Designation: ~~E2781 – 16~~ E2781 – 24

Standard Practice for Evaluation of Methods for Determination of Kinetic Parameters by Calorimetry and Differential Scanning Calorimetry[1]

This standard is issued under the fixed designation E2781; 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*~~Scope

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

1.3 *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~~safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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
E2041 Test Method for Estimating Kinetic Parameters by Differential Scanning Calorimeter Using the Borchardt and Daniels Method
E2070 Test Methods for Kinetic Parameters by Differential Scanning Calorimetry Using Isothermal Methods

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[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.

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

3. Terminology

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

3.1.1 Specific technical terms used in this practice are defined in Terminologies E473 and E1142, including *activation energy*,*differential scanning calorimetry*,*Kelvin*,*kinetics*,*pre-exponential factor*,*reaction*, and *reaction order*.

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 J mol^{-1} K^{-1}),~~
R = gas constant (=8.314 J/mol·K),
~~T = absolute temperature (K), and~~
T = temperature (K), and
~~Z = pre-exponential factor (1/sec).~~
Z = pre-exponential factor (1/s).

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 an n~~th~~th order reaction.

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

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

4.4 The study of kinetics involves the determination of ~~values of~~ E,Z,m, and n for a given reaction.

NOTE 1—Activation energy and pre-exponential factor are not independent parameters but are inter-related.

NOTE 2—The descriptions provided in Eq 1-3 are only mathematical models. That is, they represent the fitting of mathematical equations to often "noisy" experimental data. In practice, no such model will faithfully describe the complete reaction(s) under all conditions for the materials described in this practice.

4.5 Values for the kinetic ~~parameter are typically in the ranges indicated below:~~parameters typically fall within the following ranges:

~~*log Z*: 8 to 30 with *Z* in s^{-1}~~
log Z: 8 to 30 with *Z* in 1/s
~~*E*: 50 to 250 kJ/mol~~
E: 50 kJ/mol to 250 kJ/mol
n: 0.0 to 2.0
m: 0.0 to 2.0

4.6 By their nature, thermally reactive materials may change with time. For this reason, certified reference materials are not

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