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 ($\approx$10 K) temperature range. Test Method A is applicable to low nth 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 Methods 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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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:

$$f_1(\alpha) = (1 - \alpha)^n \qquad (2)$$
$$f_2(\alpha) = \alpha^m (1 - \alpha)^n \qquad (3)$$
$$f_3(\alpha) = p(1 - \alpha)[-1 n (1 - \alpha)]^{(p-1)/p} \qquad (4)$$

[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.

where:

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

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

$$d\alpha/dt = k(T) \alpha^m (1 - \alpha)^n \qquad (5)$$
$$\ln[d\alpha/dt] = \ln[k(T)] + m \ln[\alpha] + n \ln[1 - \alpha] \qquad (6)$$

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 m equals zero thereby reducing the number of kinetic parameters to be determined.

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

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

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 = $\ln[1 - \alpha]$

$d = n$, 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:

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

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 (l/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:

$$\ln[dH/dt] = -E/RT + b = m/T + b \tag{12}$$

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.

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 nth order and accelerating reactions. Activation energy, 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 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 nth order or accelerating models.

7.4 Typical nth 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 nth 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.

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.
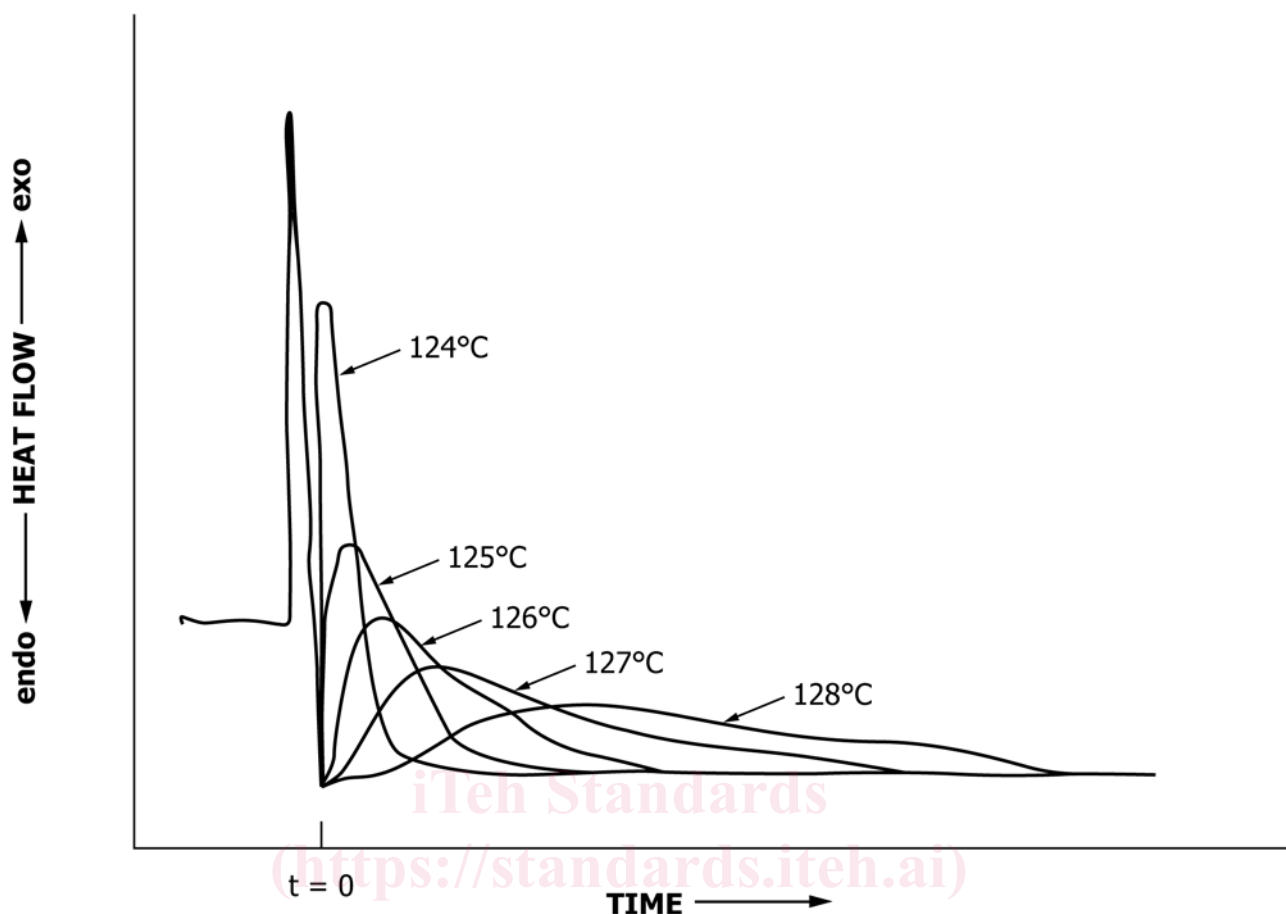
NOTE 1—This figure is for a crystallization application in which the reaction rate increases with decreasing temperature. Chemical reactions show an increase in reaction rate with increasing temperature.

