



# Standard Method for Estimating Kinetic Parameters by Differential Scanning Calorimeter Using the Borchardt and Daniels Method<sup>1</sup>

This standard is issued under the fixed designation E 2041; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method describes the determination of the kinetic parameters of activation energy, Arrhenius pre-exponential factor, and reaction order using the Borchardt and Daniels<sup>2</sup> treatment of data obtained by differential scanning calorimetry. This test method is applicable to the temperature range from 170 to 870 K (–100 to 600°C).

1.2 This treatment is applicable only to smooth exothermic reactions with no shoulders, discontinuous changes, or shifts in baseline. It is applicable only to reactions with reaction order  $n \leq 2$ . It is not applicable to autocatalyzed reactions and, therefore, is not applicable to the determination of kinetic parameters for most thermoset curing reactions or to crystallization reactions.

1.3 Electronic instrumentation or automated data analysis systems or treatments equivalent to this test method may be used.

NOTE 1—The user is advised that all electronic data treatment may not be equivalent. It is the responsibility of the user of such electronic data treatment to verify applicability to this test method.

1.4 SI values are the standard.

1.5 This test method is similar, but not equivalent to, ISO Method 11357, Part 5, which contains provisions for additional information not supplied by this test method.

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.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

E 473 Terminology Relating to Thermal Analysis<sup>3</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and the direct responsibility of Subcommittee E37.01 on Test Methods and Recommended Practices.

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<sup>2</sup> Borchardt, H.J., Daniels, F., *J. Amer. Chem. Soc.* Vol 79, pp.41–46 (1957).

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 14.02.

- E 537 Test Method for Assessing the Thermal Stability of Chemicals by Methods of Differential Thermal Analysis<sup>3</sup>
- E 698 Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials<sup>3</sup>
- E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers<sup>3</sup>
- E 968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters<sup>3</sup>
- E 1142 Terminology Relating to Thermophysical Properties<sup>3</sup>
- E 1145 Terminology Relating to Hazardous Properties of Chemicals<sup>3</sup>
- E 1641 Test Method for Decomposition Kinetics by Thermogravimetry<sup>3</sup>
- E 1970 Practice for Statistical Treatment of Thermoanalytical Data<sup>3</sup>
- 2.2 ISO Standards:
  - ISO 11357 Part 5: Determination of Temperature and/or Time of Reaction and Reaction Kinetics<sup>4</sup>

## 3. Terminology

3.1 *Definitions*—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 heated at a linear rate in a differential scanning calorimeter or other suitable calorimeter through a region of exothermic reaction behavior. The rate of heat evolution, developed by a chemical reaction, is proportional to the rate of reaction. Integration of the heat flow as a function of time yields the total heat of a reaction.

4.2 The Borchardt and Daniels<sup>2</sup> data treatment is used to derive the kinetic parameters of activation energy, Arrhenius pre-exponential factor, and reaction order from the heat flow and total heat of reaction information obtained in 4.1 (see Section 5).

<sup>4</sup> Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

## 5. Basis of Methodology

5.1 Kinetic reactions may be modeled with a number of suitable equations. The Borchardt and Daniels<sup>2</sup> method makes use of the general rate equation to describe the dependence of the rate of reaction on the amount of material present.

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

where:

$d\alpha/dt$  = reaction rate ( $\text{min}^{-1}$ )  
 $\alpha$  = fraction reacted (dimensionless),  
 $k(T)$  = rate constant at temperature  $T$  ( $\text{min}^{-1}$ ), and  
 $n$  = reaction order (dimensionless)

5.2 For a reaction conducted at temperature ( $T$ ), the rate equation of Eq 1, may be cast in its logarithmic form:

$$\ln[d\alpha/dt] = \ln[k(T)] + n \ln[1 - \alpha] \quad (2)$$

This equation has the form of a straight line,  $y = mx + b$ , where a plot of the logarithm of the reaction rate ( $\ln[d\alpha/dt]$ ) versus the logarithm of the fraction remaining  $\ln[1 - \alpha]$  yields a straight line, the slope of which is equal to  $n$  and the intercept is equal to  $\ln[k(T)]$ .

5.3 The Borchardt and Daniels model also makes use of the Arrhenius equation to describe how the reaction rate changes as a function of temperature:

$$k(T) = Z e^{E/RT} \quad (3)$$

where:

$Z$  = Arrhenius pre-exponential factor ( $\text{min}^{-1}$ ),  
 $E$  = Activation energy ( $\text{J mol}^{-1}$ ),  
 $T$  = Absolute temperature (K), and  
 $R$  = Gas constant ( $= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ).

