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Designation: ~~E2958 – 19~~ E2958 – 21

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] (Test Method A) or modulated thermogravimetry (**2**) (Test Methods B and C) 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.

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

ASTM E2958-21

1.6 *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:*[3]

E473 Terminology Relating to Thermal Analysis and Rheology
E1142 Terminology Relating to Thermophysical Properties
E1582 Test Method for Temperature Calibration of Thermogravimetric Analyzers
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

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[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.

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

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E2550 Test Method for Thermal Stability by Thermogravimetry
E3007 Practice for Selection and Use of Kinetic Reference Values in the Study of Decomposition Reactions by Thermogravimetry

3. Terminology

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

4. Summary of Test Methods

4.1 These test methods consist of heating a test specimen weighing ~~a few milligrams~~ 2 mg to 4 mg 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~~If a first-order reaction model (n = ~~1), the additional~~ 1) is assumed, the 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.

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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.

5.2 The kinetic parameters ~~determine~~determined by these test methods may be used in quality assurance, specification acceptance, research, and development.

ASTM E2958-21
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5.3 The kinetic parameters of activation energy and logarithm of the pre-exponential factor determined by these test methods 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 these test methods.

6. Apparatus

6.1 The essential equipment required to provide minimum thermogravimetric analytical capability of these test methods 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 readable to within ~~±0.1~~±0.01 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 these test methods are mass, mass rate-of-change, temperature, and time.

6.1.4 Auxiliary instrumentation or data analysis capability considered useful in conducting these test methods include:

6.1.4.1 For Test Method B, the ability to apply a sinusoidal temperature program of a 100 s to 300 s period and ±0.01 K to ±6 K amplitude upon the underlying linear temperature program or isothermal conditions.

6.1.4.2 For Test 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.

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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.~~

ASTM E2958-21
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7.2.1 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.~~manual including positioning the temperature sensor as close as practical to the test specimen.

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

NOTE 3—The value of 5 % mass loss of the specific decomposition step is commonly used as a default value 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.

TEST 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 4—Other specimen size to ±1 mg may be used but shall be reported.

NOTE 5—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 at least 20 K below the known decomposition onset temperature. Establish the mass scale at the conversion fraction of zero ($\alpha = 0.0$ %).

NOTE 6—The decomposition onset temperature may be obtained from a scouting experiment using Test Method E2550 at 5 K/min.

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ASTM E2958-21
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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~~ K, avoiding overshoot, 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 7—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 4. 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, Eq 3, and Eq 4. 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 8—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:

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

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

$$\log[Z\ , \mathrm{min}^{-1}] = \log[(d\alpha/dt)/(1 - \alpha/100\ \%)] + 0.434\ E/RT \tag{3}$$

$$T = (T_p + T_v)/2 \tag{4}$$

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

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ASTM E2958-21
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TEST 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 10—Other specimen size to ±1 mg may be used but shall be reported.

NOTE 11—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 at least 20 K below the known decomposition onset temperature. Establish the percent mass loss scale at 100 % (α = 0 %).

NOTE 12—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 to ±5.1 K (that is, 9.8 K to 10.2 K peak-to-peak) and a period of 300 s.

NOTE 13—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 14—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 Using Eq 5 and Eq 6, calculate the activation energy (*E*) and natural logarithm (ln[*Z*, min^{-1}]) of the pre-exponential factor as a function of conversion

12.6 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 15—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).

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

TEST METHOD C
MODULATED THERMOGRAVIMETRY METHOD

13. Procedure

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

NOTE 16—Other specimen size to ±1 mg may be used but shall be reported.

NOTE 17—Powdered or granular specimens should be distributed evenly over the specimen holder so as to maximize the exposed surface.

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13.2 Equilibrate the specimen for 1 minute at a temperature at least 20 K below the known decomposition onset temperature. Establish the percent mass loss scale at 100 % ($\alpha = 0$ %).

NOTE 18—The decomposition onset temperature may be obtained from a scouting experiment using Test Method E2550 at 5 K/min.

13.3 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 to ±5.1 K (that is, 9.8 K to 10.2 K peak-to-peak) and a period of 300 s.

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NOTE 19—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 20—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.

13.4 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.

13.5 Using Eq 8, calculate the activation energy (*E*) and Eq 6 to calculate natural logarithm (ln[*Z*, min^{-1}]) or Eq 7 to calculate logarithm (log[*Z*, min^{-1}]) of the pre-exponential factor as a function of conversion.

13.6 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 21—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).

13.7 Report the mean activation energy (*E*), its percent relative standard deviation (σ*E*/*E*), the mean logarithm of the preexponential factor (ln[*Z*]), its percent standard deviation (σln[*Z*]/*Z*) and the mean temperature (*T*) at the failure criterion conversion of 8.2.

14. Calculations

14.1 Using sinusoidal temperature modulation, Eq 1 reduces to:

$$E = \{R\ (T^2 - A^2)L\}/2A \tag{5}$$

$$\ln[Z\ , \mathrm{min}^{-1}] = \ln[(d\alpha/dt)/(1 - \alpha/100\ \%)] + E/RT \tag{6}$$

$$\log[Z\ , \mathrm{min}^{-1}] = \log[(d\alpha/dt)/(1 - \alpha/100\ \%)] + 0.434\ E/RT \tag{7}$$

$$E = (B_1\ \ R\ \ \ T_a^2)/(B_0\ \ A) \tag{8}$$

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 $d\alpha/dt$ curve at conversion α,

$d\alpha_v/dt$ = minimum value for the $d\alpha/dt$ 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,

T = average specimen temperature over a period of one cycle,

B_0 = average conversion rate of change ($d\alpha/dt$) over a period of one cycle, min^{-1}, and

B_1 = measured modulation conversion rate amplitude over a period of one cycle, min^{-1}.

NOTE 22—L = maximum value of the envelope of $\ln[d\alpha/dt]$ or $\ln[dw/dt]$ signal.

15. Report

15.1 Report the following information:

15.1.1 The test method of this standard used (that is, A, B, or C).

15.1.2 A complete description of the material under test, including the name of the manufacturer, lot number, and chemical composition when known.

15.1.3 A complete description of the thermogravimetric analyzer such as manufacturer and model.

15.1.4 A complete description of the experimental conditions used including, test method used (A, B, or C), 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.

15.1.5 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).

15.1.6 The specific dated version of these test methods used.

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Document Preview
ASTM E2958-21
https://standards.iteh.ai/catalog/standards/sist/3a0a8716-548e-4381-aa9e-2d35e39a6a1d/astm-e2958-21

TABLE 1 Comparison of Results Between Test Method E1641 and Test Method B of Test Method ~~E2985~~E2958 (2)

Material	Activation Energy, Kj/mol		Log Pre-Exponential Factor, min^{-1}	
	E1641	~~E2985~~E2958	E1641	~~E2985~~E2958
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