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

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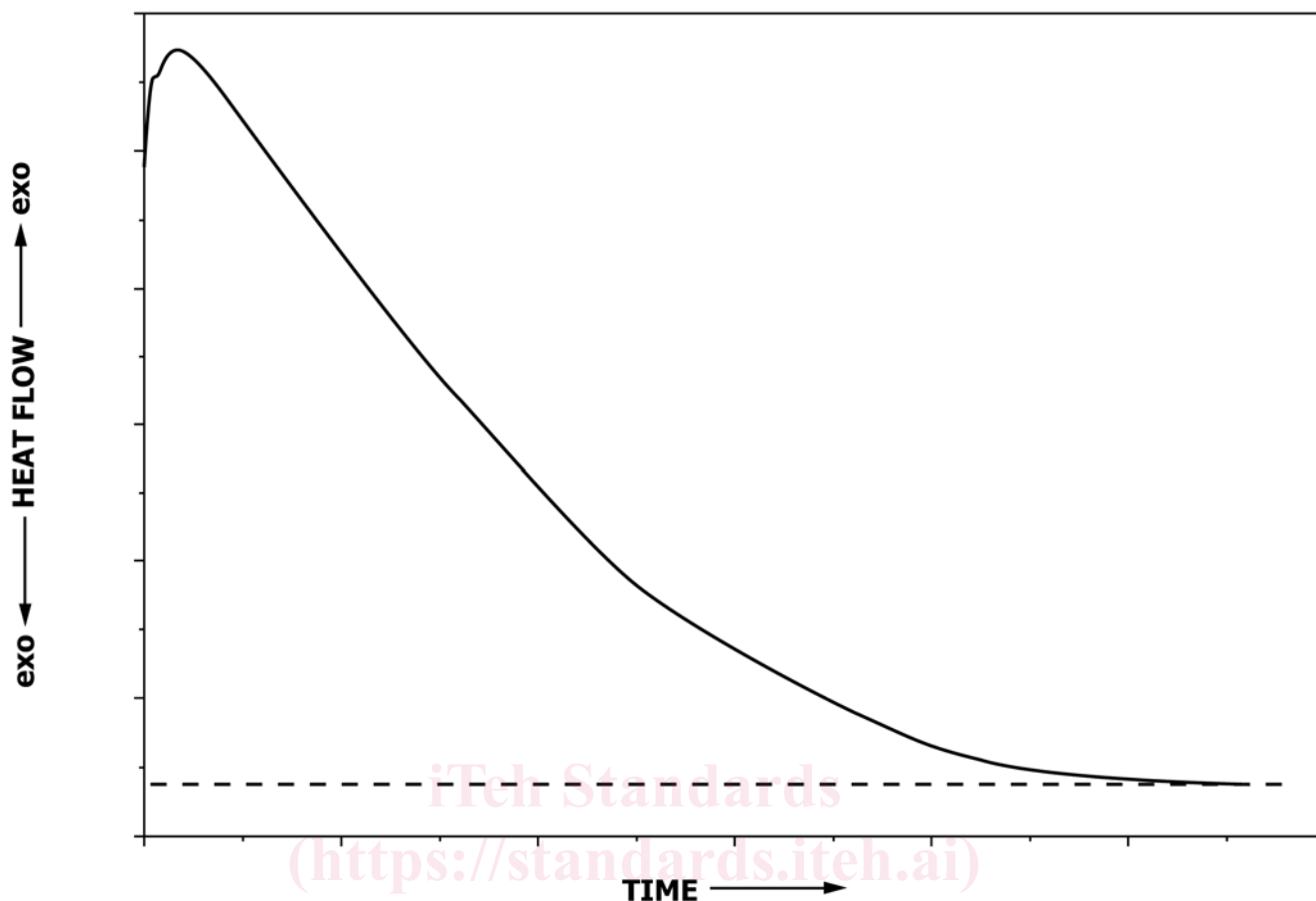
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FIG. 2 Heat Flow Curve for an *n*th Order Reaction