5.4 The Arrhenius equation Eq 3 also may be cast in its logarithmic form:

$$\ln[k(T)] = \ln[Z] - E/RT \quad (4)$$

The equation has the form of a straight line,  $y = mx + b$ , (where  $y \equiv \ln[k(T)]$ ,  $m \equiv E/R$ ,  $x \equiv 1/T$  and  $b \equiv \ln[Z]$ ) where a plot of the logarithm of the reaction rate constant ( $\ln[k(T)]$ ) versus the reciprocal of absolute temperature ( $1/T$ ) produces a straight line, the slope of which is equal to  $-E/R$  and the intercept of which is  $\ln[Z]$ .

5.5 As an alternate to Eq 2 and 4, the rate and Arrhenius equations may be combined and cast in its logarithmic form:

$$\ln[d\alpha/dt] = \ln[Z] + n \ln[1 - \alpha] - E/RT \quad (5)$$

The resultant equation has the form  $z = a + bx + cy$  (where  $z \equiv \ln[d\alpha/dt]$ ,  $\ln[Z] \equiv a$ ,  $b \equiv n$ ,  $x \equiv \ln[1 - \alpha]$ ,  $c \equiv E/R$ , and  $y \equiv 1/T$ ) and may be solved using multiple linear regression data treatment.

5.6 The values for  $d\alpha/dt$ ,  $(1 - \alpha)$  and  $T$  needed to solve Eq 2, Eq 4 and Eq 5, are experimental parameters obtained from a single linear heating rate DSC experiment scanning through the temperature region of the reaction exotherm as shown in Fig. 1.

5.7 Kinetic results obtained by this test method may be compared with those obtained by E 698.

## 6. Significance and Use

6.1 This test method is useful in research and development.,

6.2 The determination of the appropriate model for a chemical reaction or transformation and the values associated with its kinetic parameters may be used in the estimation of reaction performance at temperatures or time conditions not easily tested. This use, however, is not described in this test method.

## 7. Interferences

7.1 Because of its simplicity and ease of use, the Borchardt and Daniels method is often the method of choice for characterization of the kinetic parameters of a reaction system. The Borchardt and Daniels method, like all tools used to evaluate kinetic parameters, is not applicable to all cases. The user of this test method is expressly advised to use this test method and its results with caution.

7.2 Tabulated below are some guidelines for the use of the Borchardt and Daniels method.

7.2.1 The approach is applicable only to exothermic reactions.

NOTE 2—Endothermic reactions are controlled by the kinetics of the heat transfer of the apparatus and not by the kinetics of the reaction.

7.2.2 The reaction under investigation must have a constant mechanism throughout the whole reaction process. In practice, this means that the reaction exotherm upon heating must be smooth, well shaped (as in Fig. 1) with no shoulders, multiple peaks or discontinuous steps.

7.2.3 The reaction must be  $n$ th order. Confirmation of an  $n$ th order reaction may be made by an isothermal experiment such as that described in Appendix X1.

7.2.4 Typical reactions which are not  $n$ th order and to which Borchardt and Daniels kinetic may not be applied for predictive purposes include many thermoset curing reactions and crystallization transformations.

7.2.5 The  $n$ th order kinetic reactions anticipate that the value of  $n$  will be small, non-zero integers, such as 1 or 2. Values of  $n$  greater than 2 or which are not simple fractions, such as  $1/2 = 0.5$ , are highly unlikely and shall be viewed with caution.

7.2.6 The Borchardt and Daniels method assumes temperature equilibrium throughout the whole test specimen. This means that low heating rates, (that is,  $< 10 \text{ K/min}$ ), small specimen sizes ( $< 5 \text{ mg}$ ) and highly conductive sealed specimen containers, for example, aluminum, gold, platinum, etc., should be used.

7.3 Since milligram quantities of specimen are used, it is essential that the specimen be homogeneous and representative of the test sample from which they are taken.

7.4 Toxic or corrosive effluents, or both, may be released when heating the test specimen and may be harmful to personnel or to the apparatus. Operating with a venting or exhaust system is recommended.

