Designation: ~~E1641 – 13~~ E1641 – 15

Standard Test Method for
Decomposition Kinetics by Thermogravimetry Using the Ozawa/Flynn/Wall Method[1]

This standard is issued under the fixed designation E1641; 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 This test method describes the determination of the kinetic parameters, Arrhenius activation energy, and preexponential factor by thermogravimetry, based on the assumption that the decomposition obeys first-order kineticsusing the Ozawa/Flynn/Wall isoconversional method **(1, 2)**.[2]

1.2 This test method is generally applicable to materials with well-defined decomposition profiles, namely, a smooth, continuous mass change with a single maximum rate.

1.3 This test method is normally applicable to decomposition occurring in the range from 400 to 1300K (nominally 100 to 1000°C). The temperature range may be extended depending on the instrumentation used.

1.4 This test method is similar to ISO 11358-2 but differs in its mathematical treatment.

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

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E473 Terminology Relating to Thermal Analysis and Rheology
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E1142 Terminology Relating to Thermophysical Properties
E1582 Practice for Calibration of Temperature Scale for Thermogravimetry
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

2.2 *Other Standard:*[4]

ISO 11358-2 Plastics Thermogravimetry (TG) of Polymers Part 2: Determination of Kinetic Parameters

3. Terminology

3.1 *Definitions*—Technical terms used in this test method are defined in Terminologies E473 and E1142 and include *activation energy, Celsius, failure, failure criterion*, and *thermogravimetric analyzer*.

4. Summary of Test Method

4.1 This test method is based upon the general rate equation that takes the form of:

$$d\alpha/dT = A(1 - \alpha) \exp[- E /R \ T]/\beta \tag{1}$$

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[2] The boldface numbers in parentheses refer to the 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.

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

where:

α	=	fraction reacted (dimensionless),
A	=	pre-exponential factor (min^{-1}),
β	=	heating rate (K/min),
E	=	activation energy (J/mol),
R	=	gas constant (=8.316 J/(mol K)),
T	=	absolute temperature (K),
exp	=	Euler's number exponential, and
$d\alpha/dT$	=	rate of change of α with T.

4.2 Using the method of Ozawa, Flynn and Wall [1, 2], Eq 1 may be solved for activation energy:

$$E = (R / b) \, \Delta \log[\beta] / \Delta(1 / T) \qquad (2)$$

where:

E = the derivative of the Doyle approximation [3] with values tabulated in Table 1.

4.3 Using a point of constant conversion from a series of decomposition curves obtained at different heat rates, $\Delta \log[\beta] / \Delta(1 - T)$ is obtained by linear regression.

4.4 Assuming an initial value of $b = 0.457$, a first approximation of activation energy (E') is obtained using Eq 2.

4.5 This approximate activation energy is then used to determine a new value of b' using Table 1.

4.6 This iterative process is continued until the value of activation energy no longer changes with the next iteration.

4.7 For first order reactions ($n = 1$), the value of the pre-exponential factor (A) may be determined using Eq 3 [4].

$$A = (-\beta R / E) \, (\ln [1 - \alpha]) \, 10^a \qquad (3)$$

where:

a = the Doyle approximation value from Table 1.

4.8 This test method consists of heating a series of four or more test specimens, taken from the original sample, each at a different heating rate between 1 and 10 K/min, through their decomposition region. The specimen mass is recorded continuously as a function of temperature. The temperatures for constant conversion are determined from the resultant mass loss curves. The Arrhenius activation energy is then determined from a plot of the logarithm of heating rate versus the reciprocal of the absolute temperature at constant conversion level.

4.9 This activation energy may then be used to calculate thermal endurance and an estimate of the lifetime of the material at a certain temperature using Test Method E1877.

5. Significance and Use

5.1 Thermogravimetry provides a rapid method for determining the temperature-decomposition profile of a material.

5.2 This test method can be used for estimating lifetimes of materials, using Test Method E1877 provided that a relationship has been established between the thermal endurance test results and actual lifetime tests.

