



Designation: E698 – 16

Standard Test Method for Kinetic Parameters for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method¹

This standard is issued under the fixed designation E698; 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.

INTRODUCTION

The kinetics of exothermic reactions are important in assessing the potential of materials and systems for thermal explosion. This test method provides a means for determining Arrhenius activation energies and pre-exponential factors using differential thermal methods. This test method is to be used in conjunction with other tests to characterize the hazard potential of chemicals.

1. Scope*

1.1 This test method covers the determination of the overall kinetic parameters for exothermic reactions using the Flynn/Wall/Ozawa method and differential scanning calorimetry.

1.2 This technique is applicable to reactions whose behavior can be described by the Arrhenius equation and the general rate law.

1.3 *Limitations*—There are cases where this technique is not applicable. Limitations may be indicated by curves departing from a straight line (see 11.2) or the isothermal aging test not closely agreeing with the results predicted by the calculated kinetic values. In particular, this test method is not applicable to reactions that are partially inhibited. The technique may not work with reactions that include simultaneous or consecutive reaction steps. This test method may not apply to materials that undergo phase transitions if the reaction rate is significant at the transition temperature.

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 may involve hazardous materials, operations, and equipment. 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.*

¹ This test method is 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. Referenced Documents

2.1 *ASTM Standards*:²

E473 Terminology Relating to Thermal Analysis and Rheology

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters

E1142 Terminology Relating to Thermophysical Properties

E1231 Practice for Calculation of Hazard Potential Figures of Merit for Thermally Unstable Materials

E1445 Terminology Relating to Hazard Potential of Chemicals

E1860 Test Method for Elapsed Time Calibration of Thermal Analyzers

E1970 Practice for Statistical Treatment of Thermoanalytical Data

E2890 Test Method for Kinetic Parameters for Thermally Unstable Materials by Differential Scanning Calorimetry Using the Kissinger Method

3. Terminology

3.1 Technical terms used in this test method are defined in Terminologies E473, E1142, and E1445 including *activation energy, Arrhenius equation, Celsius, differential scanning calorimetry, enthalpy, general rate law, Kelvin, kinetics, peak value, pre-exponential factor, reaction, reaction order, and temperature.*

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.

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

4. Summary of Test Method

4.1 A specimen is placed in a suitable container and positioned in a differential scanning calorimeter (DSC).

4.2 The temperature surrounding the specimen is increased at a linear rate and any exothermic reaction peaks recorded.

4.3 Steps 4.1 and 4.2 are repeated for several heating rates in the range from 1 to 10 K min⁻¹.

4.4 Temperatures at which the reaction peak maxima occur are plotted as a function of their respective heating rates.

4.5 Kinetic values calculated from the peak temperature-heating rate relationship are used to predict a reaction half-life at a selected temperature.

4.6 A specimen is aged at the selected temperature for the predicted half-life time.

4.7 The aged specimen is temperature programmed in a differential scanning calorimeter and its reaction peak area compared with that for an unaged sample run under the same conditions.

4.8 If the normalized area for the aged specimen is approximately half that for the unaged sample, the kinetic values are confirmed for the temperature selected.

5. Significance and Use

5.1 The kinetic parameters combined with the general rate law and the reaction enthalpy can be used for the determination of thermal hazard using Practice E1231 (1).³

6. Apparatus

6.1 *General*—The equipment used in this test method should be capable of displaying quantitative changes of enthalpy as a function of time (*t*) or temperature (*T*), should be linearly programmable and have the capabilities of subjecting the sample cell to different atmospheres. The heat sensing element should be external to the sample.

6.2 *Differential Scanning Calorimeter (DSC)*:

6.2.1 A test chamber composed of:

6.2.1.1 A *furnace*, to provide uniform controlled heating (cooling) of a specimen and reference to a constant temperature or at a constant rate within the applicable temperature range of this test method.