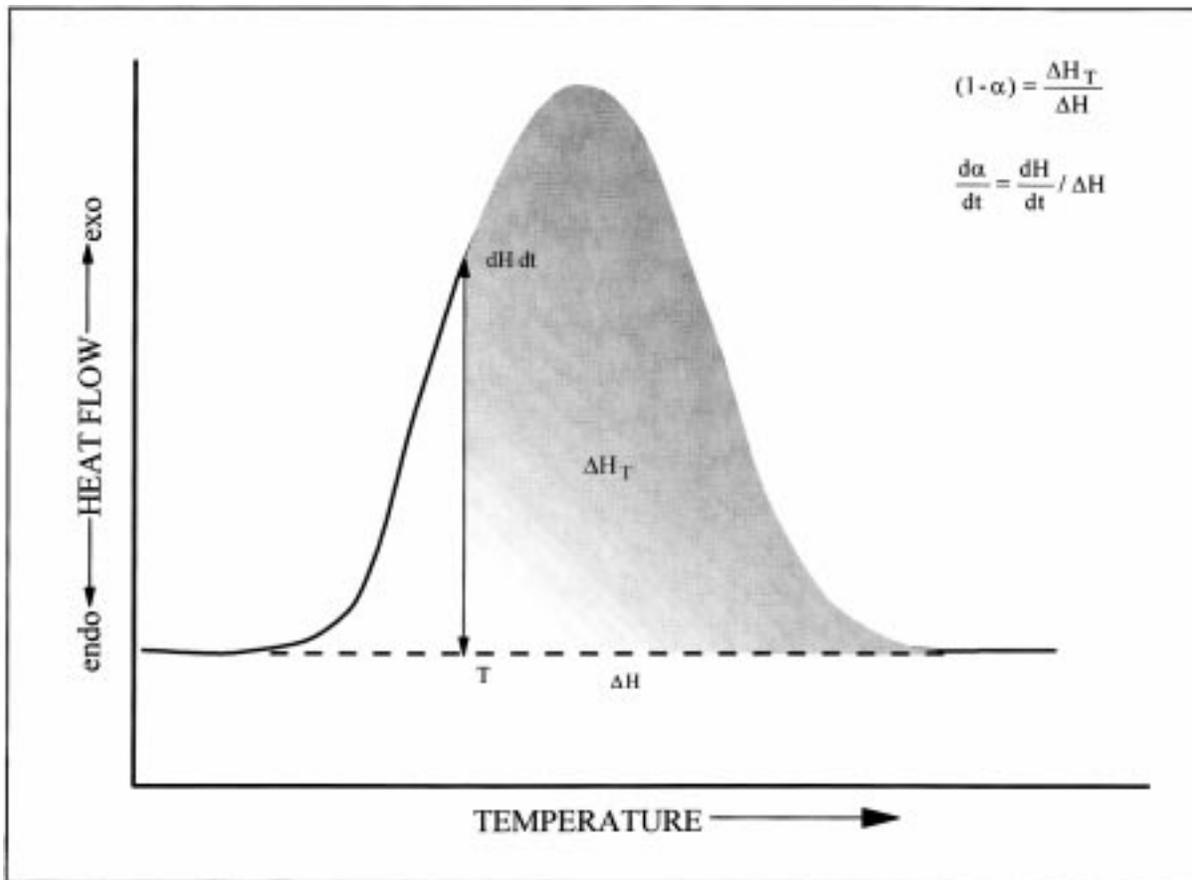


FIG. 1 Idealized DSC Curve

## 8. Apparatus

8.1 *Differential Scanning Calorimeter (DSC)*—The instrumentation required to provide the minimum differential scanning calorimetric capability for this method includes the following:

8.1.1 *DSC Test Chamber*, composed of the following:

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

8.1.1.2 *Temperature Sensor*, to provide an indication of the specimen/furnace temperature to  $\pm 0.01$  K.

8.1.1.3 *Differential Sensor*, to detect heat flow difference between the specimen and reference equivalent to  $1 \mu\text{W}$ .

8.1.1.4 A means of sustaining a test chamber environment of purge gas at a rate of  $10$  to  $50 \pm \text{mL/min}$ .

NOTE 3—Typically, 99.9% pure nitrogen, helium, or argon is employed. Use of dry purge gas is recommended and is essential for operation at subambient temperatures.

8.1.2 *Temperature Controller*, capable of executing a specific temperature program by operating the furnace(s) between selected temperature limits, that is,  $170$  to  $870$  K, at a rate of temperature change of up to  $10$  K/min constant to  $\pm 0.1$  K/min.

8.1.3 *Recording Device*, capable of recording and displaying any fraction of the heat flow signal (DSC curve), including the signal noise, on the Y-axis versus temperature on the X-axis.

8.2 *Containers* (pans, crucibles, vials, etc.), that are inert to the specimen and reference materials, and which are of suitable structural shape and integrity to contain the specimen and reference in accordance with the specific requirements of this test method.

8.3 While not required, the user will find useful calculator or computer and data analysis software to perform the necessary least squares best fit or multiple linear regression data treatments required by this test method.

8.4 *Balance*—to weigh specimens, or containers, or both, to  $\pm 10 \mu\text{g}$  with a capacity of at least  $100$  mg.

