



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

This standard is issued under the fixed designation E 2070; 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 Method A determines 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. This treatment is applicable to low n th order reactions and to autocatalyzed reactions such as thermoset curing or pyrotechnic reactions and crystallization transformations in the temperature range from 300 to 900 K (30 to 630 °C). This test method is applicable only to these types of exothermic reactions when the thermal curves do not exhibit shoulders, discontinuities or shifts in baseline.

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

1.3 Test Method C determines the activation energy and initial heat flow from a series of isothermal experiments over a small temperature range. Because this approach only determines kinetic parameter of activation energy, no knowledge of the kinetic model is required. Therefore it is considered to be “model free”. This approach is broadly applicable to a variety of complicated reactions including those not well understood.

1.4 SI units are the standard.

1.5 This test method is similar but not equivalent to **ISO 11357**, Part 5, and provides more information than the ISO standard.

1.6 *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

- D 3550** Practice for Thick Wall, Ring-Lined, Split Barrel, Drive Sampling of Soils
- D 3895** Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry
- D 4565** Test Methods for Physical and Environmental Performance Properties of Insulations and Jackets for Telecommunications Wire and Cable
- D 5483** Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry
- D 6186** Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC)
- E 473** Terminology Relating to Thermal Analysis and Rheology
- E 537** Test Method for The Thermal Stability Of Chemicals By Differential Scanning Calorimetry
- E 698** Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method
- E 967** Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers
- E 968** Practice for Heat Flow Calibration of Differential Scanning Calorimeters
- E 1142** Terminology Relating to Thermophysical Properties
- E 1445** Terminology Relating to Hazard Potential of Chemicals
- E 1860** Test Method for Elapsed Time Calibration of Thermal Analyzers
- E 1958** Guide for Sensory Claim Substantiation
- E 1970** Practice for Statistical Treatment of Thermoanalytical Data

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 Thermal Test Methods and Practices.

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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.

E 2041 Method for Estimating Kinetic Parameters by Differential Scanning Calorimeter Using the Borchardt and Daniels Method

E 2046 Test Method for Reaction Induction Time by Thermal Analysis

2.2 ISO Standard:

ISO DIS 11357 Part 5 Determination of Temperature and/or Time of Reaction and Reaction Kinetics³

3. Terminology

3.1 Specific technical terms used in this test method are defined in Terminologies **E 473**, **E 1142**, and **E 1445**.

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 autocatalytic, 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. 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 (min^{-1}),

α = fraction reacted or conversion (dimensionless),

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

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

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

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

where:

n and m = partial reaction order terms.

NOTE 1—There are a large number of conversion function expressions for $[f(\alpha)]^4$. Those described here are the more common but are not the

only functions suitable for this method. Eq 2 is known as the general rate equation while Eq 3 is the autocatalytic (or Sestak-Berggren) equation^{5,6}. Eq 2 is used for n^{th} order reactions while Eq 3 is used for thermoset cure and crystallization transformations.

5.3 For a reaction conducted at temperature (T), the autocatalytic rate equation of **5.2** may be cast in its logarithmic form.

$$d\alpha/dt = k(T) \alpha^m (1 - \alpha)^n \quad (4)$$

$$\ln[d\alpha/dt] = \ln[k(T)] + m \ln[\alpha] + n \ln[1 - \alpha] \quad (5)$$

This equation has the form $z = a + bx + cy$ and may be solved using multiple linear regression analysis.

NOTE 2—Subsequent discussions use the autocatalytic form of the rate equation (Eq 3). It 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 The Arrhenius equation describes how the reaction rate changes as a function of temperature:

$$k(T) = Z e^{-E/RT} \quad (6)$$

where:

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

E = activation energy (J 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.

5.5 Eq 6 cast in its logarithmic form is:

$$\ln[k(T)] = \ln[Z] - E/RT \quad (7)$$

Eq 7 has the form of a straight line, $y = x + b$, 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 $\ln[Z]$.

5.6 As an alternative to **5.3** and **5.5**, the rate and Arrhenius equations combined and cast in logarithmic form is:

$$\ln[d\alpha/dt] = \ln[Z] - E/RT + m \ln[\alpha] + n \ln[1 - \alpha] \quad (8)$$

Eq 8 has the form, $z = a + bw + cx + dy$, and may be solved using multiple linear regression analysis.

5.7 If activation energy values only are of interest, Eq 8 may be solved under conditions of constant conversion to yield:

$$\ln[\Delta t] = E/RT + c \quad (9)$$

where:

Δt = lapsed time, (min), at isothermal temperature, T , and

c = constant.

Eq 9 has the form of a straight line, $y = x + b$, 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 .

5.8 If activation energy values only are of interest, Eq 8 may be solved under conditions of constant conversion and the equality $d/dt = dH/dt/H$ to yield:

$$\ln[dH/dt] = E/RT + b = m/T + b \quad (10)$$

where:

H = total heat of reaction (J/g),

dH/dt = instantaneous heat flow (W/g),

³ Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

⁴ Sbirrazzuoli, N.; Brunel, D.; Elegant, L., *J. Therm. Anal.*, 38, 1509-1524, 1992.

⁵ Sestak, J.; Berggren, G.; *Thermochim. Acta*, 3, 1, 1971.

⁶ Gorbachiev, V.M., *J. Therm. Anal.*, 18, 193-197, 1980.

b = constant, and
 m = slope (kK)

Eq 10 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 .

5.9 A series of isothermal experiments by Test Method A described in Section 11 at four or more temperatures, determines the kinetic parameters of activation energy, pre-exponential factor and reaction order. Alternatively, a series of isothermal experiments by Test Method A described in Section 11 at four or more temperatures may be used to determine activation energy and initial heat flow by test Method C described in Section 15. 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 B, described in Section 12, may be used to determine activation energy only.

