



Designation: E2041 – 13^ε¹

Standard Test Method for Estimating Kinetic Parameters by Differential Scanning Calorimeter Using the Borchardt and Daniels Method¹

This standard is issued under the fixed designation E2041; 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.

^ε¹ NOTE—Warning statements were editorially corrected throughout in September 2013.

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 Daniels² 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 acceleratory reactions and, therefore, is not applicable to the determination of kinetic parameters for most thermoset curing reactions or to crystallization reactions.

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 11357, Part 5, that contains provisions for additional information not supplied by this test method.

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.*

2. Referenced Documents

2.1 ASTM Standards:³

¹ This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and the direct responsibility of Subcommittee E37.01 on Calorimetry and Mass Loss.

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² Borchardt, H.J., Daniels, F., *Journal of the American Chemical Society*, Vol 79, 1957, pp. 41–46.

³ 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.

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

E1641 Test Method for Decomposition Kinetics by Thermogravimetry Using the Ozawa/Flynn/Wall Method

E1970 Practice for Statistical Treatment of Thermoanalytical Data

2.2 ISO Standards:⁴

ISO 11357 Part 5: Determination of Temperature and/or Time of Reaction and Reaction Kinetics

3. Terminology

3.1 *Definitions*—Specific technical terms used in this test method are defined in Terminologies E473, E1142, and E1445, including *calibration*, *calorimeter*, *differential scanning calorimetry*, *enthalpy*, *peak*, *reaction*, *repeatability*, *reproducibility*, and *slope*.

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 Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

4.2 The Borchardt and Daniels² 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).

5. Basis of Methodology

5.1 Kinetic reactions may be modeled with a number of suitable equations. The Borchardt and Daniels² method makes use of the 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 (min^{-1})
 α = fraction reacted (dimensionless),
 $k(T)$ = rate constant at temperature T (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:

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

This equation has the form of a straight line, $y = mx + b$, where a plot of the logarithm of the reaction rate ($\ln[da/dt]$) 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 Daniels² 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 (min^{-1}),
 E = Activation energy (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:

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

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

5.6 The values for da/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 Test Method E698.

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 Daniels² 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 Daniels² method.

7.2.1 The approach is applicable only to exothermic reactions.

NOTE 1—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 Daniels² 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 that 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 Daniels² 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

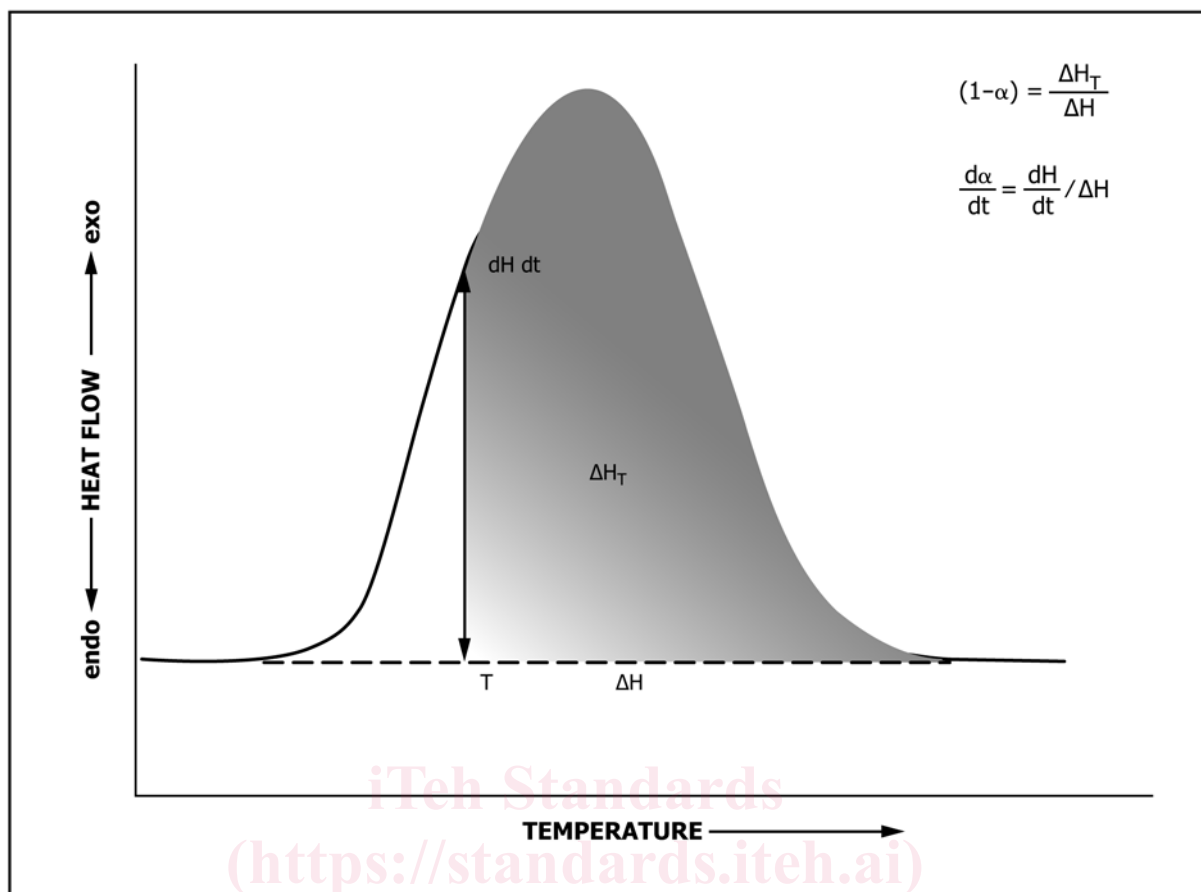


FIG. 1 Idealized DSC Curve

personnel or to the apparatus. Operating with a venting or exhaust system is recommended.

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 ± 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 mL/min.

NOTE 2—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 ± 0.1 K/min.

8.1.3 *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.

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 Test Method E967.

9.3 Calibrate the DSC heat flow signal using Practice E968.

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 3—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 4—This temperature may be determined from a previously recorded exploratory run using Test Method E537.

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 5—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 3).

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

11.4 Identify the temperatures that 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 (ΔH_T) in mJ as illustrated in Fig. 1.

NOTE 6—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 (da/dt) using the following equation:

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

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

NOTE 7—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 8—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 7).

NOTE 9—Often, it is convenient to report the value of reciprocal temperature in units of kK^{-1} .

11.9 Calculate the natural logarithm of the rate of reaction ($\ln[da/dt]$) for each of the values determined in 11.6 and 11.7 (see Note 7).

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 7).

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

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

for each value determined in 11.6 and 11.7 (see Note 7).

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

NOTE 10—The uncertainty introduced into results by linearizing non-linear data are discussed in *Journal of Chemical Education*.⁵

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 multiple linear regression technique (see Practice E1970), 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 $1/\text{kK}$. 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 $\ln[Z]$ (that is, $s_{\ln Z}$) from the values of b and s_b in 11.11.5.

⁵ Zielinski, T. J., and Allendoerfer, R. D., “Least squares fitting of nonlinear data in the undergraduate laboratory,” *Journal of Chemical Education*, Vol 74, 1997, pp. 1001–1007.