## 9. Calibration

9.1 Perform any calibration procedures recommended by the apparatus manufacturer in the instrument operator's manual.

9.2 Calibrate the DSC temperature signal over the range of the reaction using Practice E 967.

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

## 10. Procedure

10.1 Weigh  $1$  to  $10$  mg of test specimen to a precision of  $\pm 10 \mu\text{g}$  into a sample container and hermetically seal the container. Weigh the specimen and container to  $\pm 10 \mu\text{g}$ . Load the test specimen into the apparatus using an equivalent empty specimen container as the reference. Close the DSC sample chamber and prepare the apparatus for an experimental run.

NOTE 4—This test method is based upon a “non-self heating” assumption. Combinations of specimen size and reaction kinetics that produce heat flow greater than 8 mW fail this assumption and produce erroneous results. Small specimen sizes may be used to obtain this critical non-self heating assumption.

10.2 Equilibrate the specimen at a temperature 40 K below the first exothermic behavior.

NOTE 5—This temperature may be determined from a previously recorded exploratory run using Test Method E 537.

10.3 Heat the test specimen at a rate of 5 K/min to a temperature 10 K higher than the completion of the exothermic reaction as indicated by the return to baseline. Record the heat flow and sample temperature throughout this region.

NOTE 6—Other heating rates (< 10 K/min) may be used but shall be indicated in the report. Agreement of results undertaken at several heating rates will provide confidence in the method and efficacy of the results.

10.4 Cool the specimen container to ambient temperature and reweigh. Record and report any change in mass from that observed in 10.1 prior to the test.

10.5 Calculate reaction order ( $n$ ), activation energy ( $E$ ), and Arrhenius pre-exponential factor ( $Z$ ) according to the procedures in Section 11.

## 11. Calculation

11.1 Construct a linear baseline from a point on the baseline before the reaction exotherm to a point on the baseline after the reaction.

11.2 Construct a perpendicular line from the baseline to the peak of the thermal curve and record this value in mW. Only results for which the maximum heat flow (as expressed by this line) are less than 8 mW shall be used in these calculations. If the heat flow at the peak maximum is greater than 8 mW, reduce the specimen size or heating rate and rerun the experiment (see Note 4).

11.3 Integrate the total peak area bounded by the peak itself and the constructed baseline to obtain the heat of the reaction ( $\Delta H$ ) in mJ.

11.4 Identify the temperatures which correspond approximately to 10 and 90 % of the peak area obtained in 11.3.

11.5 Select a temperature interval which provides a minimum of ten equally-spaced values between the temperature limits determined in 11.4.

11.6 At each of the ten temperatures identified in 11.5, record the rate of reaction ( $dH/dt$ ) in mW, temperature ( $T$ ) in K and heat of reaction remaining ( $\Delta H_T$ ) in mJ as illustrated in Fig. 1.

NOTE 7—It is convenient to prepare a table of these values.

11.7 For each of the fractional areas obtained in 11.6, determine the fraction remaining ( $1 - \alpha$ ) and the fractional rate of reaction ( $d\alpha/dt$ ) using the following equation:

$$(1 - \alpha) = \Delta H_T / \Delta H \quad (6)$$

$$d\alpha/dt = (dH/dt) / \Delta H \quad (7)$$

NOTE 8—In this and all subsequent calculations, retain all available significant figures rounding only the final result to the number of significant figures described in Section 13.

NOTE 9—The values for  $(1 - \alpha)$  should range between 0.9 and 0.1

depending upon the values selected in 11.4 and 11.5

11.8 Calculate the reciprocal of absolute temperature for each value determined in 11.6 and 11.7 (see Note 8).

NOTE 10—Often, it is convenient to report the value of reciprocal temperature in units of  $\text{kK}^{-1}$ .

11.9 Calculate the natural logarithm of the rate of reaction ( $\ln[d\alpha/dt]$ ) for each of the values determined in 11.6 and 11.7 (see Note 8).

11.10 Determine the values for  $n$ ,  $s_n$ ,  $E$ ,  $s_E$ ,  $\ln[Z]$ , and  $s_{\ln[Z]}$  by either Method A or Method B below.

11.11 Method A:

11.11.1 Assume a value for  $n = 1.0$ .

11.11.2 Calculate the value for  $n \ln[1 - \alpha]$  for each value determined in 11.6 and 11.7 (see Note 8).

11.11.3 Calculate the value for  $\ln[k(T)]$  using:

$$\ln[k(T)] = \ln[d\alpha/dt] - n \ln[1 - \alpha] \quad (8)$$

for each value determined in 11.6 and 11.7 (see Note 8).

