



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

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1. Scope

1.1 This test method covers the determination of the kinetic parameters of activation energy, Arrhenius frequency 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 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 The values stated in SI units are to be regarded as 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 Analysis²
- E 537 Test Method for Assessing the Thermal Stability of Chemicals by Methods of Differential Thermal Analysis²
- E 698 Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials²

¹ This test method is under the jurisdiction of ASTM Committee E-37 on Thermal Measurements and the direct responsibility of Subcommittee E37.01 on Test Methods and Recommended Practices.

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

E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers²

E 968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters

E 1142 Terminology Relating to Thermophysical Properties²

E 1145 Terminology Relating to Hazardous Properties of Chemicals²

E 1970 Practice for Statistical Treatment of Thermoanalytical Data

2.2 ISO Standards:

ISO 11357 Part 5: Determination of Temperature and/or Time of Reaction and Reaction Kinetics^{3,4}

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 Daniels² data treatment is used to derive the kinetic parameters of activation energy, Arrhenius frequency 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 general rate equation to describe the dependence of the rate of reaction on the amount of material present.

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

³ *Annual Book of ASTM Standards*, Vol 14.02.

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

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 5.1, 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 Borchartt 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 frequency factor (time^{-1}),
- E = Activation energy (J/mol),
- T = Absolute temperature (K), and
- R = Gas constant = $8.314 \text{ J/mol} \cdot \text{K}$.

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, development, quality assurance, and for specification acceptance purposes.

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

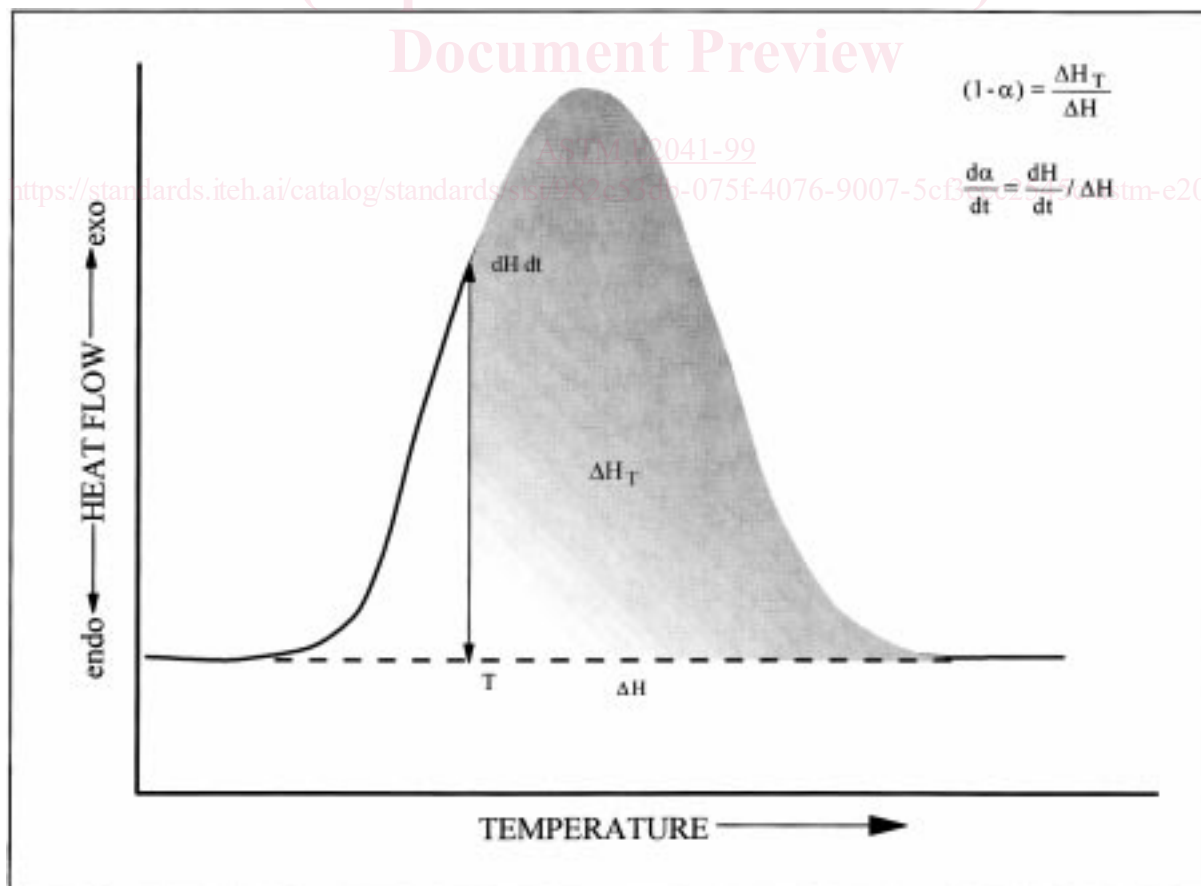


FIG. 1 Idealized DSC Curve

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 $\frac{1}{2} = 0.5$, 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 K/min), small specimen sizes (< 5 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.

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 $50 \pm \text{mL/min}$.

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 ± 0.1 K/min.

8.1.3 *Recording Device*, either digital or analog, 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 Practice 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 m W 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.