5.10 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 5, Eq 7, and Eq 8.

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 provides dH/dt and T to solve Eq 10

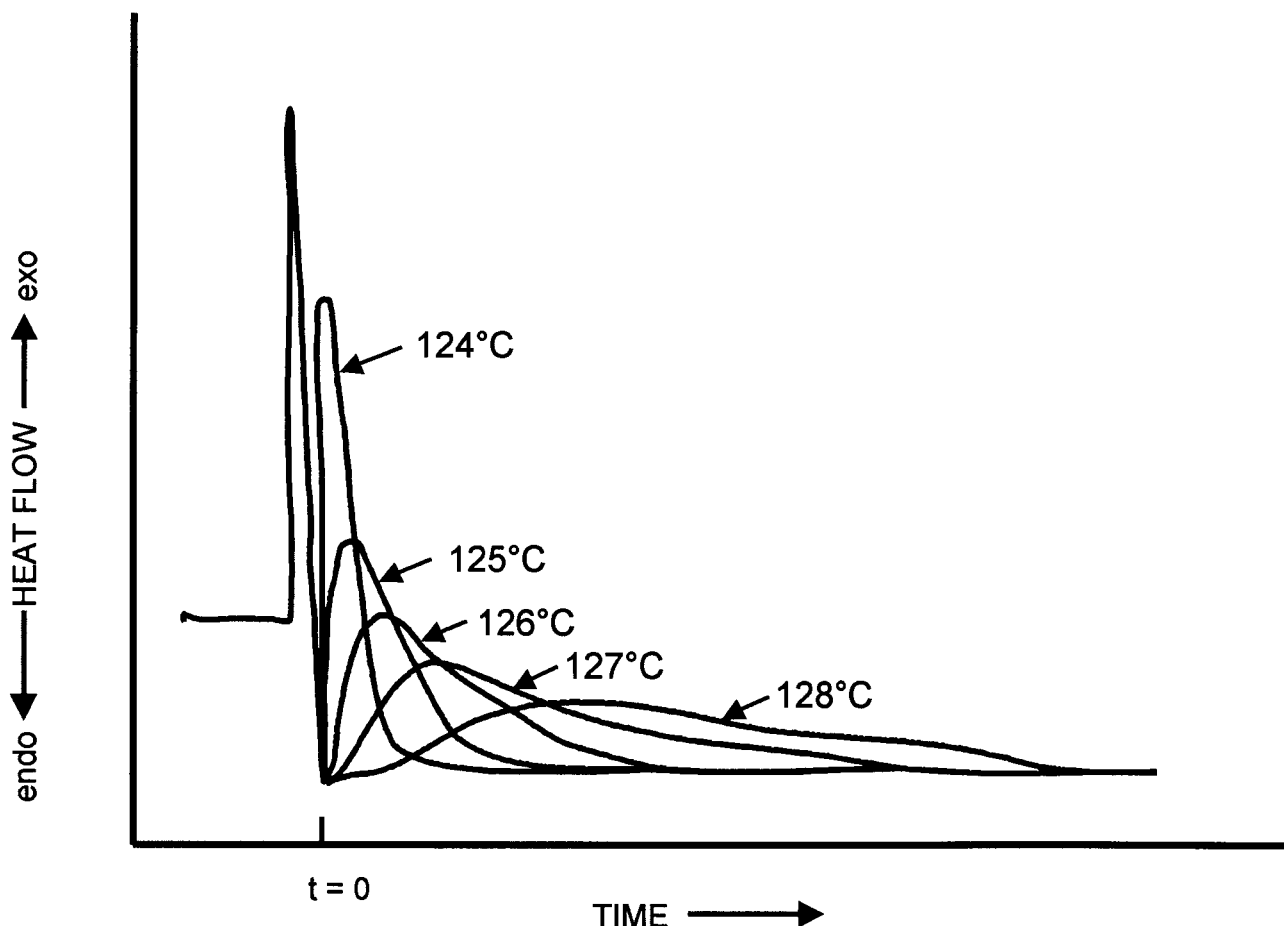
5.12 A variety of time-to-event experiments such as oxidation induction time methods (Test Methods D 3350, D 3895, D 4565, D 5483, D 6186, and E 1958) and reaction induction time methods (E 2046) provide values for Δt and T to solve equation 5.7.

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 method may be compared with those obtained from Test Method E 698 for n th order and autocatalytic reactions. Activation energy,



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

pre-exponential factor and reaction order results by this method may be compared to those for Test Method E 2041 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 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 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 Appendix X1, may confirm the selection of the n th order or autocatalytic 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 autocatalytic 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 $\frac{1}{2} = 0.5$.

7.7 Autocatalytic kinetic reactions anticipate that m and n are fractions between 0 and 1 and that their sum ($m + n$) is less than 2.

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

7.9 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 7.)