6.2.1.2 A *temperature sensor*, to provide an indication of the specimen/furnace temperature to ± 0.1 K.

6.2.1.3 A *differential sensor*, to detect a difference in heat flow between the specimen and reference equivalent to 10 μ W.

6.2.1.4 A means of sustaining a *test chamber environment*, of an inert purge gas at a rate of 10 – 50 mL/min.

NOTE 1—Typically, 99+ % pure nitrogen, argon, or helium are employed when oxidation in air is a concern. Unless effects of moisture are to be studied, use of dry purge gas is recommended; especially for operation at subambient temperature.

6.2.2 A *temperature controller*, capable of executing a specific temperature program by operating the furnace(s)

between selected temperature limits at a rate of temperature change between 0.5 and 10 K/min constant to ± 0.1 K/min or at an isothermal temperature constant to ± 0.1 K.

6.2.3 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 differential scanning calorimetry are heat flow, temperature, and time.

6.3 *Containers (pans, crucibles, vials, etc.)*, which are inert to the specimen and reference materials and which are suitable structural shape and integrity to contain the specimen and reference in accordance with the specific requirements of this test method.

6.4 A *balance*, with a capacity of at least 100 mg, to weigh specimens or containers (pans, crucibles, vials, etc.) to within 10 μ g.

6.5 Auxiliary equipment useful for conducting this test method below ambient temperature.

6.5.1 A *coolant system*, which can be directly coupled with the controller to the furnace to hasten its recovery from elevated temperatures, to provide constant cooling rates, or to sustain an isothermal subambient temperature, or a combination thereof.

7. Safety Precautions

7.1 The use of this test method on materials whose potential hazards are unknown requires that precaution be taken during sample preparation and testing.

7.2 Where particle size reduction by grinding is necessary, the user of this test method should presume that the material is dangerous.

7.3 Toxic or corrosive effluents, or both, may be released when heating the material and could be harmful to the personnel or the apparatus. Use of an exhaust system to remove such effluents is recommended.

8. Sampling

8.1 Specimen size is kept small to minimize temperature gradients within the sample. In general, a sample mass resulting in a maximum heat generation of less than 8 mJ/s (8 mW) is satisfactory.

8.2 Specimens shall be representative of the material being studied and should be prepared to achieve good thermal contact between sample and container (see Figs. 1 and 2).

8.3 The specimen container should be nonreactive with the sample or reaction products.

8.4 The reference for the sample is normally an empty container or one filled with inert material.

8.5 Specimens which have appreciable volatility over the temperature range of interest may require sealing in hermetic containers or a high-pressure cell, or both, to prevent vaporization interference and weight loss of unreacted material.

8.6 The specimen atmosphere should closely represent the conditions of usage.

³ The boldface numbers in parentheses refer to the list of references at the end of this standard.