6. Apparatus

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

6.1.1 A *thermobalance*, composed of (*a*) a *furnace* to provide uniform controlled heating of a specimen at a constant rate within the temperature range from ambient to 1300 K; (*b*) a *temperature* sensor to provide an indication of the specimen/furnace temperature to ±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 to 50 ± 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 between 1 and 10 K/min to within ±0.1 K/min.

NOTE 1—The precision of results is strongly dependent upon the precision of the heating rate; the greater the heating rate precision, the greater the precision of results. The precision described here should be considered to be the minimum suitable for this test.

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, temperature, and time.

6.1.4 *Containers (pans, crucibles, and so forth)* which are inert to the specimen and that will remain dimensionally stable over the temperature range from ambient to 1300 K.

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

TABLE 1 Numerical Integration Constants

E/RT	a	b (1/K)
8	5.3699	0.5398
9	5.8980	0.5281
10	6.4167	0.5187
11	6.928	0.511
12	7.433	0.505
13	7.933	0.500
14	8.427	0.494
15	8.918	0.491
16	9.406	0.488
17	9.890	0.484
18	10.372	0.482
19	10.851	0.479
20	11.3277	0.4770
21	11.803	0.475
22	12.276	0.473
23	12.747	0.471
24	13.217	0.470
25	13.686	0.469
26	14.153	0.467
27	14.619	0.466
28	15.084	0.465
29	15.547	0.463
30	16.0104	0.4629
31	16.472	0.462
32	16.933	0.461
33	17.394	0.461
34	17.853	0.459
35	18.312	0.459
36	18.770	0.458
37	19.228	0.458
38	19.684	0.456
39	20.141	0.456
40	20.5967	0.4558
41	21.052	0.455
42	21.507	0.455
43	21.961	0.454
44	22.415	0.454
45	22.868	0.453
46	23.321	0.453
47	23.774	0.453
48	24.226	0.452
49	24.678	0.452
50	25.1295	0.4515
51	25.5806	0.4511
52	26.0314	0.4508
53	26.4820	0.4506
54	26.9323	0.4503
55	27.3823	0.4500
56	27.8319	0.4498
57	28.2814	0.4495
58	28.7305	0.4491
59	29.1794	0.4489
60	29.6281	0.4487

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

6.3 Auxiliary apparatus considered necessary or useful in conducting this test method include:

6.3.1 *Cryogenic Mill* to grind or mill test specimens to a fine powder at temperatures below –173 K (–100°C).

7. Precautions

7.1 It is essential that the samples be representative since milligram quantities of specimen are to be used.

7.2 The value of the calculated activation energy is independent of reaction order in the early stages of decomposition. This assumption does not hold for the later stages and shall be used with caution. An upper limit of 10 % decomposition is suggested, although 20 % is justified in certain cases. suggested. It is strongly suggested that calculations be made at several different levels of decomposition, for example, 5, 10, 15, and 20 %. Variations in the results among these determinations could indicate the inapplicability of one of them. For instance, volatile, low-level impurities would affect the results of the lowest conversion determination more than those at higher conversions. Consistent results for all conversions validate the method for the range of conversions examined.

7.3 Toxic or corrosive effluents, or both, may be released during the heating process and may be harmful to the personnel or apparatus.

8. Sampling

8.1 Powdered or granular specimens that have a high surface-to-volume ratio, are preferred, although films, fibers, and fabrics may be used providing that care is taken to make all of the specimens uniform in size and shape. Under circumstances in which material parts are available, the specimens should be prepared by filing or rasping the part. All specimens should be mixed thoroughly prior to sampling if possible, and they should be sampled by removing portions from various parts of the container. These portions should in turn be combined and mixed well to ensure a representative specimen for the determination.

NOTE 3—Care should be exercised during sample preparation to avoid contamination.
NOTE 4—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. Uniformity in particle size can be achieved, without the loss of volatiles, by using a cryogenic mill to grind the sample to a fine powder. To prevent the condensation of moisture, the mill should be opened only after returning fully to ambient temperature, or the operation should be performed in a glove box filled with dry gas.

8.2 In the absence of other information, the samples are assumed to be analyzed as received except for the mechanical treatment noted in 8.1. If some heat treatment, such as drying, is applied to the sample prior to analysis, this treatment and any resulting mass loss must be noted in the report.

