



Designation: E 1641 – 99

Standard Test Method for Decomposition Kinetics by Thermogravimetry¹

This standard is issued under the fixed designation E 1641; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This test method covers determination of the kinetic parameters, Arrhenius activation energy, and preexponential factor by thermogravimetry, based on the assumption that the decomposition obeys first-order kinetics.

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 (100 to 1000°C). The temperature range may be extended depending on the instrumentation used.

1.4 Computer or electronic-based instruments, techniques, or data treatment equivalent to this test method may also be used.

NOTE 1—Users of this test method are expressly advised that all such instruments or techniques may not be equivalent. It is the responsibility of the user of this test method to determine the necessary equivalency prior to use. Only the manual procedures described in this test method are to be considered valid in the case of dispute.

1.5 The values stated in SI units are to be regarded as the 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:

E 473 Terminology Relating to Thermal Analysis²

E 1142 Terminology Relating to Thermophysical Properties²

E 1582 Practice for Calibration of Temperature Scale for Thermogravimetry²

¹ This test method is under the jurisdiction of ASTM Committee E-37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Test Methods.

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² Annual Book of ASTM Standards, Vol 14.02.

E 1877 Practice for Calculating Thermal Endurance of Materials From Thermogravimetric Decomposition Data

3. Terminology

3.1 Technical terms used in this test method are defined in Terminologies E 473 and E 1142.

4. Summary of Test Method

4.1 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 10K/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. This activation energy may then be used to calculate thermal endurance and an estimate of the lifetime of the material at a certain temperature.

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 E 1877 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 900 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 μ g; 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.

6.1.3 A recording device, either analog or digital, capable of recording and displaying the change in mass with of ± 50 μg and temperature with a resolution of 0.1 K.

6.1.4 Containers (*pans, crucibles, and so forth*) which are inert to the specimen and which will remain dimensionally stable over the temperature range from ambient to 900 K.

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

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

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. 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, which 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 sample 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 9.5. Uniformity in particle size can be achieved, without the loss of volatiles, by using a liquid nitrogen 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. Procedure

9.1 Calibrate the instrument mass balance in accordance with the procedure recommended for the instrument in use.

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 E 1582 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 Place 3 ± 1 mg of the specimen under test into a clean, tared instrument specimen holder. Other specimen sizes may be used but shall be indicated in the report.

NOTE 6—The specimen holder should be tared in the fully assembled system, with the purge gas flowing.

NOTE 7—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.

9.6 Equilibrate the specimen at a temperature, in kelvins (K), of ten times the heating rate in kelvins per minute below the known decomposition temperature. If the percentage mass loss is to be recorded, establish zero percent loss at this time.

NOTE 8—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.

9.7 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.

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

9.9 Repeat the procedures described in 9.4-9.8 at three additional heating rates covering the range from 1 to 10 K/min. Other heating rates, and more than four, may be used but shall be noted in the report.

NOTE 9—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.

10. Calculation

10.1 From each of the thermal curves obtained in 9.5-9.9, 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 %) may be used in the determination, but it must be noted in the report.

NOTE 10—These calculations are simplified if the percent mass loss rather than actual mass is recorded on the ordinate.

NOTE 11—The value is determined from the difference of the initial and final sample mass, 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 %, then $\alpha = 0.05$ corresponds to 0.05 (100.3 to 80.0) or 1.02 % mass loss. Thus, 5 % decomposition occurs on the ordinate at 99.3 % (100.3 % - 1.02 % = 99.28 %).

10.2 Plot the logarithm of the heating rate expressed as kelvins per minute against the reciprocal of the absolute temperature at which the conversion level, selected in 10.1, was reached. A straight line, similar to that in Fig. 2, should result. This test procedure is not applicable if the curve is nonlinear.

NOTE 12—An apparent nonlinearity may result from erroneous determinations. It is recommended that any nonlinear points be repeated for verification.

10.3 Using the least-squares method fit a straight line to these data without weighing factors, and determine the slope

$$\Delta(\log\beta)/\Delta(1/T)$$

NOTE 13—If the values obtained from this test method are to be used in Test Method E 1877, 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 $m = \Delta(\log\beta)/\Delta(1/T)$. If the calculation tool used to obtain the slope of the straight line provides an estimation of uncertainty in the determined slope (δm), record it. Otherwise, the uncertainty in the slope may be obtained using the procedure in Appendix XI.

10.4 The following definitions apply to 10.2-10.9:

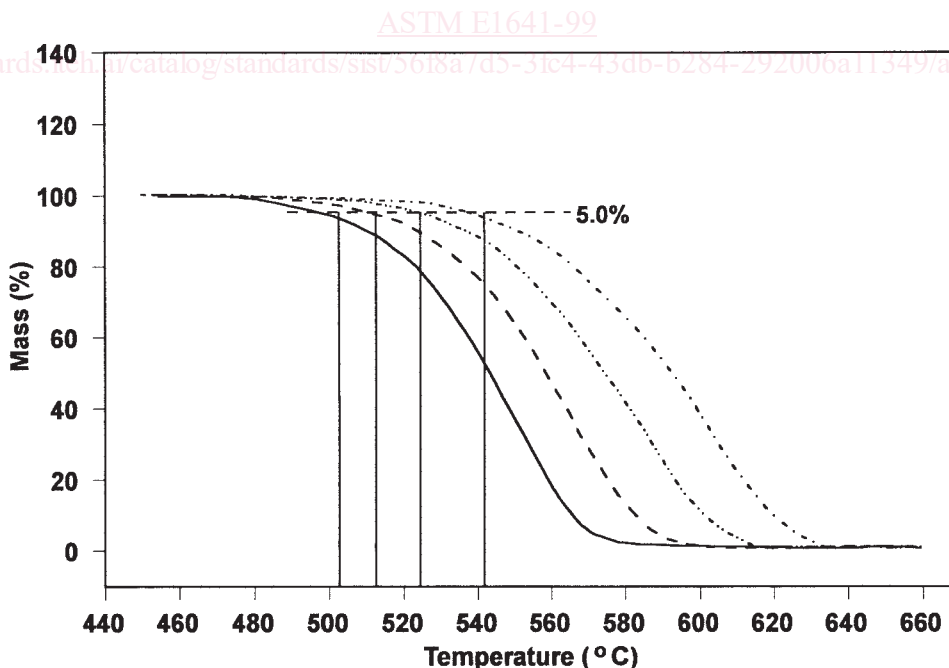


FIG. 1 Examples of Mass Loss Curves at the Following Heating Rates: 1°C/min, 2°C/min, 5°C/min, 10°C/min