Designation: ~~E2070 – 08~~ 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 ~~Method A determines~~ 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~~ (≈10 K) temperature range. ~~This treatment~~ Test Method A is applicable to low nth order ~~reactions and to autocatalyzed~~ 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 ~~(30 to 630 °C).~~ (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 ~~Method B~~ 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.~~ 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.~~

1.3 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 ~~toISO DIS 11357,~~ 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]
~~D3550~~ D3350 ~~Practice for Thick Wall, Ring-Lined, Split Barrel, Drive Sampling of Soils~~ 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

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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.

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 autocatalytic, accelerating (Sestak-Berggren or Avrami models), n^{th} 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. parameter as a function of time under isothermal experimental conditions. DSC is useful for the measurement of the total heat of a reaction and the rate of the reaction as a function of time and temperature.

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

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

where:

$d\alpha/dt$	=	reaction rate (min^{-1}),
$d\alpha/dt$	=	reaction rate (s^{-1}),
α	=	fraction reacted or conversion (dimensionless),
α	=	fraction reacted (dimensionless),
$k(T)$	=	specific rate constant at temperature T (min^{-1}),
$k(T)$	=	specific rate constant at temperature T (s^{-1}),
$f(\alpha)$	=	conversion function. Commonly used functions include:

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

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

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

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

where:

n and m	=	partial reaction order terms.

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

NOTE 1—There are a large number of conversion function expressions for [f(α)][f(α)].[4] Those described here are the moremost common but are not the only functions suitable for this test method. Eq 21 is known as the general rate equation while Eq 3 is the autocatalyticaccelerating (or

[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.Sbirrazzuoli, N., Brunel, D., and Elegant, L., *Journal of Thermal Analysis*, Vol 38, 1992, pp. 1509–1524.
[5] Sestak, J.; Berggren, G.; *Thermochim. Acta, 3*, 1, 1971.Sestak, J., and Berggren, G., *Thermochimica Acta*, Vol 3, 1971, p. 1.
[6] Gorbachiev, V.M.; *J. Therm. Anal., 18*, 193–197, 1980.Gorbachiev, V.M., *Journal of Thermal Analysis*, Vol 18, 1980, pp. 193–197.

Sestak-Berggren) ~~equation~~equation.[5,6].~~.~~ Eq 4 is the accelerating Avrami equation. Eq 2 is used for *n*th order reactions while Eq 3 ~~is~~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 ~~autocatalytic~~accelerating rate Eq 3~~equation of~~ and the rate equation Eq 1 ~~5.2~~may be cast in ~~its~~their logarithmic form.

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

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

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

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

This equation has the form $z = a + bx + cy$ and may be solved using multiple linear regression ~~analysis.~~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—~~Subsequent discussions use the autocatalytic form of the~~ The rate equation (Eq 3)~~. It~~) reduces to the simpler general rate equation (Eq 2) when the value of reaction order parameter ~~m~~n equals zero thereby reducing the number of kinetic parameters to be determined.

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

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

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

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

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

where:

Z = ~~pre-exponential factor (min^{-1}),~~
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 ~~6~~8 cast in its logarithmic form is:

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

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

Eq ~~7~~9 has the form of a straight line, $y = ~~x~~mx + b$, where a plot of the logarithm of the reaction rate constant ~~(~~(ln[~~ln~~ $k(T)$]) versus the reciprocal of absolute temperature ~~(1/T)~~(1/T) is linear with the slope equal to $-E/R$ and an intercept equal to $ln[Z]$.

5.7 As an alternative to ~~5.3~~Eq 6 and ~~5.5~~Eq 7, the rate and Arrhenius equations combined and cast in logarithmic form is:

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

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

Eq ~~8~~10 has the form, $z = a + ~~bw~~bx + ~~cx~~cy + ~~dy,~~dw,$ 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 = $\ln[1-\alpha]$
d = n, and
w = $\ln[1-\alpha]$.

5.8 If activation energy values only are of interest, Eq ~~8~~11 may be solved under conditions of constant conversion to yield:

$$\ln[\Delta t] = E/RT + c \tag{11}$$

$$\ln[\Delta t] = E/RT + b \tag{11}$$

where:

Δt = ~~lapsed time, (min), at isothermal temperature, T, and~~
c = ~~constant.~~

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

Eq ~~9~~11 has the form of a straight line, *y* = ~~x~~*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 (l/*T*) is linear with a slope equal to *E/R*.

5.9 If activation energy values only are of interest, Eq ~~8~~11 may be solved under conditions of constant conversion and the equality ~~*dα/dt*~~*dα/dt* = ~~*dH/dt/H*~~*dH/dt* / (*H*) to yield:

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

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

where:

H = ~~total heat of reaction (J/g),~~
H = total heat of reaction (mJ),
~~*dH/dt*~~ = ~~instantaneous heat flow (W/g),~~
dH/dt = instantaneous heat flow (mW),
b = constant, and
m = ~~slope (kK)~~
m = slope (K)

Eq ~~10~~12 has the form of a straight line *y* = m*x* + *b*, where a plot of the logarithm of the heat flow ~~((ln[~~*ln[dH/dt]dH*~~]/dt]~~)/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~~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, ~~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,~~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 *dα/dt*, α, (1 − α) and *T* to solve Eq ~~5~~6, Eq 7, Eq 9, and Eq ~~8~~10.

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 ~~10~~12

5.13 A variety of time-to-event experiments such as oxidation induction time methods (Practice ~~D3550~~D3350 and Test Methods D3895, D4565, D5483, ~~and~~ D6186, and Guide ~~E1958~~E1858) and reaction induction time methods (Test Method E2046) provide values for Δ*t* and *T* to solve equation Eq 11~~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 test method may be compared with those obtained from Test Method E698 for *n*th order and ~~autocatalytic~~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 ~~Method~~ Test method precision is enhanced with the selection of the appropriate conversion function [*f*(α)] that minimizes the number of experimental parameters determined. The shape of the thermal curve, as described in Section ~~Appendix X1~~11, may confirm the selection of the *n*th order or ~~autocatalytic~~accelerating models.
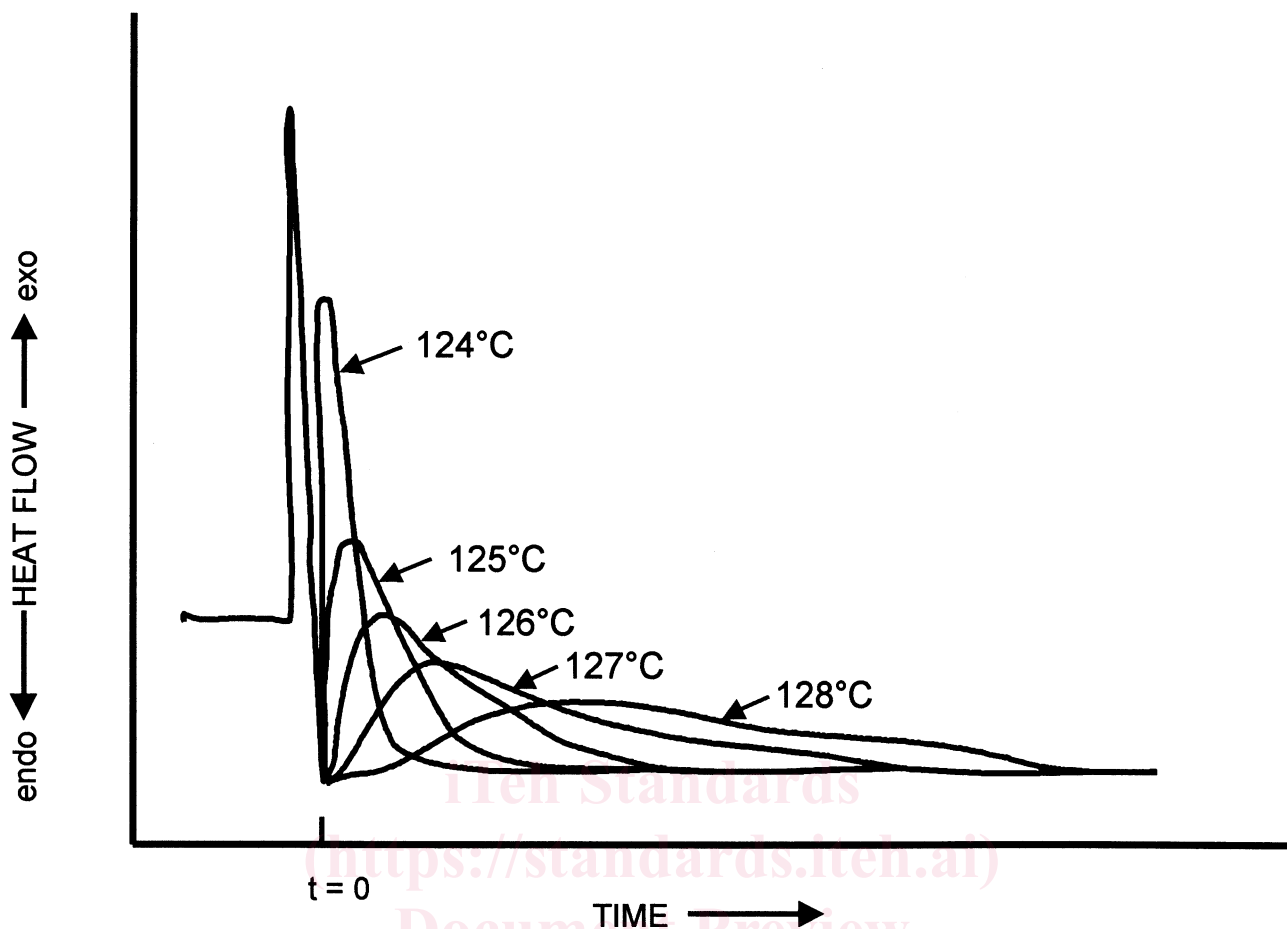
Note 1—This figure is for a crystallization application in which the reaction rate increases with decreasing temperature. Chemical reactions show an increase in reaction rate with increasing temperature.