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

9. Calibration

9.1 Prepare the thermogravimetric analyzer using any procedures described in the manufacturer's Operations manual.

9.2 Place the temperature sensor within 2 mm of the outside of the specimen holder. Care must be taken to ensure that the specimen holder is not touched in any way by the sensor and that it is not moved after temperature calibration.

9.3 Maintain a constant flow rate of purge gas in the range from 20 to 50 mL/min throughout the experiment.

NOTE 5—In the case of samples that may be sensitive to oxidative degradation, it will be necessary to maintain inert gas purging for a time sufficient to ensure that all residual oxygen is removed from the system prior to the start of the temperature program. It may be necessary to evacuate the system prior to initiating inert gas purging for some instruments.

9.4 Calibrate the instrument furnace temperature in accordance with the calibration procedure in Practice E1582 using the same heating rate, purge gas, and flow rate to be used for the specimens. The temperature calibration shall be performed both prior to every change in heating rate and at that heating rate.

9.5 Calibrate the mass signal using Test Method E2040.

10. Procedure

10.1 Place 3 ± 1 mg of the specimen under test into a clean, tared instrument specimen holder.

NOTE 6—Other specimen sizes may be used but shall be indicated in the report.
NOTE 7—The specimen holder should be tared in the fully assembled system, with the purge gas flowing.
NOTE 8—Powdered or granular specimens should be distributed evenly over the specimen holder so as to maximize the exposed surface. A one-grain thick layer would be optimal.

10.2 Select an equilibrium temperature based upon the heating rate and known decomposition temperature of the specimen, where the equilibrium temperature equals the decomposition temperature – (10 min × heating rate). If the percentage mass loss is to be recorded, establish zero percent loss at this time.

NOTE 9—If zero percent mass loss is established at the time at which the specimen is placed into the instrument, the specimen mass at the equilibration temperature can be greater than 100 % due to buoyancy effects. A blank should be run for accurate determination of the buoyancy effect throughout the temperature range of the experiment. The blank can be a piece of platinum of approximately the same volume as the specimen. The balance drift at any temperature can be determined in this manner.

10.3 Heat the specimen at a constant rate through the decomposition profile until a constant mass is obtained or the temperature is well beyond the useful temperature range of the material tested. Record the accompanying thermal curve, with mass or percentage mass loss displayed on the ordinate and specimen temperature on the abscissa.

10.4 Once the decomposition of the test specimen is complete, cool the instrument to room temperature, remove, clean, and replace the specimen holder, and ~~retare~~ re-tare the instrument in preparation for additional experiments. Use the same specimen holder for the entire series of runs to eliminate buoyancy problems.

10.5 Repeat the procedures described in 10.1 – 10.4 at three additional heating rates covering the range from 1 to 10 K/min.

