



Standard Practice for Evaluation of Methods for Determination of Kinetic Parameters by Thermal Analysis¹

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

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:

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

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

¹ This practice is under the jurisdiction of ASTM Committee E27 on Hazard Potential of Chemicals and is the direct responsibility of Subcommittee E27.02 on Thermal Stability and Condensed Phases.

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.

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 = (Observed Value $\times$ 100 %)/(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. 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.

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- <i>t</i> -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.

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 $\pm$ 2.8	11.51 $\pm$ 0.33	1.19 $\pm$ 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 $\pm$ 9.9	16.3 $\pm$ 1.2			30 to 60 % in toluene	(10)
146.7 $\pm$ 7.0	15.0 $\pm$ 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 $\pm$ 3.4	15.68 $\pm$ 0.44	1.29	0.925 $\pm$ 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 $\pm$ 0.58	15.94 $\pm$ 0.07			in vapor phase	(18)
157.7 $\pm$ 0.63	15.71 $\pm$ 0.08				(19, 20)
138.4 $\pm$ 2.5	13.16 $\pm$ 0.31				(16)
146.7 $\pm$ 6.7	14.04 $\pm$ 0.83				(21)
161.3 $\pm$ 3.1	16.30 $\pm$ 0.39				(22)
164.5 $\pm$ 1.0	16.63 $\pm$ 0.24			in diethylketone	(23)
158.4 $\pm$ 1.2	15.82 $\pm$ 0.18				(24)
152.6 $\pm$ 1.5	15.33 $\pm$ 0.13			in vapor phase	(25)
160.1 $\pm$ 1.3	16.07 $\pm$ 0.14				(26)
158.1 $\pm$ 0.25	15.80 $\pm$ 0.03		(1.00)	Gas phase “best” literature average	(24)
154.7	15.634			Solution	(27)
163.03	15.95-				(28)
157.3 $\pm$ 2.1	15.94 $\pm$ 0.34		(1.00)	15 % in toluene	(29)
		1.25 $\pm$ 0.04			(30)
152.0 $\pm$ 6.1			(1.00)	20 % in toluene	(31)
158.2 $\pm$ 4.9	19.62 $\pm$ 0.59		1.0 $\pm$ 0.05	20 % in toluene and benzene	(32)
161					(33)

^A Values in parenthesis are assumed.

TABLE 3 Literature Values for Azobenzene from which the Recommended Values for Table 1 are Obtained

NOTE 1—where:

E = activation energy,
 Z = pre-exponential factor,
 n = reaction order, and
 H = enthalpy of reaction of the pure material.

E , kJ/mol	$\log (Z, 1/s)$	H , kJ/g	n^A	Conditions	Reference
103.4 $\pm$ 1.6	12.2 $\pm$ 0.25	264.5 $\pm$ 1.6	(1.00)		(34)
103.5 $\pm$ 1			(1.00)		(35)
102.5 $\pm$ 0.2	11.98 $\pm$ 0.1	253.7 $\pm$ 5.4	(1.00)	Melt	(36)

^A Values in parenthesis are assumed.

TABLE 4 Literature Values for Azidotriphenylmethane (Trityl azide) from which the Recommended Values for Table 1 are Obtained

NOTE 1—where:

E = activation energy,
 Z = pre-exponential factor,
 n = reaction order, and
 H = enthalpy of reaction of the pure material.

E , kJ/mol	$\log (Z, 1/s)$	H , kJ/g	n^A	Conditions	Reference
145 $\pm$ 11	17.0 $\pm$ 1.7		(1.00)	Test Method E698	RR:E27-1002 ^B
165.1 $\pm$ 17	19.0 $\pm$ 2.0		1.32 $\pm$ 0.30	Test Method E2041	RR:E37-1028 ^C

^A Values in parenthesis are assumed.

^B Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E27-1002.

^C Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1028.

TABLE 5 Literature Values for Azobisisobutyronitrile (AIBN) from which the Recommended Values for Table 1 are Obtained

NOTE 1—where:

E = activation energy,
 Z = pre-exponential factor,
 n = reaction order, and
 H = enthalpy of reaction of the pure material.

E , kJ/mol	$\log (Z, 1/s)$	H , kJ/g	n^A	Conditions	Reference
182					(37)
129	15.20		(1.00)		(38)
121.3 $\pm$ 9.2	14.42 $\pm$ 1.3		1.02		(39)
117.9 $\pm$ 2.7	14.11 $\pm$ 1.0		1.03		(39)
99.7	13.24		(1.00)	Test Method E698	(39)
128.5 $\pm$ 8.4	15.12 $\pm$ 1.1	1238 $\pm$ 78	(1.00)		(40)

^A Values in parenthesis are assumed.