9. Apparatus

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

9.1.1 A DSC Test Chamber, composed of:

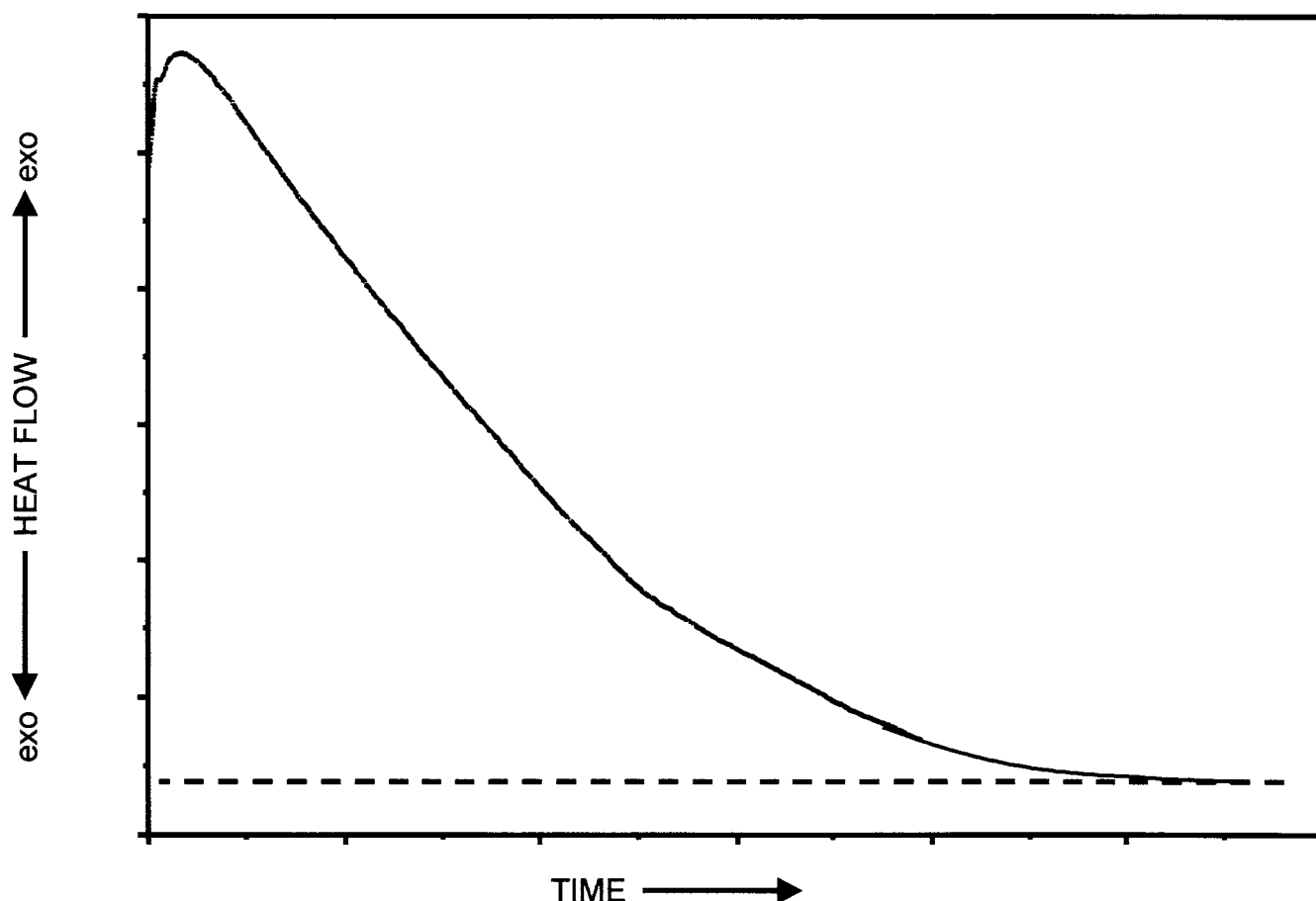


FIG. 2 Heat Flow Curve for an n th Order Reaction

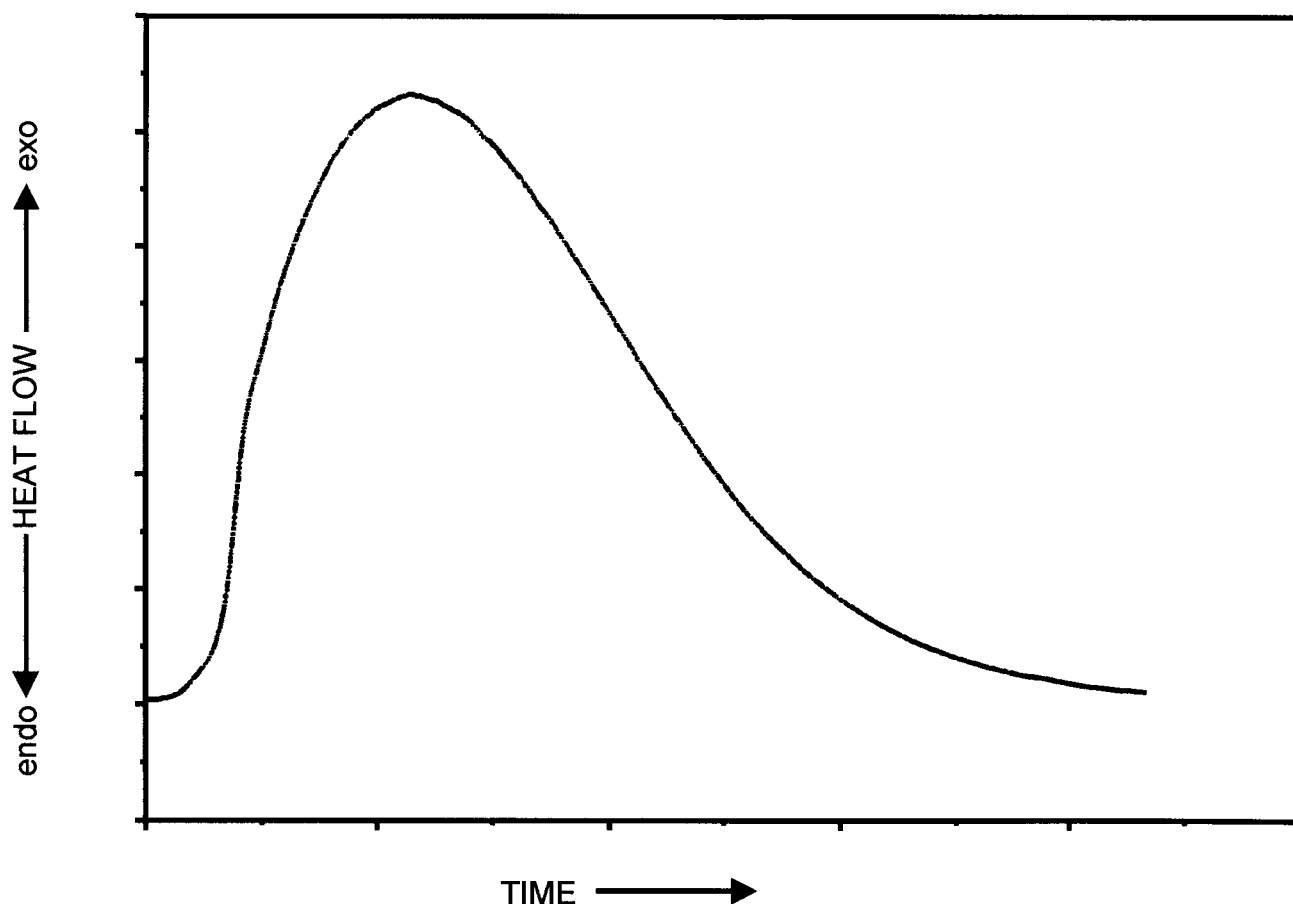


FIG. 3 Heat Flow Curve for an Autocatalyzed Reaction

9.1.1.1 A *Furnace(s)*, that provides uniform controlled heating of a specimen and reference to constant temperature at a constant rate within the applicable temperature range of this test method.

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 $1 \mu\text{W}$.

9.1.1.4 A means of sustaining a purge gas rate of 10 to $50 \pm \text{mL/minute}$ 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*, for furnace(s) temperature programs between selected temperature limits (that is, 300 to 900 K) capable of controlling the rate of temperature change of up to 100 K min^{-1} constant to $\pm 0.1 \text{ K min}^{-1}$.

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 in accordance with the requirements of this test method.

9.3 A *Balance*, to weigh specimens and/or containers to $\pm 10 \mu\text{g}$ 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 E 967.

10.3 Calibrate the DSC heat flow signal using Test Method E 968.

10.4 Confirm that the elapsed time conformity of the thermal analyzer "clock" is better than 0.1 % using Test Method E 1860.

11. Procedure (Test Method A and C)

11.1 Weigh 4 to $7 \pm 1 \text{ mg}$ of test specimen in a tared sample container. Seal the container. Record the total weight of the specimen and the container to $\pm 10 \mu\text{g}$.

11.2 Place the test specimen and a similar empty reference container in the apparatus. Close the DSC sample chamber and prepare the apparatus for an experimental run.

11.3 Use a temperature program of 20 K min^{-1} to raise the furnace temperature quickly from room 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 when the specimen test temperature reaches ± 1 K of the isothermal test temperature.

NOTE 5—A dynamic test, such as Test Method E 537 may be used to determine the experimental isothermal test temperatures. Isothermal test temperatures typically are selected to be those between 1 and 10 % of the total reaction by Test Method E 537.

NOTE 6—In some instruments that do not measure the specimen temperature directly, temperature may be determined from a known relationship between heat flow and the reference or program temperature (for example; 20 mW $\approx$ 1 K).