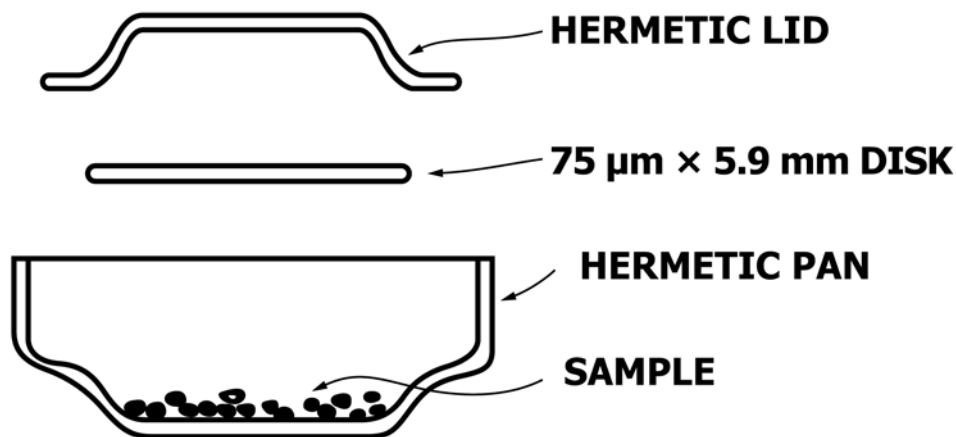


FIG. 1 Arrangement for Good Sample Contact with Container

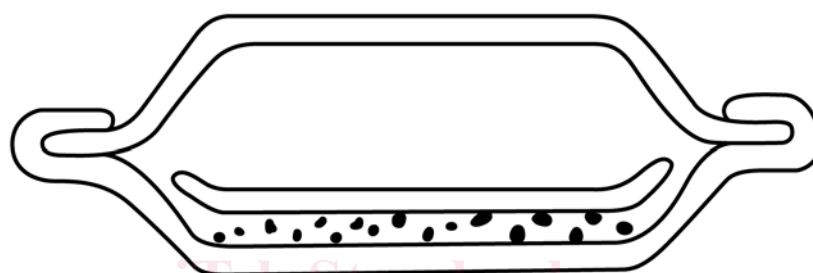


FIG. 2 Specimen Pan Collapsed and Collected

9. Calibration

9.1 Perform any calibration procedures recommended by the manufacturer as described in the operator's manual.

9.2 Calibrate the heat flow and elapsed time signals using Practice E968 and Test Method E1860, respectively, using the same type of specimen container to be used in the subsequent kinetic tests.

9.3 Calibrate the temperature signal at 10 K/min using Practice E968 and Test Method E1860, respectively, using the same type of specimen container to be used in the subsequent kinetic tests.

9.4 Determine the temperature calibration corrections for other heating rates by programming a sharply melting standard (for example, pure indium metal) at these heating rates and observing the deviation of the known melt temperature as a function of the rate.

NOTE 2—This table of temperature calibration correction values, once determined for a particular apparatus and specimen container, may be used for subsequent experiments following temperature calibration at 10 K/min heating rate in 9.3.

9.5 The thermal resistance of the instrument sample cell is determined by measuring the temperature lag observed for the melting of a pure metal standard. See Fig. X1.2 in Appendix X1.

10. Procedure

10.1 Perform an initial experiment using a specimen of 5 mg or less to determine proper specimen sizes and starting temperatures.

10.2 Place the specimen and reference materials in the instrument heating unit. Use a specimen size as recommended in 8.1.

10.3 Heat the specimen at 10 K/min from a point starting at least 50 K below the first observed exothermic peak deflection.

10.4 Record the differential heat flow signal as a function of temperature. Continue heating until the peak maximum of interest is recorded.

10.5 Repeat 10.2 – 10.4 for various heating rates between about 1 and 10 K/min.

NOTE 3—A minimum of four determinations at heating rates between 1 and 10 K/min are recommended.

NOTE 4—Reaction curve baselines should be level to minimize slope error in peak maxima measurements.

11. Calculation

11.1 Temperatures of reaction peak maxima are corrected for temperature scale nonlinearity, heating rate changes, and thermal lag as in the example in Appendix X1.

11.2 Plot $\log_{10} \beta$ (heating rate, K min⁻¹) versus $1/T$, where T is the corrected peak maximum temperature in Kelvin. Calculate and construct a least squares “best fit” line through these points (see Practice E1970). The slope of this “best fit” line is taken as the value for $d \log_{10} \beta / d(1/T)$.

11.3 Calculate an approximate value for E (activation energy) as follows (2):

$$E \cong -2.19R [d \log_{10} \beta / d(1/T)] \quad (1)$$

where R = gas constant (=8.314 J mol⁻¹ K⁻¹).

11.4 Refine value of E by:

11.4.1 Calculate E/RT approximately.

11.4.2 Find corresponding value of D from **Table X2.1**.

11.4.3 Calculate new value for E as follows:

$$E = (-2.303R/D)[d \log_{10} \beta/d(1/T)] \quad (2)$$

Refining the value of E a second time usually results in a close approach to its final value. An alternative calculation method is shown in **Appendix X3**.

11.5 The pre-exponential factor can be calculated as follows under the assumption of a first-order reaction:

$$Z = \beta E e^{E/RT}/RT^2 \quad (3)$$

where:

β = a heating rate from the middle of the range.

11.6 For the confirming isothermal test, calculate k for various temperatures from the Arrhenius equation and the above E and Z values.

11.7 From $t = 0.693/k$, calculate aging times (t) for each temperature.

11.8 Select a temperature requiring at least 1-h aging time, and age the sample isothermally for the calculated half-life in a thermal instrument or other facility capable of ± 1 K control. Quench immediately to some temperature at least 50 K below the aging temperature so that no significant reaction occurs during subsequent holding time.

11.9 Heat the aged specimen in a thermal instrument and record its reaction peak and determine temperature.

11.10 Heat a similar but unaged specimen in the same way and record its reaction peak and determine temperature.

11.11 On an equal mass basis, the peak area or displacement from baseline of the aged specimen shall be approximately one half that of the unaged sample. If so, the reaction kinetics are confirmed for the temperature range explored.

12. Report

12.1 The report shall include the following:

12.1.1 Identification of the sample by name or composition, stating the source, past history, and weight of each specimen together with its purity (if available).

12.1.2 Description of apparatus and type of container used.

12.1.3 Identification of specimen environment as to degree of confinement, composition of atmosphere, and whether the atmosphere is static, self-generated, or dynamic through or over the sample.

12.1.4 Description of test conditions, including the heating rates and peak temperature range investigated.

12.1.5 The specific dated version of this test method.

13. Precision

13.1 An interlaboratory study (ILS) was conducted in 2000 involving participation by eight laboratories using apparatus

from three manufacturers and six instrument models. Each laboratory characterized trityl azide (azidotriphenylmethane) at five heating rates. The ILS results were treated by Practice **E691** and Practice **E1970**. The results of this interlaboratory study are on file at ASTM Headquarters.⁴

13.2 Precision:

13.2.1 Within laboratory variability may be described using the repeatability value (r) obtained by multiplying the repeatability standard deviation by 2.8. The repeatability value estimates the 95 % confidence limit. That is, two within laboratory results should be considered suspect if they differ by more than the repeatability value (r).

13.2.1.1 The pooled repeatability relative standard deviation for activation energy (E) was 3.7 %.

13.2.1.2 The pooled repeatability relative standard deviation for logarithm of the pre-exponential factor was 4.1 %.

13.2.2 Between laboratory variability may be described using the reproducibility value (R) obtained by multiplying the reproducibility standard deviation by 2.8. The reproducibility value estimates the 95 % confidence limit. That is, two between laboratory results should be considered suspect if they differ by more than the reproducibility value (R).

13.2.2.1 The relative reproducibility standard deviation for activation energy was 6.5 %.

13.2.2.2 The relative reproducibility standard deviation for logarithm of the pre-exponential factor was 8.4 %.

13.3 Bias:

13.3.1 Bias is the difference between a test result and an accepted reference value. There is no accepted reference value for activation energy or logarithm of the pre-exponential factor for trityl azide. Therefore, no bias information can be provided.

13.3.2 The mean value for the activation energy and logarithm of the pre-exponential factor were observed to be:

$$E = 145 \text{ kJ/mol}$$

$$\text{Ln } [Z(\text{min}^{-1})] = 35.1$$

13.3.3 Bias of the kinetic constants may be checked by an isothermal aging procedure (such as a 60 minute test at a temperature determined from the kinetic parameters to yield a 50 % reaction conversion in 60 minutes). A difference of less than 10 % relative between predicted and observed results is considered a confirmation of the kinetic values determined.

14. Keywords

14.1 Arrhenius kinetic parameters; differential scanning calorimetry; hazard potential; kinetics; thermal analysis; thermal hazard; thermal stability

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E27-1002. Contact ASTM Customer Service at service@astm.org.