TABLE 6 Literature Values for Phenyltetrazolthiol from which the Recommended Values for Table 1 are Obtained

NOTE 1—where:

E = activation energy,
 Z = pre-exponential factor,
 n = reaction order,
 m = reaction order, and
 H = enthalpy of reaction of the pure material.

E , kJ/mol	$\log (Z, 1/s)$	H , kJ/g	n	m	Conditions	Reference
143 $\pm$ 17	20.4 $\pm$ 2.4		1.68 $\pm$ 0.49	1.32 $\pm$ 0.14	Test Method E2070	RR:E37-1029 ^A

^A Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1029.

REFERENCES

- (1) Sestak, J., and Berggren, G., "Study of the Kinetics of the Mechanism of Solid-Solid Reactions at Increasing Temperature," *Thermochimica Acta*, Vol 3, 1971, pp. 1–12.
- (2) Yasutake, H., *Kogyo Kayku (Journal of the Industrial Explosives Society (Japan))*, Vol 52, 1991, p. 350.
- (3) Wrabetz, K., and Wong, J., *Fresenius Zeitschrift fur Analytische Chemie*, Vol 329, 1987, p. 487.
- (4) Torfs, J.C.M., Leen, D., Dorrepaal, A.J., and Heijens, J.C., *Analytical Chemistry*, Vol 56, 1984, p. 2863.
- (5) Gimzewski, E., and Audley, G., "Thermal Hazards: Calculating Adiabatic Behavior from DSC Data," *Thermochimica Acta*, Vol 214, 1993, pp. 129–140.
- (6) Griffiths, J.F., Gilligan, M.F., and Gray, P., *Combustion and Flame*, Vol 24, 1975, p. 11.
- (7) MacNeil, D.D., Christensen, L., Landucci, J., Paulsen, J.M., and Dahn, J.R., *Journal of the Electrochemical Society*, Vol 147, 2000, p. 970.
- (8) Oxley, J.C., Smith, J.L., Rogers, E., Ye, W., Ardai, A.A., and Henly, T.J., *Energy Fuels*, Vol 14, 2000, p. 1252.
- (9) MacNeil, D.D., Trussler, S., Fortier, H., and Dahn, J.R., "A Novel Hertz Differential Scanning Calorimeter Sample Crucible," *Thermochimica Acta*, Vol 386, 2002, pp. 153–160.
- (10) Aldeeb, A.A., Rogers, W.J., and Mannan, M.S., "Theoretical and Experimental Methods for the Evaluation of Reactive Chemical Hazards," *Transactions of the Institution of Chemical Engineers*, Vol 80, 2002, pp. 141–149.
- (11) Hofelich, T.C., Frurip, D.J., and Powers, J.B., "The Determination of Compatibility via Thermal Analysis and Mathematical Modeling," *Process Safety Progress*, Vol 13, 1994, pp. 227–233.
- (12) Townsend, D.I., and Tou, J.C., *Thermochimica Acta*, Vol 37, 1980, pp. 1–30.
- (13) Whiting, L.F., LaBean, M.S., and Eadie, S.S., *Thermochimica Acta*, Vol 136, 1988, pp. 231–245.
- (14) Grever, T., *Thermal Hazards of Chemical Reactions*, Elsevier, New York, 1994, p. 394.
- (15) Ball, E., Rust, F., and Vaughn, W., *Journal of the American Chemical Society*, Vol 72, 1950, p. 337.
- (16) Murawaski, J., Roberts, J.S., and Szwarc, M., *Journal of Chemical Physics*, Vol 19, 1951, p. 698.
- (17) Raley, J., Rust, F., and Vaughan, W., *Journal of the American Chemical Society*, Vol 70, 1948, pp. 1136, 2767.
- (18) Birss, F.W., Danby, C.J., and Hinshelwood, C.N., *Proceedings of the Royal Society A*, Vol 239, 1957, p. 154.
- (19) Blatt, L., and Benson, S.W., *Journal of Chemical Physics*, Vol 36, 1962, p. 895.
- (20) Blatt, L., and Benson, S.W., *Journal of Chemical Physics*, Vol 38, 1963, p. 3031.
- (21) Jauiss, M.T., Roberts, J.S., and Szwarc, M., *Journal of the American Chemical Society*, Vol 74, 1952, p. 6005.
- (22) Pritchard, G.O., Pritchard, H. O., and Trotman-Dickenson, A.F., *Journal of the Chemical Society*, 1954, p. 1425.