NOTE 7—In some apparatus it may not be possible to achieve less than 1K 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, however, protective safety equipment shall be used to ensure the safety of the operator from thermal burns and from premature rupture of the specimen container.

11.4 Record the sample temperature 5 min into the experiment.

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

11.6 Cool the apparatus to ambient room temperature and reweigh the specimen. Record and report the specimen weight change measured in 11.1.

11.7 Repeat 11.1-11.6 with freshly prepared test specimens at least three additional isothermal test temperatures. Select experimental temperatures so that isothermal test times to record the exothermic transition are between fifteen and one hundred minutes.

11.8 Calculate partial reaction order parameters (n and m), activation energy, and pre-exponential factor (Z) according to the procedure described in Section 13 or activation energy (E) and initial heat flow $(dH/dt)_0$ according to the procedure described in Method C in Section 15.

12. Procedure (Test Method B)

12.1 For each thermal curve obtained in 11.1-11.7, determine the lapsed time from the initiation of the experiment in 11.3 to the exothermic peak (this lapsed time is the lapsed time for the test specimen to reach constant conversion).

12.2 Using the lapsed time from 12.1 and temperatures from 11.4, calculate activation energy (E) using calculation Section 14.

13. Calculation (Test Method A)

13.1 For each isothermal experiment, construct a linear baseline from a point on the baseline before the reaction exotherm to a point on the baseline after the reaction.

NOTE 8—An n th order reaction may require extrapolation of the baseline at the end of the experiment forward as in Fig. 2.

13.2 Integrate the total peak area bounded by the peak itself and the constructed baseline to obtain the heat of the reaction (in mJ). This value is ΔH .

NOTE 9—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 10—In n th order reactions, an appreciable fraction of the reaction may take place before temperature equilibrium of test specimen is achieved. In such cases, the value for ΔH may be taken from a temperature programmed experiment such as Test Method E 537.

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

13.4 Select a time interval that provides a minimum of ten equally time spaced 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 the reaction completed (ΔH_c) in mJ and the heat of reaction remaining (ΔH_r) in mJ as illustrated in Fig. 4.

NOTE 11—It is convenient to prepare a table of these values.