NOTE 10—Other heating rates, and more than four, may be used but shall be noted in the report.
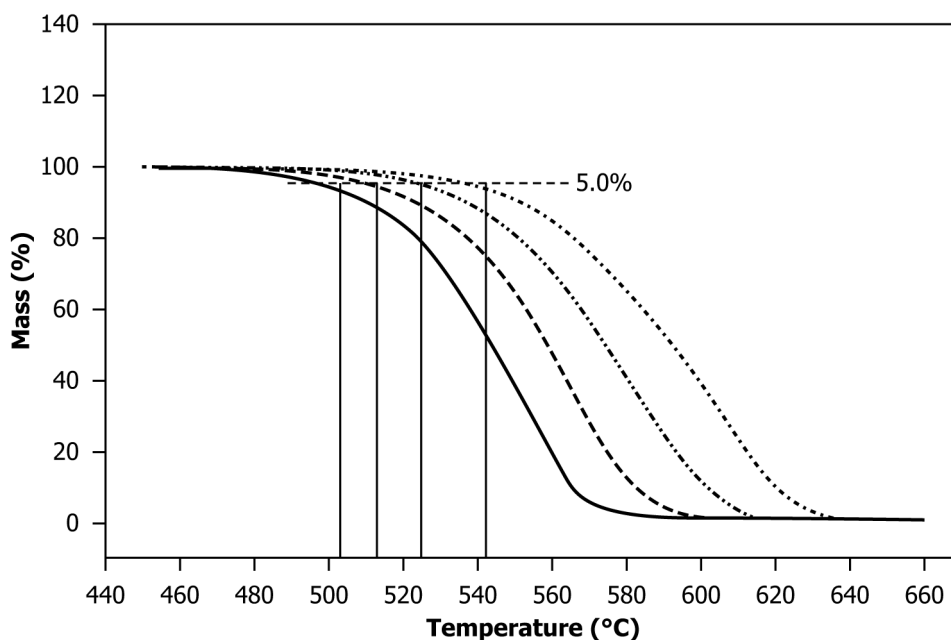
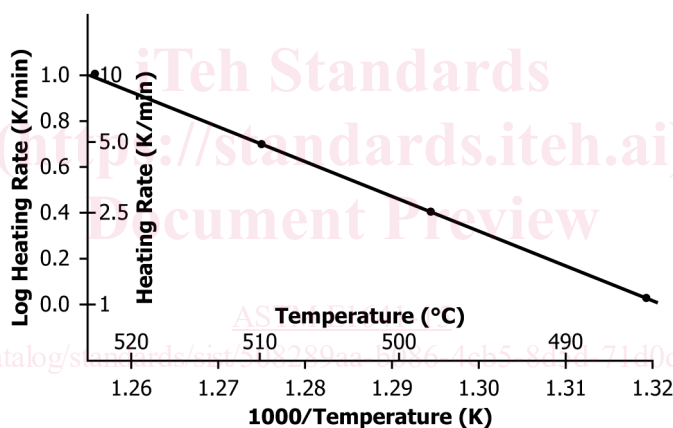FIG. 1 Examples of Mass Loss Curves at the Following Heating Rates: 1°C/min, 2°C/min, 5°C/min, 10°C/min

FIG. 2 Arrhenius Plot of Heating Rate, Temperature of Constant Conversion Data

NOTE 11—The use of heating rates greater than 10 K/min affects both the precision of the temperature measurement and the kinetics of the decomposition. Diffusion of volatiles from the sample may become the rate-controlling process at high heating rates.

11. Calculation

11.1 Select some mass loss (conversion) as the failure criterion.

NOTE 12—5 % mass loss is commonly selected as the failure criterion. Other values may be used but shall be reported.

11.2 From each of the thermal curves obtained in 10.1 – 10.5, determine the absolute temperature at constant conversion, α, for each of the constant conversion values to be used in the calculations as noted in 7.2. For example, see Fig. 1. The temperature corresponding to other conversion levels (not greater than ~~20 %)~~ 20 % and preferably less than 10 %) may be used in the determination, but it must be noted in the report.

NOTE 13—These calculations are simplified if the percent mass loss rather than actual mass is recorded on the ordinate.
NOTE 14—The value is determined from the difference of the initial and final sample conversion, with the initial mass taken as the mass at the equilibration temperature and the final mass taken once the plateau has been reached at the end of weight loss. For example, if the initial mass is 100.3 % and the final mass is 80 %, 100 % decomposition corresponds to (100.3 to 80.0) or 20.3 % mass loss. Thus, 5 % decomposition occurs at (0.05 × 20.3) or 1.02 % mass loss, which occurs on the ordinate at 99.3 % (100.3 % − 1.02 % = 99.28 %).

11.3 Display the logarithm of the heating rate expressed in K/min against the reciprocal of the absolute temperature in K at which the conversion level (failure criterion), selected in 11.1, was reached. A straight line, similar to that in Fig. 2, should result. This test procedure is not applicable if the curve is nonlinear.

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NOTE 15—An apparent nonlinearity may result from erroneous determinations. It is recommended that any nonlinear points be repeated for verification.

11.4 Using the ~~least-squares method~~linear regression fit a straight line (see Practice E1970) to these data without weighing factors, and determine the slope (m) and its standard deviation (δ_m):

$$m = \Delta(\log\beta)/\Delta(1/T) \tag{4}$$

NOTE 16—If the values obtained from this test method are to be used in Test Method E1877, an estimation of the uncertainty for activation energy (E) and preexponential factor (A) is required. These uncertainties may be derived from the uncertainty in the slope value of ~~$m = \Delta(\log\beta)/\Delta(1/T)$ m.~~$= \Delta$ ~~(log β)/Δ (1/ T).~~If the calculation tool used to obtain the slope of the straight line provides an estimation of uncertainty in the determined slope ~~(δm),~~(δm), record it. Otherwise, the uncertainty in the slope may be obtained using the procedure in Appendix X1.