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

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~~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 ~~Autocatalytic~~Accelerating kinetic reactions anticipate that *m* and *n* are fractions between 0 and ~~1~~2 and that their sum (*m* + *n*) is less than ~~2.~~3.

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~~(see Note ~~7~~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 ~~within the applicable temperature range of this test method.~~between 300 and 900 K.
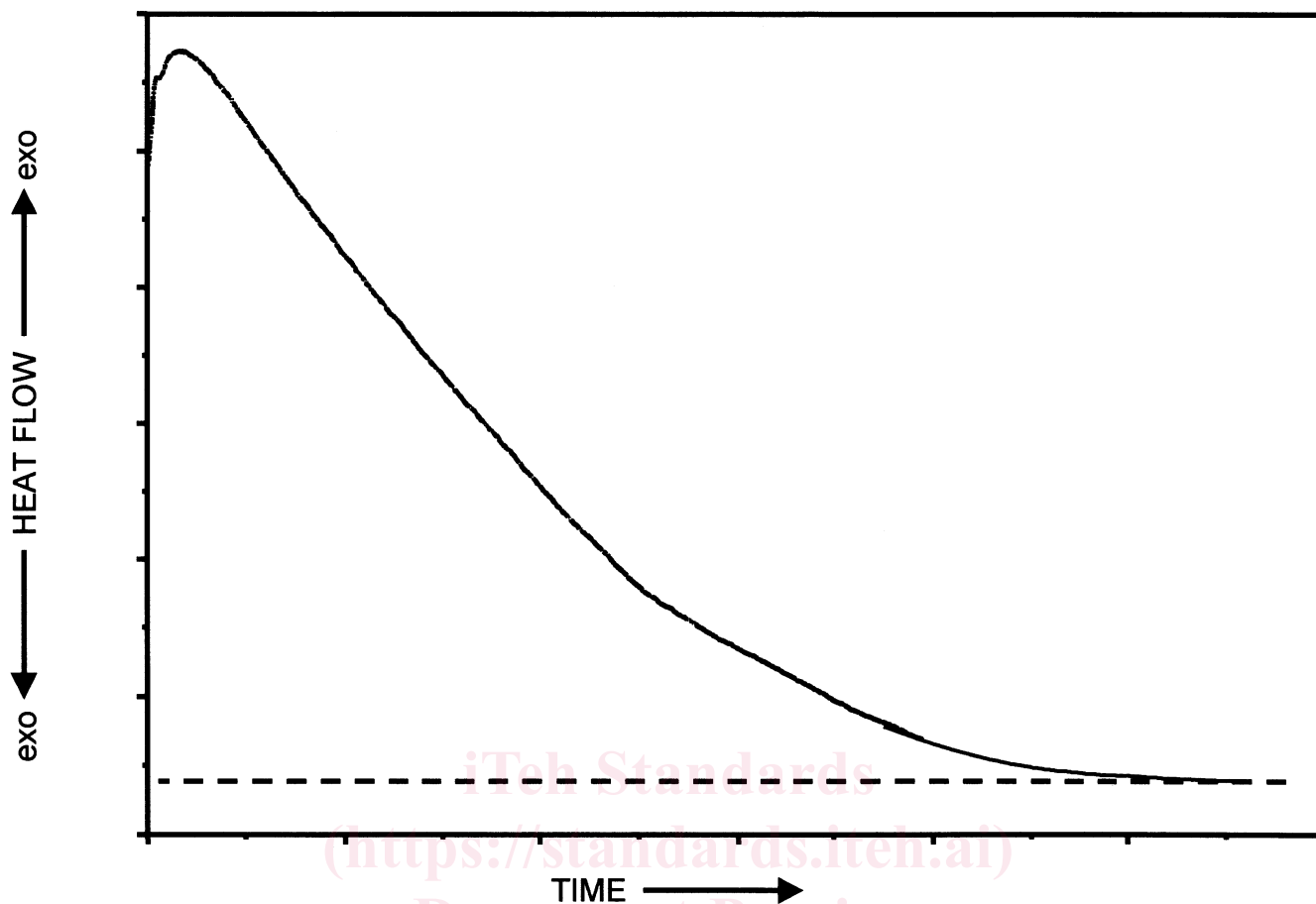
5

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

9.1.1.2 *A Temperature Sensor,* that indicates the specimen/furnace temperature to ± 0.01 ±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,* for furnace(s) temperature programs between selected temperature limits (that is, 300 to 900 K) capable of controlling thecapable 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 ±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 in accordance with the requirements of this test method.reference.

9.3 *A Balance,* to weigh specimens and/or containers to ± 10 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"clock is better than 0.1 % using Test Method E1860.