known standard values for the kinetic parameters for phenyltetrazolthiol and so bias may not be evaluated.

22.3.2 The mean values determined by Test Method A for activation energy, logarithm of the pre-exponential factor expressed in min^{-1} (log[*Z*]), and reaction orders *m* and *n* were found to be 143.1 kJ mol^{-1}, 18.59, 1.32 and 1.68, respectively.

23. Keywords

23.1 activation energy; accelerating reactions; Avrami equation; crystallization reactions; differential scanning calorimetry (DSC); frequency factor; kinetics; *n*th order reactions; pre-exponential factor; reactions; Sestak-Berggren equation; thermal analysis; thermoset cure

APPENDIX

X1. TEST METHOD D—EXAMPLE CALCULATION

X1.1 Shown below is a sample activation energy calculation using Test Method D.

X1.2 A chart on the side of a commercial milk carton lists the storage temperature and shelf life information (see Table X1.1).

X1.3 Convert the storage temperature and shelf life information into Kelvin (K = [{°F - 32} • 5/9] + 273.2) and minutes (min = days • 1440), respectively. These results are shown in Columns A and B in Table X1.2.

X1.4 Calculate the reciprocal of absolute temperature. The results appear in Column C in Table X1.2. For convenience, these values are in kK^{-1} units.

X1.5 Calculate the natural logarithm of time for each value in Column A. The results appear in Column D of Table X1.2.

TABLE X1.1 Milk Carton Chart

Storage Temperature (°F)	Self-Life (days)
32	24
40	10
47	5
70	0.5

TABLE X1.2 Calculation Results

Column	A	B	C	D
	Time (min)	Temperature (K)	(1/*T*) (kK^{-1})	ln[*t*] (ln[min])
	34 560	273.2	3.660	10.450
	14 400	277.6	3.602	9.575
	7 200	281.5	3.552	8.882
	720	294.3	3.398	6.579

X1.6 Prepare a plot of ln[Δt] versus 1/*T*, see Fig. 5. There appears to be a linear relationship between *ln*[Δt] and 1/*T*.

X1.7 Calculate the slope (m) and the standard deviation of the slope for 1/*T* values (X values) from Column C in Table X1.2) and ln[Δt] values (Y values from Column D in Table X1.2), using Practice E1970.

$$m = 14.75\ \text{kK} \qquad (X1.1)$$

$$s_m = 0.24\ \text{kK} \qquad (X1.2)$$

X1.8 Calculate the value for activation energy and its standard deviation (see 14.7)

$$E \pm s_E = (-m \pm s_m)\ R \qquad (X1.3)$$

$$E = -122\ 600 \pm 2\ 000\ \text{J mol}^{-1} \qquad (X1.4)$$

$$= -122.6 \pm 2.0\ \text{kJ mol}^{-1}$$

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