11.11.4 Prepare a plot of  $\ln[k(T)]$  versus  $1/T$  such as that in Fig. 2.

NOTE 11—The uncertainty introduced into results by linearizing non-linear data are discussed in *J. Chem. Ed.*, 74, 1001 (1997).

11.11.4.1 This plot should result in a straight line. If it does not, assume a new value for  $n$  and repeat the steps in 11.11.2-11.11.4.1 until a straight line is obtained. Report the value of  $n$ , which yields a straight line. A curve that is concave upward indicates that the value of  $n$  is too large while one that is concave downward indicates that  $n$  is too small.

11.11.5 Using a least squares best fit technique (see Practice E 1970), determine a slope ( $m$ ), intercept ( $b$ ), standard deviation in slope ( $s_m$ ) and standard deviation in intercept ( $s_b$ ) for this straight line. The slopes  $m$  and  $s_m$  have the units of  $1/\text{K}$ . Intercepts  $b$  and  $s_b$  are dimensionless.

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

$$E = -m \cdot R \quad (9)$$

$$s_E = s_m \cdot R \quad (10)$$

where:

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}.$$

11.11.7 Determine the value of  $\ln[Z]$  and standard deviation in  $\ln[Z]$  (i.e.,  $s_{\ln Z}$ ) from the values of  $b$  and  $s_b$  in 11.11.5.

$$\ln[Z] = b \quad (11)$$

$$s_{\ln Z} = s_b \quad (12)$$

11.11.8 Calculate the logarithm of the reaction rate constant at any temperature of interest using the values from 11.11.6, 11.11.7, and Eq 14.

11.12 Method B:

11.12.1 Alternatively, the values for  $n$ ,  $s_n$ ,  $E$ ,  $s_E$ ,  $\ln Z$  and  $s_{\ln Z}$  may be determined simultaneously using a multiple linear regression data treatment applied to the following equation:

$$\ln[d\alpha/dt] = \ln[Z] + n \ln[1 - \alpha] - E/RT. \quad (13)$$

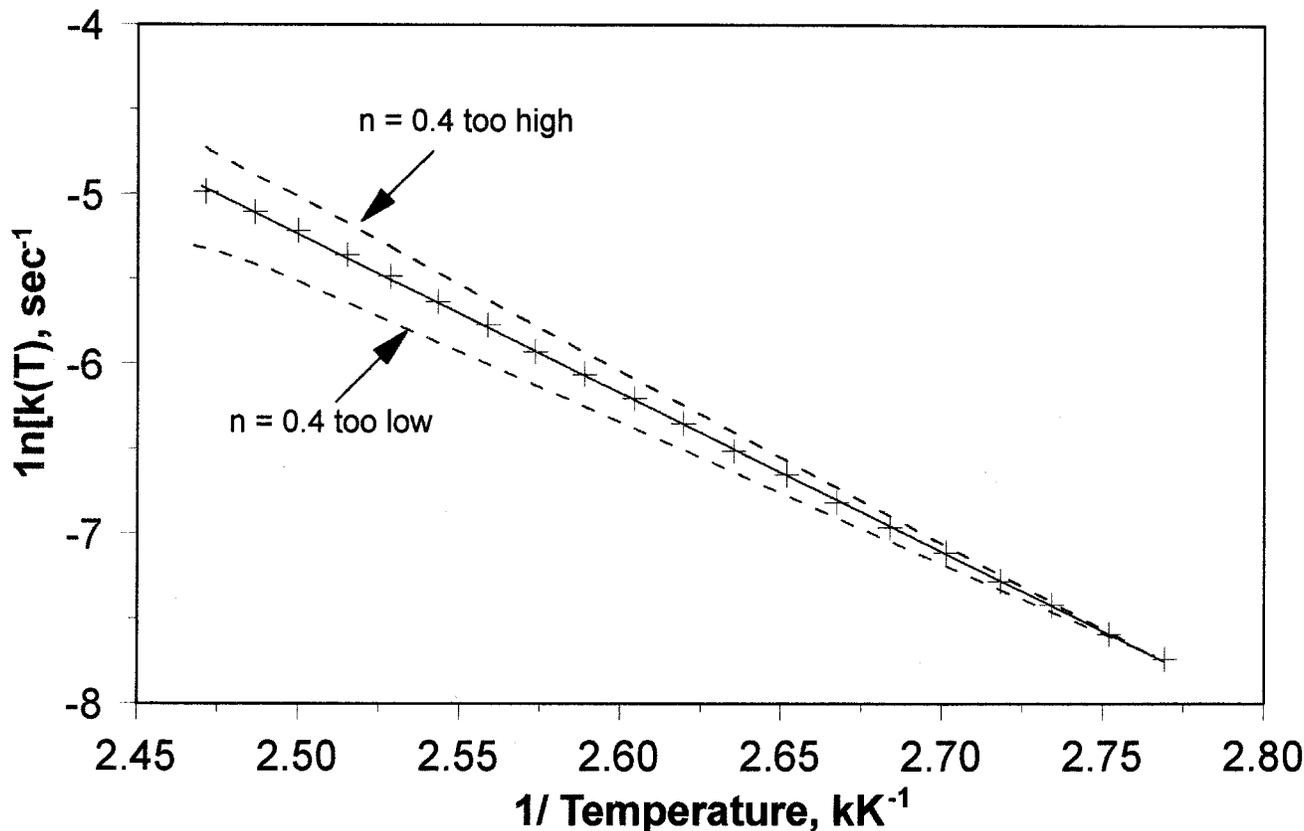


FIG. 2 Plot of  $\ln[k(T)]$  versus  $1/T$

11.13 Calculate the logarithm of the reaction rate constant at any temperature of interest using the values from 11.12.1 and the equation:

$$\ln[k(T)] = \ln[Z] - E/RT \quad (14)$$

## 12. Report

12.1 The report shall include the following information:

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

12.1.2 Description of the instrument and software used for the test.

12.1.3 Experimental conditions including test specimen mass, heating rate, temperature range of test, specimen container, purge gas type, and flow rate.

12.1.4 Description of the data treatment used including name and version of any software packages and whether Method A or Method B is used.

12.1.5 The values and their standard deviations for reaction order ( $n \pm s_n$ ) activation energy ( $E \pm s_E$ ) in kJ/mol and logarithm of the Arrhenius frequency factor ( $\ln[Z] \pm s_{\ln Z}$ ), with Z in 1/min. Report all values to one position to the right of decimal point.

12.1.6 Report any values of logarithm of the rate constant at temperature of interest.

12.1.7 The original thermal curve.

12.1.8 The dated version of this test method use.

## 13. Precision and Bias

13.1 An interlaboratory test was conducted in 2002 to determine the precision and bias of method B of E 2041-01 using trityl azide (e.g., azidotriphenylmethane). The results from a minimum of 12 laboratories, using 5 replicates each (i.e., 44 degrees of freedom) are used to provide the information (see RR: E37-1028) listed below. Seven instrument models from three manufacturers were used and the data was evaluated using three different software programs.

### 13.2 Precision—

13.2.1 Within laboratory variability may be described using the repeatability value (r) obtained by multiplying the 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.

13.2.2 The within laboratory repeatability relative standard deviation for activation energy (E), logarithm of the pre-exponential factor ( $\log [Z]$ ) and reaction order (n) was found to be 3.0, 3.4, and 6.6 %, respectively.

13.2.3 Between laboratory variability may be described using the reproducibility value (R) obtained by multiplying the 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  $R$ .

13.2.4 The between laboratory reproducibility relative standard deviation for activation energy ( $E$ ), logarithm of the preexponential factor ( $\log [Z]$ ) and reaction order ( $n$ ) was found to be 9.8, 9.8 and 22 %, respectively.

### 13.3 Bias:

13.3.1 Bias is the difference between the value obtained and that of a reference material. There are no known standard

values for kinetic parameters for trityl azide and so bias may not be estimated. See X2.1.

## 14. Keywords

14.1 activation energy; Arrhenius frequency factor; Borchardt and Daniels kinetics; differential scanning calorimetry (DSC); kinetics; pre-exponential factor; reactions

## APPENDIXES

### (Nonmandatory Information)

#### X1. TEST FOR $n$ th ORDER OR AUTOCATALYTIC REACTIONS

X1.1 The Borchardt and Daniels method is applicable only to  $n$ th order reactions. It is not applicable to autocatalyzed reaction. This appendix describes a useful test procedure for verifying a given reaction is  $n$ th order.

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 the temperature corresponding to 10 % peak area from 10.3 as the isothermal test temperature  $T$ . 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.

NOTE X1.1—**Caution:** Burn hazard. The sample chamber and its heat shields and covers are hot presenting a burn hazard to the operator. Exercise great care in this operation. Use protective safety equipment to ensure the safety of the operator.

X1.6 Observe the shape of the resultant thermal curve. Heat-flow curves, which reach a maximum heat flow value within a few seconds after placement of the test specimen in the apparatus and then decay away, are likely to be due to  $n$ th order reactions. Heat-flow curves, which begin low, build to a maximum (after tens of seconds) and then decay away, are likely to be due to autocatalyzed reactions. See Fig. X1.1 and Fig. X1.2 for example curves.

