Designation: E2958 – 14

Standard Test Methods for Kinetic Parameters by Factor Jump/Modulated Thermogravimetry[1]

This standard is issued under the fixed designation E2958; 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 These test methods describe the model-free determination of Arrhenius activation energy by thermogravimetry using the factor jump (**1**)[2] (Method A) or modulated thermogravimetry (**2**) (Method B) techniques. With the assumption of a first-order kinetic model, the pre-exponential factor is additionally determined.

1.2 These test methods are applicable to materials with well-defined decomposition profiles, namely, a smooth, continuous mass change.

1.3 These test methods are applicable to decomposition occurring in the range from 400 K to 1200 K (nominally 100°C to 900°C). The temperature range may be extended depending on the instrumentation and material used.

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

1.5 There is no ISO standard similar to this standard.

1.6 *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:*[3]

E473 Terminology Relating to Thermal Analysis and Rheology

E1142 Terminology Relating to Thermophysical Properties

E1582 Practice for Calibration of Temperature Scale for Thermogravimetry

E1641 Test Method for Decomposition Kinetics by Thermogravimetry Using the Ozawa/Flynn/Wall Method

E1877 Practice for Calculating Thermal Endurance of Materials from Thermogravimetric Decomposition Data

E1970 Practice for Statistical Treatment of Thermoanalytical Data

E2040 Test Method for Mass Scale Calibration of Thermogravimetric Analyzers

E2550 Test Method for Thermal Stability by Thermogravimetry

3. Terminology

3.1 *Definitions*—Technical terms used in this test method defined in Terminologies E473 and E1142 include *Arrhenius equation, activation energy, Celsius, failure criterion, pre-exponential factor, reaction order*, and *thermogravimetric analysis*.

4. Summary of Test Method

4.1 These test methods consist of heating a test specimen weighing a few milligrams at a heating rate of about 1 K/min with a superimposed step-and-hold (factor jump) or sinusoidal (modulated) temperature program through the decomposition temperature region. The specimen mass rate-of-change is continuously calculated and recorded as a function of temperature. The activation energy is then determined from the mass rate-of-change at two (or more) closely spaced temperature regions. The activation energy thus determined is based on no assumed reaction model or mechanism and thus is model free.

4.2 Assuming a first-order reaction model (n = 1), the additional reaction parameter logarithm-of-the-pre-exponential-factor (ln[Z]) is additionally determined.

4.3 Activation energy and logarithm-of-the-pre-exponential-factor may be displayed as a function of average temperature or conversion to provide additional information about the constancy of the decomposition reaction relative to these experimental parameters.

5. Significance and Use

5.1 The activation energy may be used to calculate thermal endurance and an estimate of the lifetime of the material at specified temperatures using Test Method E1877.

[1] These test methods are under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Calorimetry and Mass Loss.

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

[3] 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.

5.2 The kinetic parameters determine by this test method may be used in quality assurance, research and development.

5.3 The kinetic parameters of activation energy and logarithm of the pre-exponential factor determined by this method have little intrinsic value in themselves. Most practical applications of this information, such as lifetime estimation (see Test Method E1877), also require an estimation of the precision of the respective values. Determination of that precision by replicated determination is a non-manditory part of this standard.

6. Apparatus

6.1 The essential equipment required to provide minimum thermogravimetric analytical capability of this test method include:

6.1.1 A *thermobalance*, composed of (*a*) a *furnace* to provide uniform controlled heating of a specimen at a constant rate up to 100 K/min within the temperature range from ambient to 1200 K; (*b*) a *temperature* sensor to provide an indication of the specimen/furnace temperature to within ±0.1 K; (*c*) an *electrobalance* to continuously measure the specimen mass with a minimum capacity of 20 mg and a sensitivity of ±50 µg; and (*d*) a means of sustaining the specimen/container under *atmospheric control* of an inert or reactive purge gas of 99.99 % purity at a rate of 20 mL/min to 50 mL/min ± 5 mL/min.

6.1.2 A *temperature controller*, capable of executing a specific temperature program by operating the furnace between selected temperature limits at a rate of temperature change of 1 K/min to 100 K/min constant to within ±1 % or an isothermal temperature which is maintained constant to within ±0.05 K.

6.1.3 A *data collection device*, to provide a means of acquiring, storing, and displaying measured or calculated signals, or both. The minimum output signals required for this test method are mass, mass rate-of-change, temperature, and time.

6.1.4 Auxiliary instrumentation or data analysis capability considered useful in conducting this method includes:

6.1.4.1 For Method B, the ability to apply a sinusoidal temperature program of a 100 s to 300 s period and ±0 K to 6 K amplitude upon the underlying linear temperature program or isothermal conditions.

6.1.4.2 For Method B, the capability to continuously calculate activation energy and logarithm of the pre-exponential factor.

NOTE 1—Alternative capabilities are described in Refs (**3-7**).

6.2 *Containers* (pans, crucibles, and so forth) that are inert to the specimen and that will remain dimensionally stable over the temperature range from ambient to 1200 K.

6.3 *High-Purity (99.99 %) Nitrogen Supply*, for purge gas.

NOTE 2—Other atmospheres may be used but shall be reported.

6.4 *Cryogenic Mill* capable of grinding up to 4 mg of material at a temperature less than 173 K (–100°C).

7. Sampling, Test Specimens, and Test Units

7.1 Since milligram quantities of specimens are used, it is essential that the specimens be representative of the samples from which they are taken. All specimens should be thoroughly mixed prior to sampling and should be sampled by removing portions form various parts of the sample. These portions should in turn be combined and mixed well to ensure a representative specimen for the determination.

7.2 Powdered or granular specimens that have a high surface-to-volume ratio, are preferred, although films, fibers, and fabric may be used providing that care is taken to ensure that all specimens are uniform in size and shape. Where the sample is a part or is in the form of pellets, the specimen may be prepared by filling, rasping or cryogenic milling.

NOTE 3—The specimen size and surface-to-volume ratio are known to affect the results of this test. A narrow range of specimen sizes should be used as noted in 10.1 and 12.1. Uniformity in particle size can be achieved, without the loss of volatiles, by using a cryoscopy (liquid nitrogen) mill to grind the sample to a powder. To prevent the condensation of moisture, the mill should be opened only after returning to ambient temperature, or the operation should be performed in a glove box filled with dry gas.

7.3 In the absence of other information, the samples are assumed to be analyze as-received except for the mechanical treatment noted in 7.2. If some heat treatment, such as drying, is applied to the sample prior to analysis, this treatment and any resulting mass loss shall be reported.

7.4 Some materials may require more sophisticated conditioning, such as maintaining the sample in a specified temperature and relative humidity for an extended period of times. Such conditioning may be conducted, but procedural details shall be included in the report.

8. Preparation of Apparatus and Experimental Conditions

8.1 Prepare the thermogravimetric analyzer using the procedures described in the manufacturer's operations manual.

8.2 Identify the weight loss to be used as the failure criterion. Report this value.

NOTE 4—The value of 5 % mass loss of the specific decomposition step is commonly used in thermogravimetry and accelerated lifetime testing as the failure criteria (see Test Method E1641).

9. Calibration and Standardization

9.1 Calibrate the temperature scale of the thermogravimetric analyzer at 1 K/min using Practice E1582.

9.2 Calibrate the mass loss scale of the thermogravimetric analyzer using Test Method E2040.

METHOD A
FACTOR JUMP METHOD

10. Procedure

10.1 Place 2 mg to 4 mg of the specimen into a clean, tared instrument specimen container.

NOTE 5—Other specimen size may be used but shall be reported.
NOTE 6—Powdered or granular specimens should be distributed evenly

over the specimen holder so as to maximize the exposed surface.