13.6 For each fractional area obtained in 13.5, determine the fraction converted (α), the fraction remaining $(1 - \alpha)$ and the fractional rate of reaction $(d\alpha/dt)$ using the following equations:

$$\alpha = \Delta H_c / \Delta H \quad (11)$$

$$(1 - \alpha) = \Delta H_r / \Delta H$$

$$d\alpha/dt = (dH/dt) / \Delta H$$

NOTE 12—Retain all available significant figures for the calculations and round the final result to the number of significant figures described in Section 17.

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

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

13.8 Calculate the value for $\ln[\alpha]$ for each value determined in 13.5 and 13.6.

13.9 Calculate the value for $\ln[1 - \alpha]$ for each value determined in 13.5 and 13.6.

13.10 Calculate the value for $\ln[k(T)]$, m and n and their respective standard deviations, $s_{\ln(k)}$, s_m and s_n using a multiple linear regression technique and equation:

$$\ln[k(T)] = \ln[d\alpha/dt] - m \ln[\alpha] - n \ln[1 - \alpha] \quad (12)$$

13.11 Report $\ln[le(T)]$.

13.12 Calculate the reciprocal of absolute temperature $(1/T)$ for each isothermal experiment used in 13.2.

NOTE 14— $1/T$ shall be expressed in units of K^{-1} .

13.13 Prepare a plot of $\ln[k(T)]$ versus $1/T$ using the values from 13.11 and 13.12.

13.14 Using a least squares best fit technique (Test Method E 970), determine the slope and standard deviation of slope for this straight line. Values of m and s_m have the units of K^{-1} .

13.15 Calculate the value for activation energy and standard deviation in activation energy using the following equations:

$$s_E = s_m \cdot R \quad (13)$$

where:

$$R = 8314 \text{ J mol}^{-1} \text{ K}^{-1}.$$

13.16 Report activation energy and its standard deviation: $E \pm s_E$.

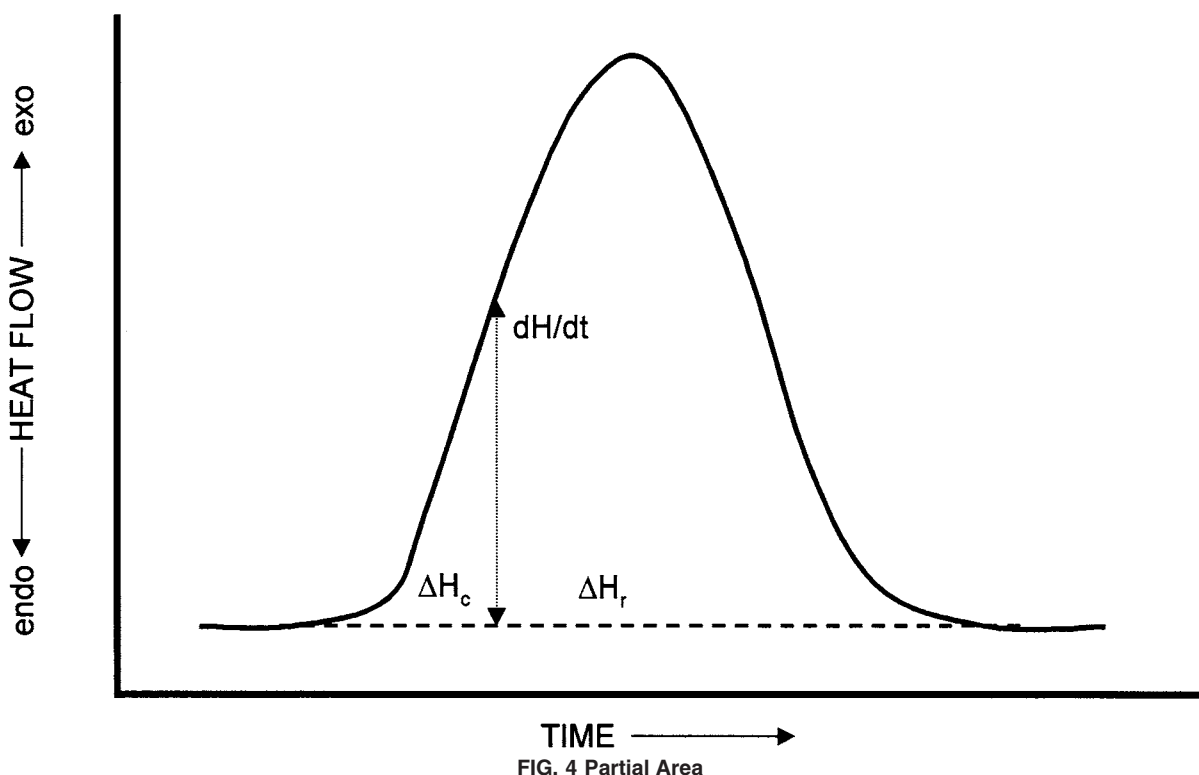


FIG. 4 Partial Area

14. Calculation (Test Method B)

14.1 Test Method B may be used to determine activation energy from a table of time-to-event and temperature data. The necessary data may be obtained by this method or may use information gathered by other measurements such as Oxidation Induction Time (OIT) Test Method D 3350, **D 3895**, **D 4565**, **D 5483**, **D 6186** or **E 1958** or from Reaction Induction Time (RIT) or may be used by selecting the point of constant conversion (such as the time to the peak) of data generated by this test method.

14.2 Gather at least four sets of data pairs for time-to-event and corresponding isothermal temperatures, such as those in Section 12.

NOTE 15—It is convenient to prepare a table of these values.

14.3 Calculate the reciprocal of absolute temperature ($1/T$) for each isothermal temperature value in 14.2.

NOTE 16— $1/T$ shall be expressed in units of K^{-1} .

14.4 Calculate the natural logarithm of the time-to-event ($\ln[\Delta t]$) for each of the values obtained in 14.2.

NOTE 17—Ensure that the units for all time values are in the same units, preferably minutes.

