Designation: E2781 – 11

StandardPractice for Evaluation of Methods for Determination of Kinetic Parameters by Thermal Analysis[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

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 Arrhenius Kinetic Constants 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 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 J mol^{-1} 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 (**1**).[3] If the value of m equals 0, then $f(\alpha)$ reduces to the form of $f(\alpha) = (1-\alpha)^n$ commonly call *n*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.

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

Current edition approved March 1, 2011. Published April 2011. DOI: 10.1520/E2781-11.

[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.

[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.

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:

log Z: 8 to 30 with Z in s^{-1}
E: 50 to 250 kJ/mol
n: 0.0 to 2.0
m: 0 to 2.0

4.6 By their nature, thermally reactive materials may change with time. For this reason, certified reference materials are not available for use in the evaluation of kinetic parameters. The user of this standard may synthesize or purchase from a commercial laboratory supply house materials of suitable purity for use in this standard.

NOTE 3—Storage of reference materials in a refrigerator may prolong shelf life. Observe manufacturers recommendations.

4.7 The recommended values for the thermal active materials identified in this standard are taken from "best values" found in the open literature as described in the accompanying tables.

5. Significance and Use

5.1 The kinetic parameters provided in this standard may be used to evaluate the performance of a standard, apparatus, techniques or software for the determination parameters (such as Test Methods E698, E1641, E2041, or E2070) using thermal analysis techniques such as differential scanning calorimetry, and accelerating rate calorimetry (Guide E1981). The results obtained by these approaches may be compared to the values provided by this practice.

NOTE 4—Not all reference materials are suitable for each measurement technique.

6. Hazards

6.1 Thermally reactive materials evolve heat as part of the indicated reaction. Build up of this heat may lead to a dangerous over-pressure condition or to a self accelerating reaction. Operators shall use caution when working with such materials. Operators shall use as small amount of material as is practical for the measurement.

6.2 The reference materials described in this standard and their decomposition products may be explosive, carcinogenic, hazardous, toxic, or corrosive. Handling of these materials should be performed by trained workers who are knowledgeable with the Material Safety Data Sheets (MSDS) for each material. Tetramethyl succinonitrile (TMSN), a decomposition product of azobisisobutyronitrile (AIBN), is considered a very toxic (neurotoxic agent) and hazardous substance.

7. Procedure

7.1 Experimentally determined kinetic parameters are compared to the values described in this practice as their quotient, expressed as percent. Thus values less than unity or 100 % indicate that the determined value is less than the reference value while those greater than unity or 100 % indicate that the determined value is greater than the reference value.

8. Calculation

8.1 Conformance = $^{(\text{Observed Value} \times 100\ \%)}/_{(\text{Referenced Value})}$

NOTE 5—Generally speaking, experimentally determined kinetic parameters E and $log\ Z$ are considered to be in agreement if they have conformance between 80 and 120 % of the values described in Table 1.

TABLE 1 Kinetic Parameters for Kinetic Reference Materials (Derived from Tables 2-6)

NOTE 1—where:
E = activation energy,
Z = pre-exponential factor,
n = reaction order,
m = reaction order,
H = enthalpy of reaction of the pure material, and
DSC = differential scanning calorimeters.

Material	*E*, kJ/mol	log (*Z*,1/s)	*n*	*m*	*H*, kJ/g	Description
Di-t-butylperoxide	158.1	15.80	1.0	0.0	1.34	Generally tested in liquid form as a 10 to 20 % solution in toluene. Kinetic parameters are solvent sensitive. Suitable for calorimeters.
Azidotriphenylmethane	165.1	19.00	1.0	0.0		Suitable for DSC.
Azobenzene	102.5	11.98	1.0	0.0	0.254	Solid material, endothermic; Suitable for DSC.
Azobisisobutyronitrile	128.5	15.12	1.0	0.0		Suitable for calorimeters and DSC.
Phenyltetrazolthiol	143	20.4	1.7	1.3		Suitable for DSC.

Experimentally determined values *m* and *n* are considered to be in agreement if they have conformance between 70 and 130 % of the values described in Table 1.

NOTE 6—The value of *log Z* depends upon the concentration of the reactant.

9. Report

9.1 Identification of the kinetic method being examined.

9.1.1 Identification of the reference material being used for the comparison, its source and purity.

9.1.2 The comparison quotient (conformance) for each kinetic parameter.

10. Precision and Bias

10.1 This practice is used to determine the bias of kinetic values determined by other standards or candidate standards.

10.2 This practice does not generate experimental data and has no precision.

11. Keywords

11.1 activation energy; kinetics; pre-exponential factor; reaction order; thermal analysis

TABLE 2 Literature Values for Di-t-butylperoxide (DTBP) from which the Recommended Values for Table 1 are Obtained

NOTE 1—where:
E = activation energy,
Z = pre-exponential factor,
n = reaction order,
H = enthalpy of reaction of the pure material,
DSC = differential scanning calorimeters, and
ARC = accelerating rate calorimeter.

E, kJ/mol	log (*Z*,1/s)	*H*, kJ/g	*n*[A]	Conditions	Reference
148	16.15				(2)
163	16.45			gas phase	(3)
154	15.11			DSC, mineral oil	(4)
158	16.36			ARC, mineral oil, or toluene	(5)
122.1 ± 2.8	11.51 ± 0.33	1.19 ± 0.02		DSC, 725 psi	(6)
136	12.87			0.1 M in diesel fuel	(7)
148	14.87			Neat	(8)
140	13.74			Neat	(9)
159.2 ± 9.9	16.3 ± 1.2			30 to 60 % in toluene	(10)
146.7 ± 7.0	15.0 ± 0.9			30 to 60 % in benzene	(10)
158.5	16.1	1.31		ARC	(11)
145.5	15.1	1.82		DSC	(11)
147.3 ± 3.4	15.68 ± 0.44	1.29	0.925 ± 0.088	ARC	(12)
158.2	16.15	1.19			(13)
		1.335			(14)
159				in t-butyl benzene	(15)
151				in toluene	(16)
142				in vapor phase	(16)
163				in vapor phase	(17)
157				in i-propylbenzene	(17)
159				in t-butylbenzene	(17)
155				in t-butylamine	(17)
159.7 ± 0.58	15.94 ± 0.07			in vapor phase	(18)
157.7 ± 0.63	15.71 ± 0.08				(19, 20)
138.4 ± 2.5	13.16 ± 0.31				(16)
146.7 ± 6.7	14.04 ± 0.83				(21)
161.3 ± 3.1	16.30 ± 0.39				(22)
164.5 ± 1.0	16.63 ± 0.24			in diethylketone	(23)
158.4 ± 1.2	15.82 ± 0.18				(24)
152.6 ± 1.5	15.33 ± 0.13			in vapor phase	(25)
160.1 ± 1.3	16.07 ± 0.14				(26)
158.1 ± 0.25	15.80 ± 0.03		(1.00)	Gas phase "best" literature average	(24)
154.7	15.634			Solution	(27)
163.03	15.95-				(28)
157.3 ± 2.1	15.94 ± 0.34		(1.00)	15 % in toluene	(29)
		1.25 ± 0.04			(30)
152.0 ± 6.1			(1.00)	20 % in toluene	(31)
158.2 ± 4.9	19.62 ± 0.59		1.0 ± 0.05	20 % in toluene and benzene	(32)
161					(33)

[A] Values in parenthesis are assumed.