Designation: E2070 – 08

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 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 ($\sim$ 10 K) temperature range. This treatment is applicable to low nth 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 This test method is similar but not equivalent to ISO DIS 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]

D3550 Practice for Thick Wall, Ring-Lined, Split Barrel, Drive Sampling of Soils

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

E1860 Test Method for Elapsed Time Calibration of Thermal Analyzers

E1958 Guide for Sensory Claim Substantiation

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

2.2 *ISO Standard:*

ISO DIS 11357 Part 5: Determination of Temperature and/or Time of Reaction and Reaction Kinetics[3]

3. Terminology

3.1 Specific technical terms used in this test method are defined in Terminologies E473, E1142, and E1445.

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, nth 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:

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

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:

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

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

where:

$n\ and\ m$ = partial reaction order terms.

NOTE 1—There are a large number of conversion function expressions for [f(α)][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 auto-catalytic rate equation of 5.2 may be cast in its logarithmic form.

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

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

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:

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

where:

Z = pre-exponential factor (min^{-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.

5.5 Eq 6 cast in its logarithmic form is:

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

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:

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

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:

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

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:

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

where:

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

---

[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.; 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.

dH/dt = instantaneous heat flow (W/g),
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 (Practice D3550 and Test Methods D3895, D4565, D5483, and D6186 and Guide E1958) and reaction induction time methods (Test Method E2046) 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 E698 for nth order and autocatalytic reactions. Activation energy,
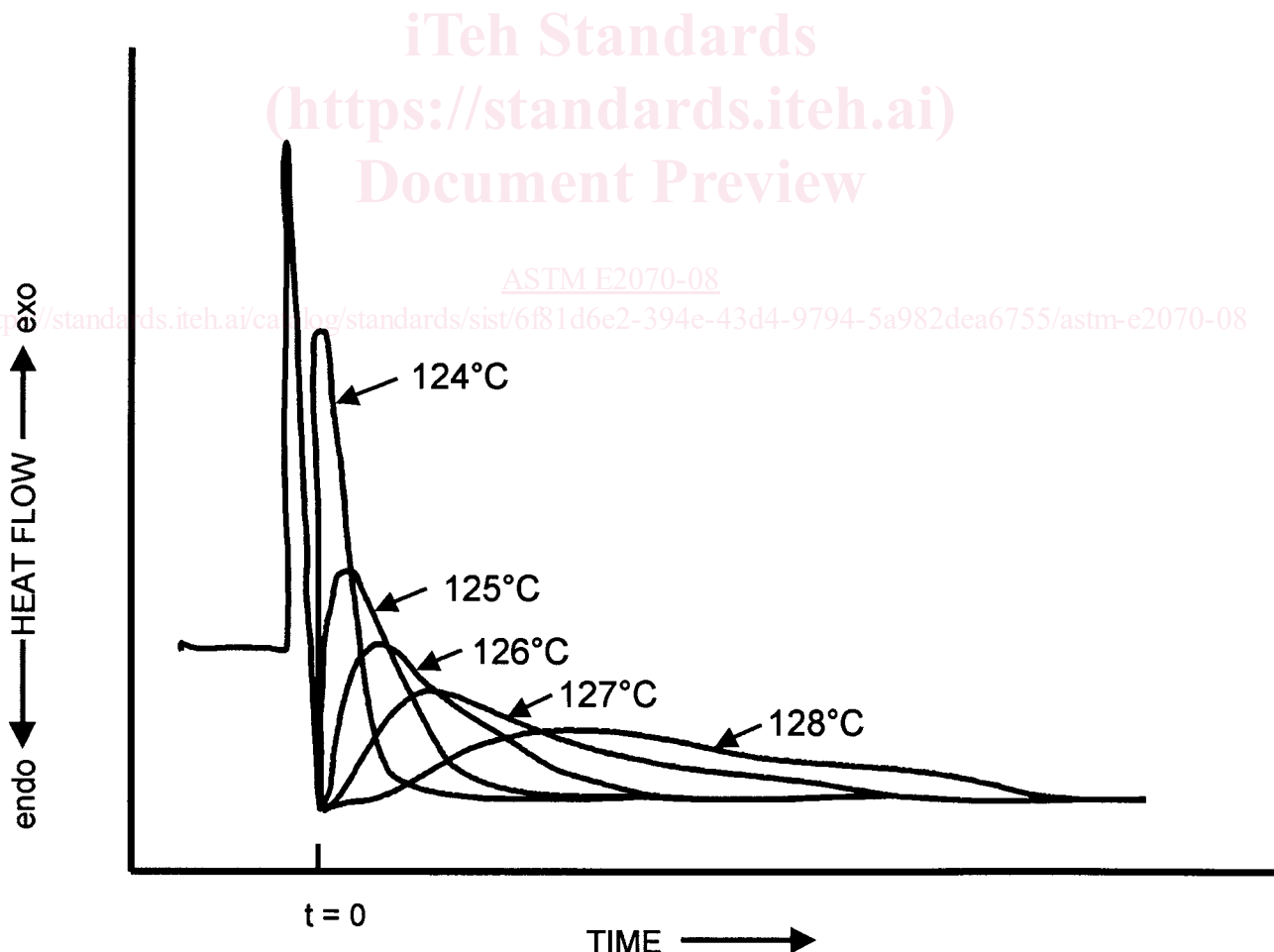
NOTE 1—This figure is for a crystallization application in which the reaction rate increases with decreasing temperature. Chemical reactions show an increase in reaction rate with increasing temperature.