14.5 Prepare a plot of $\ln[\Delta t]$ versus $1/T$ as shown in Fig. 5.

NOTE 18—Over a narrow temperature range, this plot should result in a straight line. If it does not, additional data sets may be required to determine the characteristics of the plot.

14.6 Using a least squares best fit technique (Practice **E 970**), determine the slope and standard deviation of slope (s_m) for these data. Values of s_m have the units of K^{-1} .

14.7 Calculate the value for activation energy (E) and standard deviation in activation energy (s_E) using the following equations:

$$s_E = s_m \cdot R \quad (14)$$

where:

$$R = 8314 \text{ J mol}^{-1} \text{ K}^{-1}.$$

14.8 Report activation energy and its standard deviation: $E \pm s_E$.

15. Calculation (Test Method C)

15.1 Test Method C may be used to determine activation energy and initial heat flow from a table of peak heat flow and temperature data. The necessary data may be obtained using 11.

15.2 For each isothermal experiment, construct a linear baseline from a point on the baseline before the reaction exotherm to a point on the baseline after the reaction.

NOTE 19—An n^{th} order reaction may require extrapolation of the baseline at the end of the experiment forward as in Fig. 2.

15.3 For each thermal curve, record the rate of reaction (dH/dt) in W/g and temperature (T) in K at a point of constant conversion, typically at the peak of the exothermic reaction (see Fig. 6).