10.2 Equilibrate the specimen for 1 minute at a temperature 20 K below the known decomposition onset temperature. Establish the mass scale at the conversion fraction of zero (α = 0.0 %).

NOTE 7—The decomposition onset temperature may be obtained from a scouting experiment using Test Method E2550 at 5 K/min.

10.3 Begin recording experimental data. Initiate an isothermal temperature program for 150 s. At the end of this isothermal period, measure and record the mass rate-of-change ($d\alpha_v/dt$), temperature (T_v) and conversion (α_v).

10.4 Initiate a temperature step-and-hold sequence by increasing the temperature by 10.0 K ± 0.2 K and holding that temperature to within 0.05 K for 150 s. At the end of this isothermal period, record the mass rate-of change ($d\alpha_p/dt$), temperature (T_p) and conversion (α_p).

NOTE 8—The time required to establish temperature equilibrium and to make an accurate mass rate-of-change measurement may vary by instrument and temperature. These conditions are thought to embrace those achievable by all instrument designs. Other temperature steps and isothermal hold periods may be used but shall be reported (see Appendix X1).

10.5 Using the data obtained in 10.3 and 10.4, determine the activation energy, logarithm of the pre-exponential factor and temperature (T) using Eq 1, Eq 2, and Eq 3. Record these values along with the conversion (α) at the end of the second isothermal region.

10.6 Initiate a second step-and-hold cycle by decreasing the temperature by 5.0 K ± 0.1 K and holding that temperature to within 0.05 K for 150 s. At the end of the isothermal region, record the mass-rate-of change ($d\alpha_v/dt$), temperature (T_v) and conversion (α_v).

10.7 Using the data obtained in 10.4 and 10.6, determine the activation energy, logarithm of the pre-exponential factor, and temperature using Eq 1, Eq 2, and Eq 3. Record these values along with the conversion (α) at the end of the second isothermal region.

10.8 Repeat 10.4 – 10.7 until the decomposition weight loss is complete or until the upper temperature limit of the apparatus is reached.

10.9 Create a table of activation energy and logarithm of the pre-exponential factor versus conversion. Select the activation energy and logarithm of the pre-exponential factor nearest the failure criterion conversion level from 8.2.

NOTE 9—Most uses of activation energy and logarithm of the pre-exponential factor required an estimation of their precision. Mean values and standard deviations for both values may be obtained from a minimum of three replicate determinations (see Practice E1970).

10.10 Report the mean activation energy (E) and its percent relative standard deviation ($\sigma E/E$) and the mean logarithm of the pre-exponential factor ($\ln[Z]$) and its percent relative standard deviation ($\sigma\ln[Z]/\ln[Z]$) at the temperature closest to the failure criterion of 8.2

11. Calculations

11.1 Calculations are as follows:

$$E = \{R\ T_p\ T_v\ \ln[(d\alpha_p/dt)/(d\alpha_v/dt)]\}/(T_p - T_v) \quad (1)$$

$$\ln[Z, \text{min}^{-1}] = \ln[(d\alpha_v/dt)/(1 - \alpha/100\ \%)] + E/RT \quad (2)$$

$$T = (T_p + T_v)/2 \quad (3)$$

where:

E = Activation energy, J/mol,
R = Gas constant (= 8.31451 J/(mol K)),
T_p = Temperature at the end of the higher temperature isothermal plateau, K,
T_v = Temperature at the end of the lower temperature isothermal plateau, K,
T = Average temperature between T_p and T_v, K,
$d\alpha_p/dt$ = Mass rate-of-change at the end of the higher temperature isothermal plateau, % / min,
$d\alpha_v/dt$ = Mass rate-of-change at the end of the lower temperature isothermal plateau, % / min,
ln = Natural logarithm to the Napier base e,
α = Fraction reacted or conversion, %,
Z = Pre-exponential factor, min^{-1}, and
$d\alpha/dt$ = Mean mass rate-of-change for two adjacent step-and-hold segments = $(d\alpha_v dt + d\alpha_p/dt)/2$.