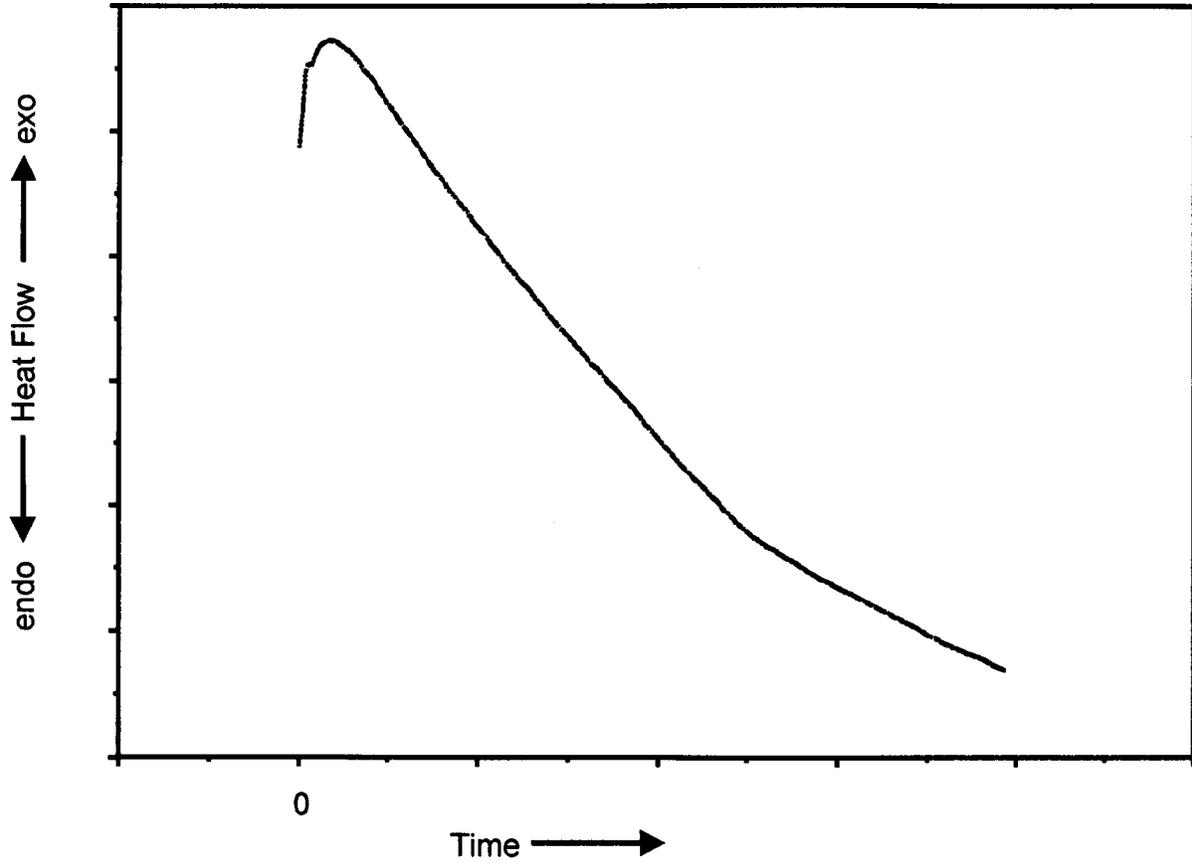


FIG. X1.1 Heat Flow Curve for an  $n$ th Order Reaction

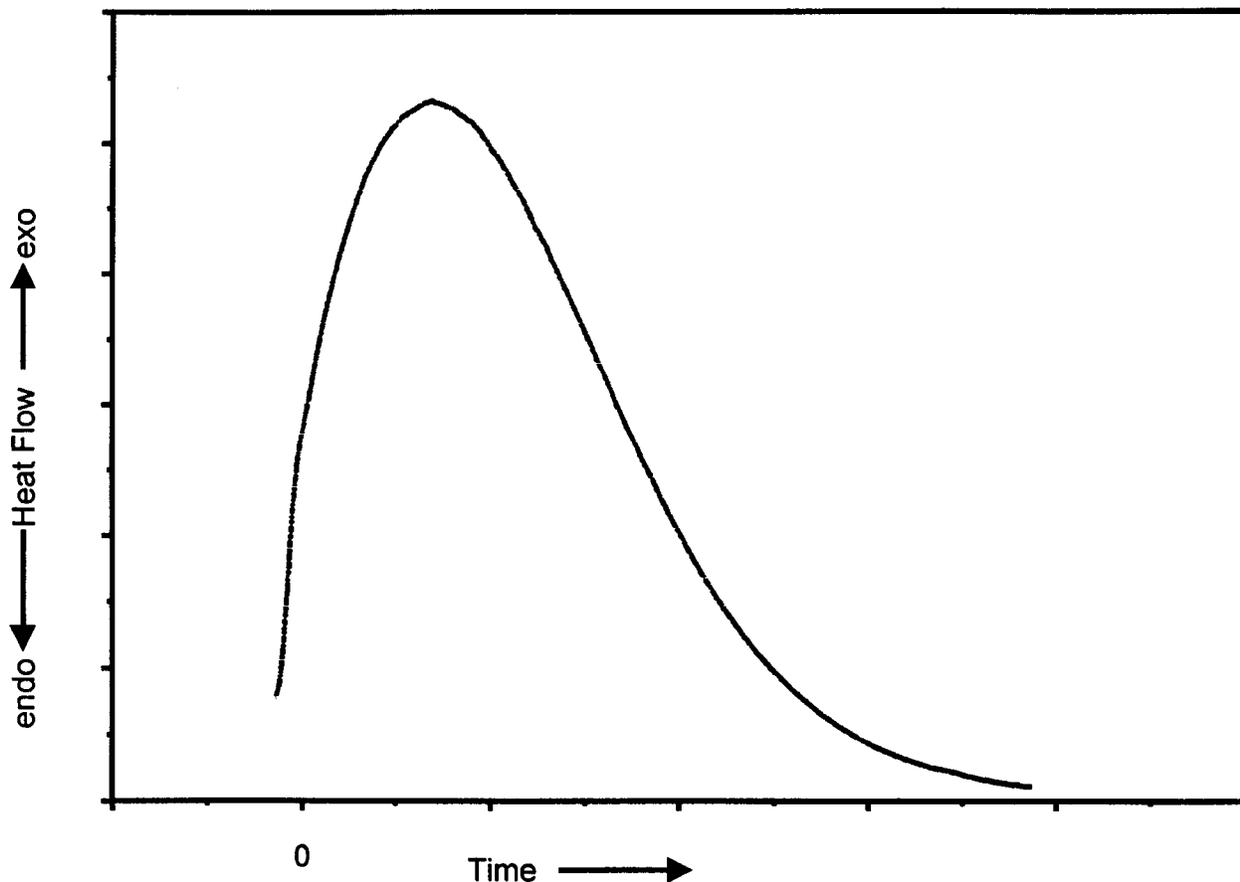


FIG. X1.2 Heat-Flow Curve for an Autocatalyzed Reaction

## X2. Comparative Results

X2.1 The trityl azide (used in the interlaboratory test referenced in Section 13) was used as a test specimen in additional interlaboratory tests. A comparison of mean values may be useful to the user.

X2.2 The mean values determined by DSC method B of E2041-01 for activation energy ( $E$ ), logarithm of the pre-exponential factor ( $\log [Z]$ ), and reaction order ( $n$ ) were found to be 165.1 kJ/mol, 17.2 (with  $Z$  expressed in  $\text{min}^{-1}$ ) and 1.32, respectively.

X2.3 Trityl azide was also used in an interlaboratory test (see RR: E27-1002) for DSC variable heating rate Test Method E 698. In that study, the mean values for activation energy and logarithm of the pre-exponential factor were 145.5 kJ/mol and 15.2 (with  $Z$  expressed in  $\text{min}^{-1}$ ), respectively (with 8 degrees of freedom). In Test Method E 698, the reaction order ( $n$ ) is fixed at 1.00. These values are statistically different (student t-test) different from those obtained in this test.

X2.4 Trityl azide was also evaluated in an intralaboratory

test using the TGA variable heating rate test standard Test Method E 1641. In this study, the mean values for activation energy and logarithm of the pre-exponential factor were 73.0 kJ/mol and 7.13 (with  $Z$  expressed in  $\text{min}^{-1}$ ), respectively. In Test Method E 1641, the reaction order ( $n$ ) is fixed at 1.00. These values are statistically different (student t-test) from those obtained in this test or those of Test Method E 698.

X2.5 Trityl azide was also evaluated in an intralaboratory test using modulated thermogravimetry an approach that is not yet an ASTM International standard<sup>5</sup> In this work, the mean values for activation energy and logarithm of the pre-exponential factor were 87.5 kJ/mol and 8.87 (with  $Z$  expressed in  $\text{min}^{-1}$ ), respectively. In modulated thermogravimetry, the reaction order ( $n$ ) is fixed at 1.00. These values are statistically different (student t-test) from those obtained in this test or those of Test Method E 698.

<sup>5</sup> Blaine, R.L., Hahn, B.K., "Obtaining Kinetic Parameters by Modulated Thermogravimetry", 1998. Volume 54, pp. 658-704

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