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

15.4 Calculate the natural logarithm of each reaction rate for each value determined in 15.3.

15.5 Calculate the reciprocal of the absolute temperature ($1/T$) for each isothermal experiment used in 15.3.

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

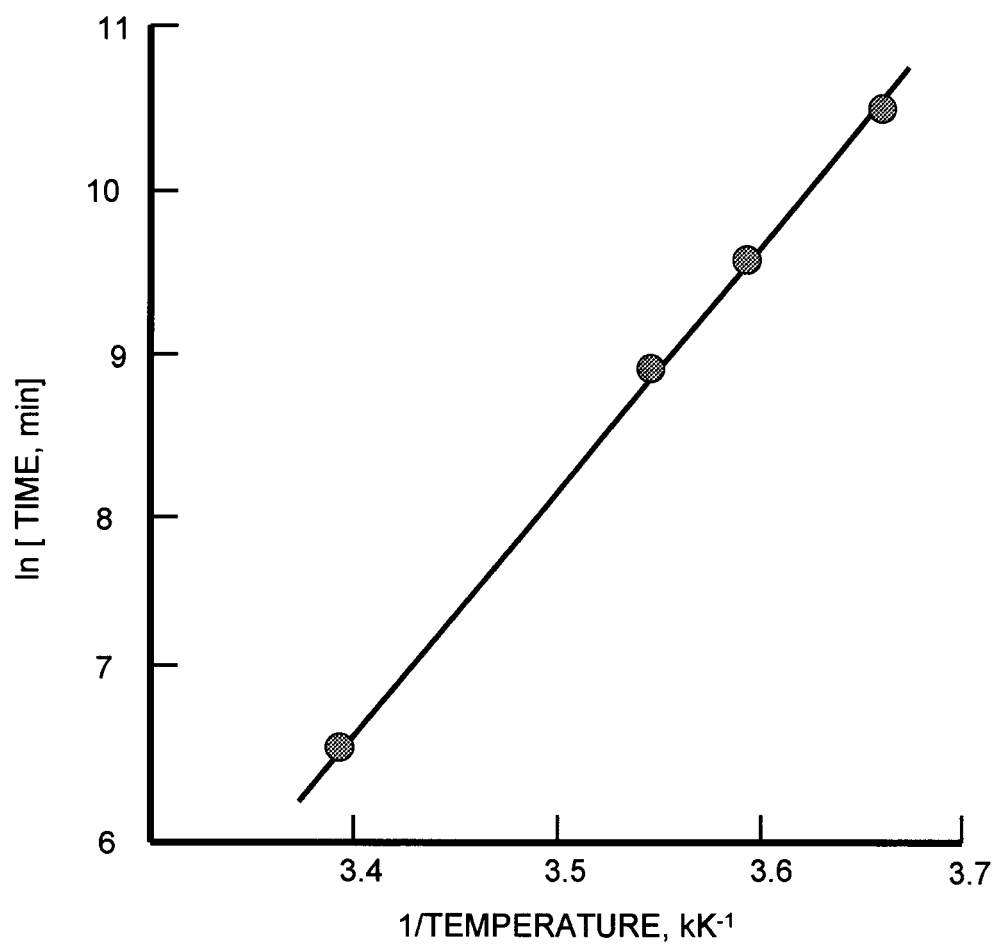


FIG. 5 Plot of $\ln[\eta]$ Versus $1/T$

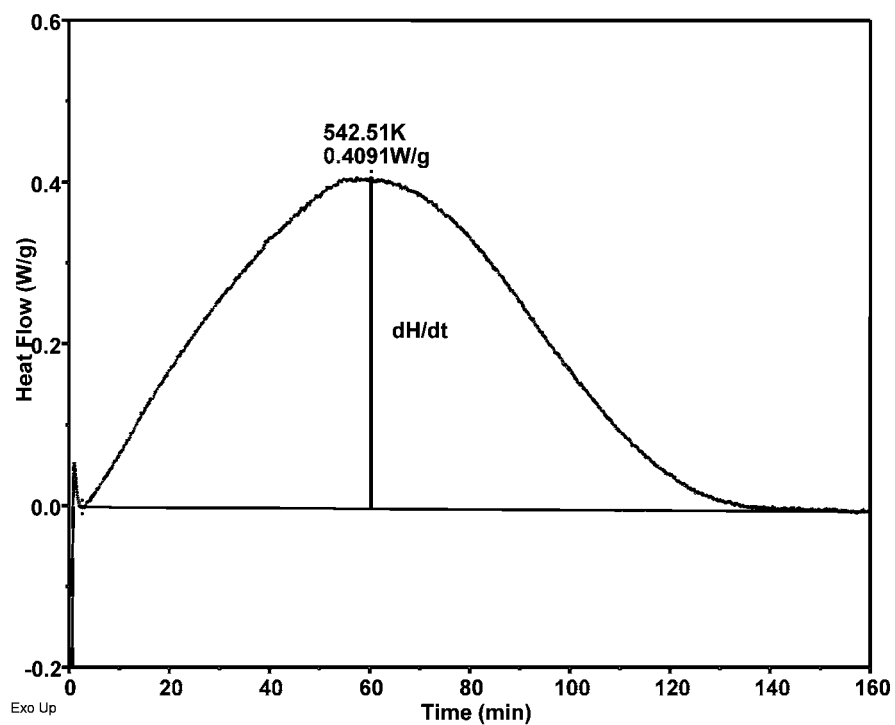


FIG. 6 Determination of Heat Flow at Peak Maxima under Isothermal Temperature

15.6 Prepare a plot of $\ln[dH/dt]$ versus $1/T$ using the values from Sections 15.4 and 15.5 (see Fig. 7).

15.7 Using a least squares best-fit technique (Test Method E 1970), determine the slope (m), intercept (b) and standard deviation of the slope (s_m) for the straight line (Eq 11) Values of m and s_m have the units of kK . b is dimensionless.

15.8 Calculate the value for activation energy (E) and its standard deviation (s_E) using: Eq 13.

15.9 Report activation energy and its standard deviation $E \pm s_E$.

15.10 Identify the initial temperature T_o for the purpose at hand. Calculate the reciprocal of the initial temperature ($1/T_o$) in units of kK^{-1} .

15.11 Using the values for m , b and T_o from Sections 15.7 and 15.10, Eq 15, determine the natural logarithm of the initial heat flow ($\ln[(dH/dt)_o]$) using:

$$\ln[(dH/dt)_o] = m/T_o + b \quad (15)$$

15.12 Take the antilogarithm of $\ln[(dH/dt)_o]$ to determine the initial heat flow.

$$(dH/dt)_o = \exp \{ \ln[(dH/dt)_o] \} \quad (16)$$

15.13 Report the initial temperature and the associate initial heat flow from Sections 15.10 and 15.12.

16. Report

16.1 Report the following information:

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

16.1.2 Description of the calorimeter and software used for the test,

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

16.1.4 Description of the software including the version number used for data treatment,

16.1.5 The values and standard deviations for reaction order ($m \pm s_m$), activation energy ($E \pm s_E$), initial heat flow, ($(dH/dt)_o$) and logarithm of the frequency factor ($\ln Z \pm s_{\ln z}$), or any combination suited for the purpose at hand. Report all values to one position to the right of the decimal point,

16.1.6 The logarithm of the rate constant at the temperature of interest,

16.1.7 The original thermal curves, and

16.1.8 The dated version of this method used.

17. Precision and Bias

17.1 An interlaboratory test was conducted in 2003 to determine the precision and bias of Method B of E 2070-00 using phenyltetrazolthiol as a test specimen.⁷ The results from a minimum of 13 laboratories, using 5 replicates each (i.e., 48 degrees of freedom), are used to provide the information listed below.

17.2 Precision:

17.2.1 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 they differ by more than the repeatability value r .

17.2.2 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 were found to be 3.12, 3.12, 5.14 and 19.9, % respectively.

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

17.2.4 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 were found to be 11.7, 11.4, 9.28 and 21.0 %, respectively.

⁷ A Research Report is available from ASTM Headquarters. Request RR: E37-1029.

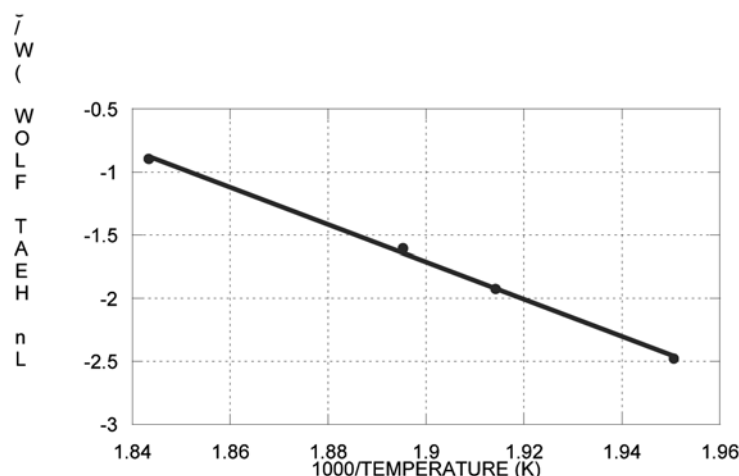


FIG. 7 Plot of $\ln[dh/dt]$ Versus $1/T$

17.3 Bias:

17.3.1 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.

17.3.2 The mean values determined by Method B for activation energy, logarithm of the pre-exponential factor expressed in $\text{min}^{-1}(\log[Z])$, and reaction orders were found to be 143.1 kJ mol⁻¹, 18.59, 1.32 and 1.68, respectively.

18. Keywords

18.1 activation energy; autocatalytic reactions; crystallization reactions; differential scanning calorimetry (DSC); frequency factor; kinetics; *n*th order reactions; pre-exponential factor; reactions; thermal analysis; thermoset cure

APPENDIXES

X1. TEST FOR *n*th ORDER OR AUTOCATALYTIC REACTIONS

X1.1 Different forms of the rate equation are used for *n*th order and autocatalytic reactions. This appendix describes a useful test procedure for identifying the reaction type applicable to the material under test.