NOTE 10—The logarithm of the pre-exponential factor ($\ln[Z]$) calculated in Eq 2 is determined assuming a first-order kinetics reaction.

METHOD B
MODULATED THERMOGRAVIMETRY METHOD

12. Procedure

12.1 Place 2 mg to 4 mg of the specimen into a clean, tared instrument specimen container.

NOTE 11—Other specimen size may be used but shall be reported.

NOTE 12—Powdered or granular specimens should be distributed evenly over the specimen holder so as to maximize the exposed surface.

12.2 Equilibrate the specimen for 1 minute at a temperature 20 K below the known decomposition onset temperature. Establish the percent mass loss scale at 100 % (α = 0 %).

NOTE 13—The decomposition onset temperature may be obtained from a scouting experiment using Test Method E2550 at 5 K/min.

12.3 Begin recording experimental data including average temperature, average mass, conversion, activation energy and logarithm of the pre-exponential factor. Initiate a modulated temperature program with amplitude of ±4.9 K – 5.1 K (that is, 9.8 K to 10.2 K peak-to-peak) and a period of 300 s.

NOTE 14—The time required to establish dynamic equilibrium may vary with instrument and temperature. These conditions are thought to embrace the dynamic equilibrium achievable by all instrument designs. Other periods and amplitudes may be used but shall be reported (see Appendix X1).

NOTE 15—The recording of other signals such as the mass rate-of-change, modulated temperature and modulated mass may be helpful to interpret the thermal decomposition.

12.4 After 150 s, initiate an underlying temperature program of 1 K/min. Terminate the experiment when the decomposition mass loss is complete or when the upper temperature of the apparatus is reached.

12.5 Create a display of activation energy and logarithm-of-the-pre-exponential-factor as a function of conversion. Select the value for activation energy and logarithm-of-the-pre-exponential-factor nearest to the failure criterion conversion.

NOTE 16—Most uses of activation energy and logarithm-of-the-pre-exponential-factor require an estimation of their precision. Mean values and standard deviations may be obtained from a minimum of three replicate determinations (see Practice E1970).

12.6 Report the mean activation energy (E), its percent relative standard deviation ($\sigma E/E$), the mean logarithm of the pre-exponential factor ($\ln[Z]$), its percent standard deviation ($\sigma\ln[Z]/Z$) and the mean temperature (T) at the failure criterion conversion of 8.2.

13. Calculations

13.1 Using sinusoidal temperature modulation, Eq 1 reduces to:

$$E = \{R\ (T^2\ -\ A^2)L\}/2A \quad (4)$$

$$\ln[Z\ ,\ \mathrm{min}^{-1}] = \ln[(d\alpha/dt)/(1\ -\ \alpha/100\ \%)] + E/RT \quad (5)$$

where:

A = Measured temperature modulation amplitude, K,
L = $\ln[(d\alpha_p/dt)/(d\alpha_v/dt)] = \ln[(dw_p/dt)/(dw_v/dt)]$,
$d\alpha_p/dt$ = Maximum value for the dα/dt curve at conversion α,
$d\alpha_v/dt$ = Minimum value for the dα/dt curve at conversion α,
dw_p/dt = Maximum value of the change-in-mass curve for cycle,
dw_v/dt = Minimum value for the change-in-mass curve for a cycle, and
T = Average specimen temperature.

NOTE 17—L = Maximum value of the envelope of $\ln[d\alpha/dt]$ or $\ln[dw/dt]$ signal.

14. Report

14.1 Report the following information:

14.1.1 Designation of the material under test, including the name of the manufacturer, lot number, and chemical composition when known.

14.1.2 Description of the thermogravimetric analyzer such as manufacturer and model.

14.1.3 The experimental conditions used including, Method used (A or B), a description of the method such as magnitude of the temperature steps and isothermal (hold) times, period and amplitude of the sinusoidal temperature program, underlying heating rate, temperature range, and failure criterion.