- (23) Blake, A.R., and Kutschke, K.O., "The Reaction of Methyl Radicals with Formaldehyde," *Canadian Journal of Chemistry*, Vol 37, 1959, pp. 1462–1468.
- (24) Shaw, D.H., and Pritchard, H.O., "Thermal Decomposition of Di-tert-Butyl Peroxide at High Pressure," *Canadian Journal of Chemistry*, Vol 46, 1968, pp. 2721–2724.
- (25) Lossing, F.P., and Ticker, A.W., *Journal of Chemical Physics*, Vol 20, 1952, p. 907.
- (26) Mulcahy, M.F.R., and Williams, D.J., *Australian Journal of Chemistry*, Vol 14, 1961, p. 534.
- (27) Iizuka, Y., and Surianarayanan, M., *Industrial & Engineering Chemistry Research*, Vol 42, 2003, pp. 2987–2995.
- (28) Wang, Y.W., Duh, Y.S., and Shu, C.M., "Evaluation of Adiabatic Runaway Reaction and Vent Sizing for Emergency Relief from DSC," *Journal of Thermal Analysis and Calorimetry*, Vol 85, No. 1, 2006, pp. 225–234.
- (29) Kersten, R.J.A., Boers, M.N., Stork, M.M., and Visser, C., "Results of a Round-Robin with Di-tertiary-Butyl Peroxide in Various Adiabatic Equipment for Assessment of Runaway Reaction Hazards," *Journal of Loss Prevention in the Process Industries*, Vol 18, 2005, pp. 145–151.
- (30) Duh, Y., Wu, X.H., and Kao, C., "Hazard Ratings for Organic Peroxides," *Process Safety Progress*, Vol 27, No. 2, 2008, pp. 89–99.
- (31) Hou, H.Y., Liao, T.S., Duh, Y.S., and Shu, C.M., "Thermal Hazard Studies for Dicumyl Peroxide by DSC and TAM," *Journal of Thermal Analysis and Calorimetry*, Vol 83, No. 1, 2006, pp. 167–171.
- (32) Duh, Y., Kao, C.-S., Lee, C., and Yu, S.W., "Runaway Hazard Assessment of Cumene Hydroperoxide from the Cumene Oxidation Process," *Transactions of the Institution of Chemical Engineers, Part B*, Vol 75, No. B2, 1997, pp. 73–78.
- (33) Wang, Q., Rogers, W.J., and Manan, M.S., "Thermal Risk Assessment and Rankings for Reaction Hazards in Process Safety," *Journal of Thermal Analysis and Calorimetry*, Vol 98, 2009, pp. 225–233.
- (34) Wolf, W., and Cammenga, H.K., *Zeitschrift fur Physikalische Chemie*, Vol 107, 1977, p. 21.
- (35) Cammenga, H. K., and Eppe, M., *Angewandte Chemie International Edition in English*, Vol 34, 1995, p. 1171.
- (36) Eckardt, N., Flammersheim, H.J., and Cammenga, H.K., "The Cis-Trans Isomerization of Azobenzene in the Molten State," *Journal of Thermal Analysis and Calorimetry*, Vol 52, No. 1, 1998, pp. 177–185.
- (37) Li, X., Wang, X., and Koseki, H., "Study of Thermal Decomposition Characteristics of AIBN," *Journal of Hazardous Materials*, Vol 159, 2008, pp. 13–18.
- (38) Van Hook, J.P., and Tobolsky, A.V., "The Thermal Decomposition of 2,2'-azo-bis-isobutyronitrile," *Journal of the American Chemical Society*, Vol 80, No. 4, 1958, pp. 779–782.
- (39) Neag, C.M., Provder, T., and Holsworth, R. M., "Statistical Evaluation of Non-Isothermal Decomposition Kinetics Analysis Methods for AIBN," *Journal of Thermal Analysis*, Vol 32, 1987, pp. 1833–1842.
- (40) Barret, K.E.J., "Determination of the Rates of Thermal Decomposition of Polymerization Initiators with a Differential Scanning Calorimeter," *Journal of Thermal Analysis and Calorimetry*, Vol 11, 1967, pp. 1617–1626.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the ASTM website (www.astm.org/COPYRIGHT/).