X1.2 Weigh 1 to 5 mg of the test specimen into a 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. Close the DSC sample chamber and prepare the apparatus for an experimental run.

X1.3 Select an isothermal test temperature corresponding to 10 % peak area from a scouting run performed by Test Method E 537. Equilibrate the apparatus at this test temperature.

X1.4 Initiate the experiment recording heat flow as a function of time.

X1.5 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). **Caution**—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 7).

X1.6 Observe the shape of the resultant thermal curve. An *n*th order reaction is likely when the heat flow curve reaches a maximum within seconds 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 autocatalyzed reaction.

X2. TEST METHOD B—EXAMPLE CALCULATION

X2.1 Shown below is a sample activation energy calculation using Test Method B.

X2.2 A chart on the side of a commercial milk carton lists the storage temperature and shelf life information (see Table X2.1).

X2.3 Convert the storage temperature and shelf life information into Kelvin ($K = [(\text{°F} - 32) \cdot 5/9] + 273.2$) and minutes ($\text{min} = \text{days} \cdot 1440$), respectively. These results are shown in Columns A and B in Table X2.2.

X2.4 Calculate the reciprocal of absolute temperature. The results appear in Column C in Table X2.2. For convenience, these values are in kK⁻¹ units.

TABLE X2.1 Milk Carton Chart

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

TABLE X2.2 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

X2.5 Calculate the natural logarithm of time for each value in column A. The results appear in column D of Table X2.2.

X2.6 Prepare a plot of $\ln[\Delta t]$ versus $1/T$, see Fig. 5. There appears to be a linear relationship between $\ln[\Delta t]$ and $1/T$. If these data do not appear to be linear, collect additional data to verify non-linearity.

X2.7 Calculate the slope (*m*) and the standard deviation of the slope for $1/T$ values (*X* values) from Column C in Table X2.2) and $\ln[\Delta t]$ values (*Y* values from Column D in Table X2.2), using Practice E 1970.

$$m = 14.75 \text{ kK} \quad (\text{X2.1})$$

$$s_m = 0.24 \text{ kK} \quad (\text{X2.2})$$

$$E \pm s_E = (-m \pm s_m) R \quad (\text{X2.3})$$

X2.8 Calculate the value for activation energy and its standard deviation (see 14.7)

$$\begin{aligned} E &= -122\,600 \pm 2\,000 \text{ J mol}^{-1} \\ &= -122.6 \pm 2.0 \text{ kJ mol}^{-1} \end{aligned} \quad (\text{X2.4})$$

X3. TEST METHOD C—EXAMPLE CALCULATION

X3.1 Shown below is a sample activation energy and initial heat flow calculation using Test method C.

X3.2 A table of experimental results for 5-chloro-2-nitrobenzoic acid is taken from the literature⁸ for the peak heat flow and corresponding isothermal temperatures and is presented in Table X3.1.

X3.3 Calculate the reciprocal of absolute temperature for each value in column F. The results appear in column G in Table X3.1. For convenience, these values are expressed in units of kK^{-1} .

X3.4 Calculate the natural logarithm of heat flow in units of W/g for each value in column E. The results appear in column H of Table X3.1.

X3.5 Prepare a plot of $\ln[dH/dt]$ versus $1/T$, see Fig. 7. A linear relationship should exist. If the data do not appear linear, collect additional data to verify non-linearity..

X3.6 Calculate the slope (m), its standard deviation(s_E), and intercept (b) for the $1/T$ (X-values) from column G and $\ln[dH/dt]$ values (Y-values) from column H in Table X3.1, using Practice E 1970.

$$\begin{aligned} m &= 14.747 \text{ kK} \\ s_m &= 1.40 \text{ kK} \\ b &= 26.306 \end{aligned}$$

X3.7 Calculate the value for activation energy and its standard deviation:

$$E \pm s_E = (-m \pm s_m) R \quad (\text{X3.1})$$

$$\begin{aligned} E &= -122\,606 \pm 11\,640 \text{ J mol}^{-1} \\ &= -123 \pm 11 \text{ kJ mol}^{-1} \end{aligned} \quad (\text{X3.2})$$

X3.8 Select a temperature of interest for the initial temperature (T_0). For example, $500 \text{ K} = 0.5 \text{ kK}$

X3.9 Calculate the logarithm of the initial heat flow using Eq X3.3 for $m = -14.747 \text{ kK}$ and $b = 26.306$.

$$\ln[(dH/dt)_0] = -14.747 \text{ kK} / 0.500 \text{ kK} - 26.306 = -3.188 \quad (\text{X3.3})$$

X3.10 Obtain $(dH/dt)_0$ by taking the antilog of Eq X3.3

$$(dH/dt)_0 = \exp\{\ln[-3.188]\} = 0.0413 \text{ W/g at } 500 \text{ K}. \quad (\text{X3.4})$$

TABLE X3.1 Calculated Results

Column	E	F	G	H
	Heat Flow (min)	Temperature (K)	$1/T$	$\ln[dH/dt]$
	(W/g)	(K)	(kK^{-1})	($\ln[\text{W/g}]$)
				
	0.4080	542.51	1.8433	-0.8965
	0.2011	527.61	1.8953	-1.6040
	0.1463	12.68	1.9505	-2.4768

⁸ Sima Chervin, Glenn Bodman, "Phenomenon of Autocatalysis in Decomposition of Energetic Chemicals", Proceedings of the 27th Conference of the North American Thermal Analysis Society, 1999, pp. 125–129.

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