14.1.4 The determined (mean) activation energy (and its percent relative standard deviation), and the (mean) logarithm of the pre-exponential factor (and its percent relative standard deviation).

14.1.5 The specific dated version of this test method used.

15. Precision and Bias

15.1 An interlaboratory test will be conducted in 2015-2020 to develop a detailed precision and bias statement for this test method. Anyone wishing to participate in this interlaboratory test may contact the ASTM International Staff Manager for Committee E37.

15.2 *Method A (Factor Jump):*

15.2.1 Within laboratory relative standard deviation in a single laboratory with nine replicate determinations on poly-(styrene) was ±1.0 % for activation energy (**8**).

15.3 *Method B (Modulated Thermogravimetry):*

15.3.1 Within laboratory relative standard deviation determined in a single laboratory with six replicate determinations on 60 % poly(ethylene vinyl acetate) found both activation energy and logarithm-of-the-pre-exponential-factor to be ±1.7 % (**2**).

NOTE 18—Activation energy and logarithm of the logarithm of the pre-exponential factor are not independent measurements but are related to each other by the kinetic compensation effect (**9**).

15.4 The statistical "F test" indicates (at the 95 % confidence level) that there is no statistical significance difference between the precision values is 15.2.1 and 15.3.1.

15.5 Bias is the difference between the determined value and an accepted reference value. There are no known certified kinetic reference materials for the evaluation of kinetic parameters by thermogravimetry.

15.6 In the absence of a suitable reference material, the values obtained by this standard may be compared with the values obtain by another test method for the same materials. Table 1 compares the results obtained for several polymers, organic and inorganic chemicals using Method B of this standard and Test Method E1641. While there is considerable

TABLE 1 Comparison of Results Between Test Method E1641 and Method B of Test Method E2985 (2)

Material	Activation Energy, Kj/mol		Log Pre-Exponential Factor, min^{-1}	
	E1641	E2985	E1641	E2985
Poly(ethylene)	190	190	12.9	12.8
Poly(tetrafluoroethylene)	316	341	19.1	21.1
Poly(styrene)	173	182	13.0	14.0
Poly(ethylene vinyl acetate) – first loss	183	167	14.5	13.2
Poly(ethylene vinyl acetate) – second loss	289	174	20.4	11.5
Dicumyl Peroxide	104	101	12.0	11.8
1,3-Diphenylbutadiyne	80	99	8.1	10.4
Calcium Oxalate•H_2O	117	121	13.8	13.5
Calcium Oxalate	207	194	14.0	12.2
Calcium Carbonate	210	188	10.5	8.7

variation among the materials, the average bias is zero for both activation energy and logarithm of the pre-exponential factor.

16. Keywords

16.1 activation energy; decomposition; kinetics; pre-exponential factor; thermogravimetric analysis; thermogravimetry

APPENDIX

(Nonmandatory Information)

X1. SELECTING ALTERNATIVE OPERATING CONDITIONS

X1.1 There are a number of constraints on the selection of experimental operating conditions. Users who wish to operate at condition different than those described in this standard should be aware of these conditions.

X1.1.1 A large temperature step or modulation amplitude is required to achieve accuracy in the differential temperature value in the denominator of Eq 1 and Eq 4. Experience shows that this temperature difference between adjacent peak-and-valleys should be on the order of 8 K to 10 K (**8**).

X1.1.2 The time to re-establish static isothermal temperature equilibrium and a stable mass rate-of-change signal following a temperature step may take several minutes. For this reason, isothermal "hold" periods for the step-and-hold method should be reduced with great care and demonstration of the stability of the logarithm of the mass rate-of-change signal (**8**).

X1.1.3 It is preferable to achieve replicate determinations over a short average temperature interval. Increasing average rate of temperature change (the underlying temperature rate) should be done with caution. At least 10 determinations should take place over the full decomposition mass change (**2**).

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