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 E2041 for nth 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 nth order or autocatalytic models.

7.4 Typical nth 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 nth order kinetic reactions, this method antici- pates 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 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 essen- tial 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:

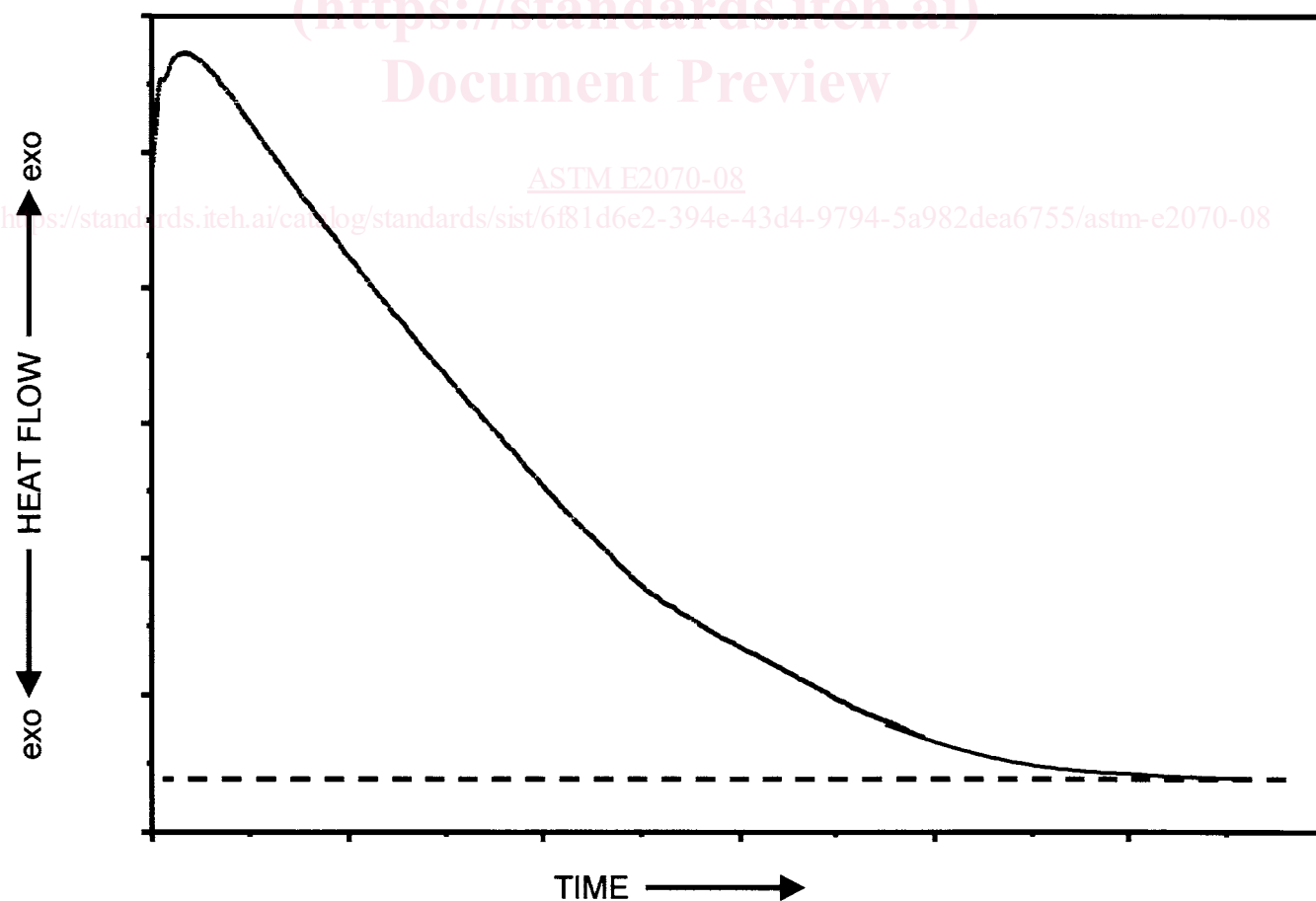9.1.1 *A DSC Test Chamber,* composed of:

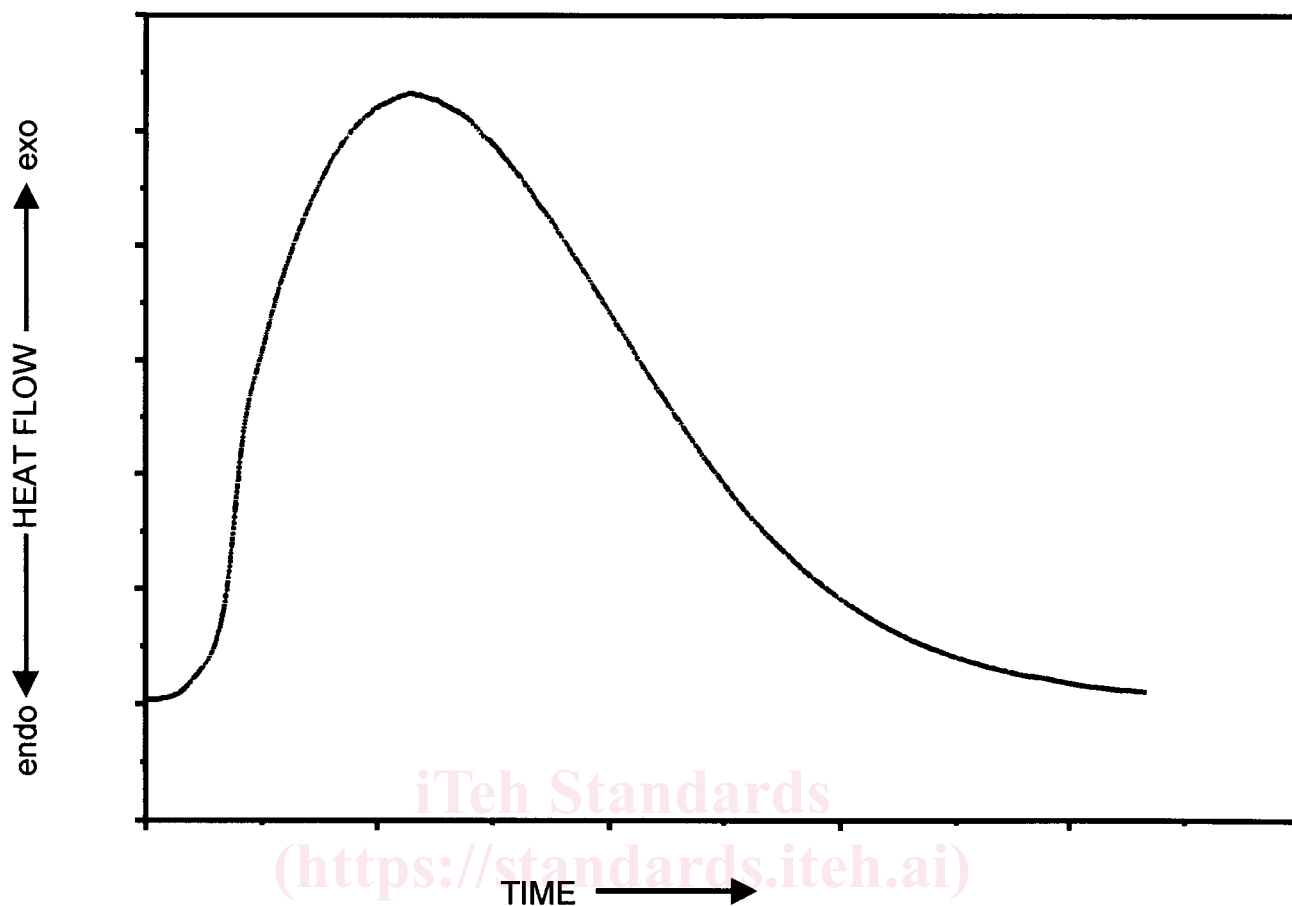FIG. 2 Heat Flow Curve for an nth Order Reaction

4

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 µW.

9.1.1.4 A means of sustaining a purge gas rate of 10 to 50 ± 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 ± 0.1 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 ± 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 (Test Method A and C)

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

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 E537 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 E537.

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 ≈ 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 $(dH/dt)_o$ 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 nth 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 nth 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 E537.

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:

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

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

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

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:

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

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 kK⁻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 (Practice E1970), determine the slope and standard deviation of slope for this straight line. Values of and s_m have the units of kK.