



Designation: E2781 – 16

Standard Practice for Evaluation of Methods for Determination of Kinetic Parameters by Calorimetry and Differential Scanning Calorimetry¹

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1. Scope*

1.1 It is the purpose of this practice to provide kinetic parameters for reference materials used for evaluation of thermal analysis methods, apparatus, and software where enthalpy and temperature are measured. This practice addresses both exothermic and endothermic, n th order, and autocatalytic reactions.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 There is no International Organization for Standardization (ISO) equivalent to this standard.

1.4 *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*:²
- E473 Terminology Relating to Thermal Analysis and Rheology
 - E698 Test Method for Kinetic Parameters for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method
 - E1142 Terminology Relating to Thermophysical Properties
 - E1641 Test Method for Decomposition Kinetics by Thermogravimetry Using the Ozawa/Flynn/Wall Method
 - E1981 Guide for Assessing Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry

¹ This practice is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.02 on Reference Materials.

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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.

E2041 Test Method for Estimating Kinetic Parameters by Differential Scanning Calorimetry Using the Borchardt and Daniels Method

E2070 Test Method for Kinetic Parameters by Differential Scanning Calorimetry Using Isothermal Methods

3. Terminology

3.1 *Definitions*—Specific technical terms used in this practice are defined in Terminologies E473 and E1142, including *differential scanning calorimetry*.

4. Summary of Practice

4.1 Kinetics is the study of the relationship of the extent of a chemical reaction to the independent parameters of time and temperature. This relationship is often described using the Arrhenius expression where:

$$d\alpha/dt = Zf(\alpha)\exp(-E/RT) \quad (1)$$

where:

- α = fraction left to react,
- $f(\alpha)$ = some function of (α) ,
- E = activation energy (J/mol),
- R = gas constant ($=8.314 \text{ J mol}^{-1} \text{ K}^{-1}$),
- T = absolute temperature (K), and
- Z = pre-exponential factor (1/sec).

4.2 For many reactions of interest the description of the function of amount left to react is of the form:

$$f(\alpha) = \alpha^m (1 - \alpha)^n \quad (2)$$

where m and n are the overall reaction orders. This form of the concentration dependence is known as the auto-catalytic form or the Sestak-Berggren reaction.³ If the value of m equals 0, then $f(\alpha)$ reduces to the form of $f(\alpha) = (1 - \alpha)^n$ commonly called n th order reaction.

4.3 Eq 1 may be evaluated in either its exponential or logarithmic form:

$$\ln(da/dt) = \ln Z + \ln(f(\alpha)) - E/RT \quad (3)$$

³ Sestak, and J., Berggren, G., "Study of the Kinetics of the Mechanism of Solid-Solid Reactions at Increasing Temperature," *Thermochimica Acta*, Vol 3, 1971, pp. 1–12.

*A Summary of Changes section appears at the end of this standard