11.5 The following definitions apply to 11.3 – 11.10:

E	=	~~activation energy, J/mol,~~
A	=	~~pre-exponential factor, min^{-1},~~
R	=	~~gas constant, 8.314 J/(mol·K),~~
~~$\Delta(\log\beta)/\Delta(1/T)$~~	=	~~slope of the line obtained in 11.4,~~
~~β~~	=	~~heating rate, K/min,~~
β'	=	heating rate nearest the midpoint of the experimental heating rates, K/min,
~~T~~	=	~~temperature at constant conversion, K,~~
~~b~~	=	~~logarithm of the approximation derivative (known as the Doyle approximation) (from Table 1 (use b = 0.457/K on first iteration),~~
$\underline{b}$	=	logarithm of the approximation derivative (known as the Doyle approximation) (from Table 1 (use b =0.457/K on first iteration),
a	=	logarithm of the approximation integral (known as the Doyle approximation) taken from Table 1,
~~α~~	=	~~conversion value of decomposition, and~~
$\underline{\alpha}$	=	fraction reacted (dimensionless), and
T_c	=	temperature for point of constant conversion for β', K.

11.6 Calculate an estimation of the activation energy using Eq ~~1~~2(1, 25), making use of the value of ~~$\Delta(\log\beta)/\Delta(1/$~~ ~~$T$)~~$\Delta(\log\beta)/\Delta(1/T)$ determined in 11.4 and a value of ~~$b = 0.457/K$~~$b = 0.457/K$ in this first ~~iteration:~~iteration.

$$E = -(R/b)*\Delta(\log\beta)/\Delta(1/T) \tag{1}$$

11.7 Calculate the value for E/RT_c, where T_c = the temperature at constant conversion for the heating rate closest to the midpoint of the experimental heating rates.

11.8 Using the value for E_e/RT_c obtained in 11.7, obtain a new estimation of b from Table 1. Resubmit this value of b to Eq ~~1~~2.

11.9 Repeat 11.6 and 11.7 until the value for the activation energy changes by less than 1 %. This refined value, E, is reported as the Arrhenius activation energy.

11.10 Select the mass loss curve for the heating rate nearest the midpoint of the experimental heating rates, and calculate the pre-exponential factor, A, using Eq ~~2~~3 (1, 2, 3, 4) and the value of the exponent, a, obtained from Table 1 for the refined value of E_e/RT_c determined in 11.9.

$$A = (\beta'R - \ln(1 - \alpha)10^a)/E \tag{2}$$

NOTE 17—This mathematical treatment to solve for E and A has been tailored specifically to make it possible to perform by hand. Commercial kinetics software may use other numerical methods of integrating the general differential form of the rate equation (the Flynn and Wall equations) and solving for the parameters. The interim values E_a, a, and b, which are part of the numerical iteration, are thus not reported.

11.11 Example calculation for E (from Fig. 2):

$$T_c = 510 °C = 783 K,$$

$$\text{and } \Delta(\log\beta)/\Delta(1/T) = [1.000 - 0.000]/[0.001258 - 0.001319]$$

$$= -16\,394 K$$

$$T_r = 510°C = 783 K, \text{ and } \Delta(\log\beta)/\Delta(1/T) = [1.000 - 0.000]/[0.001258 - 0.001319] = -16\,394 K$$

11.11.1 As the first estimation:

$$b' = 0.457/K$$

$$b = 0.457$$

11.11.2 Using Eq ~~1~~2:

$$E' = [-8.314 J/(mol \times K)(-16\,394)/\{0.457/k\}] = 298\,249 J/mol$$

$$E = 8.314 J/(mol\,K) \times (-16\,394 K) \times (0.457) = 298\,249 J/mol$$

11.11.3 Calculating the value of E'/RT_c: