Designation: E3007 – 15

Standard Practice for
Kinetic Values Used to Evaluate the Study of Decomposition Reactions by Thermogravimetry[1]

1. Scope

1.1 It is the purpose of this practice to provide kinetic parameters for reference material(s) to be used for evaluation of thermogravimetry methods, apparatus, and software where decomposition mass loss and associated temperature are measured. This practice addresses *n*th order 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 of Standards (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
E1142 Terminology Relating to Thermophysical Properties
E1641 Test Method for Decomposition Kinetics by Thermogravimetry Using the Ozawa/Flynn/Wall Method
E2958 Test Methods for Kinetic Parameters by Factor Jump/Modulated Thermogravimetry

NOTE 1—Test Methods E1641 and E2958 determine the pre-exponential factor *A* in units of min^{-1}. These results shall be converted to units of s^{-1} for comparison to values quoted in this practice using:

$$\ln[A,\ \mathrm{s}^{-1}] = \ln[A,\ \mathrm{min}^{-1}] + \ln[60\ \mathrm{s}/\mathrm{min}] = \ln[A,\ \mathrm{min}^{-1}] + 4.094$$

3. Terminology

3.1 *Definitions*—Specific technical terms used in this practice are defined in Terminologies E473 and E1142, including *Arrhenius equation, derivative, reaction,* and *thermogravimetric analysis*.

3.1.1 *decomposition, n*—the process by which a substance is broken up into constituent parts, elements or simpler compounds.

3.1.2 *kinetics, chemical, n*—the study of the dependence of the chemical reaction rate on temperature and time.

4. Summary of Practice

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

$$d\alpha/dt = A\, f(\alpha)\, \exp[-E/RT] \tag{1}$$

and:

α = fraction reacted (dimensionless),
$f(\alpha)$ = some function of α,
E = activation energy ($\mathrm{J\ mol^{-1}}$),
R = gas constant (= 8.314 $\mathrm{J\ mol^{-1}\ K^{-1}}$),
T = absolute temperature (K),
t = time (s),
exp = natural logarithm base,
$d\alpha/dt$ = fraction reaction rate (s^{-1}),
A = pre-exponential factor (s^{-1}), and
n = reaction order.

4.2 The function $f(\alpha)$ is commonly in the form:

$$f(\alpha) = (1 - \alpha)^n \tag{2}$$

and is known as an *n*th order reaction model.

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

$$\ln[d\alpha/dt] = \ln[A] + \ln[f(\alpha)] - E/RT \tag{3}$$

4.4 The study of kinetics involves the determination of values of *E, A,* and *n* for a given chemical reaction.

NOTE 2—Activation energy and pre-exponential factor are not independent parameters.

NOTE 3—The descriptions provided in Eq 1-3 are only mathematical

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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 Standard Reference Materials.

Current edition approved June 1, 2015. Published July 2015. DOI: 10.1520/E3007-15.

[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.

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 parameters are typically in the ranges of:

$$20 < E < 350 \text{ kJ/mol},$$
$$5 < \ln[A] < 50 \text{ with } A \text{ in s}^{-1}, \text{ and}$$
$$0.0 < n < 2.0$$

4.6 Some, thermally reactive materials may change with time. For this reason, certified reference materials may not be available for use in the evaluation of kinetic parameters. For any purchased reference material(s) of high purity from a commercial laboratory supply house or national metrology institute, the source, storage conditions and storage time of the material(s) shall be reported.

4.7 The recommended kinetic values for the thermally reactive materials identified in Table 1 are derived from a meta-analysis of literature values.[3] These reference values may be used for the evaluation of methods, apparatus or software where decomposition mass loss and temperature are measured.

NOTE 4—Kinetic parameters are known to be affected by specimen particle size. Large particle size is thought to retard escaping decomposition produced thereby affecting the reaction kinetics. While not specifically addressed by this practice, the user is advised to cryogenically grind samples for 1 minute prior to use.

NOTE 5—Kinetic parameters may be affected by specimen atmosphere. Kinetic results obtained in an inert atmosphere shall be used for comparison purposes (see Table 1).

5. Significance and Use

5.1 The kinetic parameters provided in this practice may be used to evaluate the performance of a standard, apparatus, technique or software for the determined mean parameters (such as Test Methods E1641 and E2958). The results obtained by these approaches may be compared to the values provided by this practice.

6. Hazards

6.1 Thermally reactive materials evolve decomposition products as part of the indicated reaction. These products may be toxic or corrosive. Operators shall use as small an amount of material as is practical for the measurement. Handling of these materials shall be performed by trained workers who are knowledgeable with their Safety Data Sheets (SDS) and adopt appropriate safety precautions according to local regulations.

7. Procedure

7.1 Experimentally determined mean kinetic parameters for a reference material are compared to the values described in this practice as their quotient, expressed as percent. The closeness of the conformance quotient to 100 % is an indication of accuracy. Values less than 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.

NOTE 6—The kinetic values for polytetrafluoroethylene are considered the standard. Other values presented in Table 1 are provided for user information.

8. Calculation

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

NOTE 7—Observed values include E, $\ln[A,\ \text{s}^{-1}]$ and n.

8.2 *Example Calculation*—If the observed experimental value for activation energy of polytetrafluoroethylene decomposition is E_o = 320 kJ/mol and the reference value of E_r taken from Table 1 is 319 kJ/mol, then:

$$\text{Conformance} = (320 \text{ kJ/mol} \times 100\ \%)/319 \text{ kJ/mol} = 100\ \%$$

9. Report

9.1 Identification of the kinetic method being examined.

9.2 Identification of the reference material being used for the comparison, its source, physical form (that is, powder, film, etc.), particle size, and purity.

9.3 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, candidate standards, apparatus, or software.

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; thermogravimetry; thermogravimetric analysis

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[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1044. Contact ASTM Customer Service at service@astm.org.

TABLE 1 Kinetic Parameters for Kinetic Reference Materials (see Note 1 in 2.1 and Note 6 in 7.1)

NOTE 1—Where: E = activation energy, A = pre-exponential factor, and n is reaction order.

NOTE 2—Derivation of these values is described in supporting data filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1044. Contact ASTM Customer Service at service@astm.org.

Material	CAS	E, kJ/mol	$\ln[A,\ \text{s}^{-1}]$	n	Description
Calcium Carbonate	471-34-1	194 ± 17 (8.7 %)	17.3 ± 1.5 (8.7 %)	0.51 ± 0.42	nitrogen
Calcium Oxalate Monohydrate	24804-31-70	97 ± 16 (16 %)	19.3 ± 3.1 (16 %)	0.83 ± 0.18	nitrogen and air
Polytetrafluoroethylene	**9002-84-0**	**319 ± 24 (7.5 %)**	**45.1 ± 3.4 (7.5 %)**	**1.00 ± 0.01**	**nitrogen**
Polyethylene	9002-88-4	255 ± 41 (16 %)	37.5 ± 6.0 (16 %)	0.96 ± 0.12	nitrogen
Polypropylene	9003-07-0	232 ± 27 (12 %)	34.3 ± 4.1 (12 %)	0.96 ± 0.12	nitrogen
Polystyrene	9003-53-6	211 ± 60 (28 %)	34.0 ± 9.5 (28 %)	0.96 ± 0.15	nitrogen

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