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.
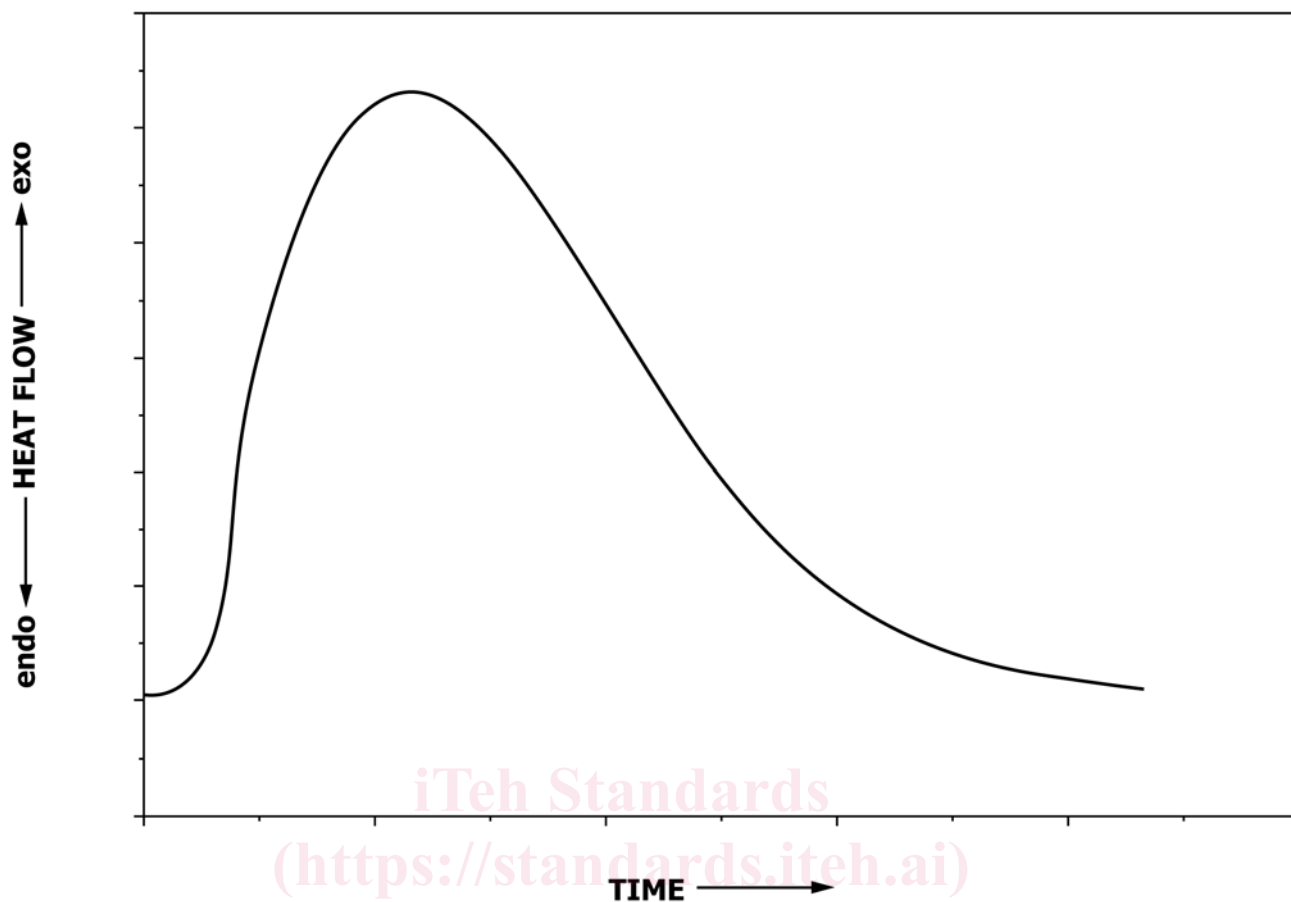
FIG. 3 Heat Flow Curve for an Accelerating Reaction

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