



# Standard Test Method for Heat of Reaction of Thermally Reactive Materials by Differential Scanning Calorimetry<sup>1</sup>

This standard is issued under the fixed designation E2160; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method determines the exothermic heat of reaction of thermally reactive chemicals or chemical mixtures, using milligram specimen sizes, by differential scanning calorimetry. Such reactive materials may include thermally unstable or thermoset materials.

1.2 This test method also determines the extrapolated onset temperature and peak heat flow temperature for the exothermic reaction.

1.3 This test method may be performed on solids, liquids or slurries.

1.4 The applicable temperature range of this method is 25 to 600°C.

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 There is no ISO method equivalent to this standard.

1.7 This standard is related to Test Method E537 and to NAS 1613, but provides additional information.

1.8 *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.*

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

E473 Terminology Relating to Thermal Analysis and Rheology

<sup>1</sup> 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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<sup>2</sup> 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.

E537 Test Method for The Thermal Stability of Chemicals by Differential Scanning Calorimetry

E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

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

E1860 Test Method for Elapsed Time Calibration of Thermal Analyzers

2.2 *Other Standard:*

NAS 1613 Seal Element, Packing, Preformed, Ethylene Propylene Rubber, National Aerospace Standard, Aerospace Industries Association of America, 1725 DeSales St., NM, Washington, DC 20036

## 3. Terminology

3.1 Specific technical terms used in this standard are defined in Terminologies E473 and E1142.

## 4. Summary of Test Method

4.1 A small (milligram) quantity of the reactive material is heated at 10°C/min through a temperature region where a chemical reaction takes place. The exothermic heat flow produced by the reaction is recorded as a function of temperature and time by a differential scanning calorimeter. Integration of the exothermic heat flow over time yields the heat of reaction. If the heat flow is endothermic, then this test method is not to be used.

4.2 The test method can be used to determine the fraction of a reaction that has occurred in a partially reacted sample. The heat of reaction is determined for a specimen that is known to be 100 % unreacted and is compared to the heat of reaction determined for the partially reacted sample. Appropriate calculation yields the fraction of the latter sample that was unreacted.

4.3 Subtracting the reaction fraction remaining from unity (1) yields the fraction reacted. The fraction reacted may be expressed as percent. If the sample tested is a thermoset resin, the percent reacted is often called the percent of cure.

4.4 The extrapolated onset temperature and peak heat flow temperature are determined for the exothermic heat flow thermal curve from 4.1.

## 5. Significance and Use

5.1 This method is useful in determining the extrapolated onset temperature, the peak heat flow temperature and the heat of reaction of a material. Any onset temperature determined by this method is not valid for use as the sole information used for determination of storage or processing conditions.

5.2 This test method is useful in determining the fraction of a reaction that has been completed in a sample prior to testing. This fraction of reaction that has been completed can be a measure of the degree of cure of a thermally reactive polymer or can be a measure of decomposition of a thermally reactive material upon aging.

5.3 The heat of reaction values may be used in Practice E1231 to determine hazard potential figures-of-merit Explosion Potential and Shock Sensitivity.

5.4 This test method may be used in research, process control, quality assurance, and specification acceptance.

## 6. Apparatus

6.1 *Differential Scanning Calorimeter (DSC)*, capable of measuring and recording heat flow as a function of temperature and time. Such a DSC is composed of:

6.1.1 *Test Chamber*, composed of:

6.1.1.1 *Furnace(s)*, to provide uniform controlled heating of a specimen and reference to a constant temperature or at a constant rate within the temperature range of 25 to 600°C.

6.1.1.2 *Temperature Sensor*, to provide an indication of the specimen or furnace temperature to within  $\pm 0.5^\circ\text{C}$ .

6.1.1.3 *Differential Sensor*, to detect a heat flow difference between the specimen and reference equivalent to 0.2 mW.

6.1.1.4 *Means of Sustaining a Test Chamber Environment*, of inert (for example, nitrogen, helium or argon) or reactive (for example, air) gas at a purge rate of  $50 \pm 5$  mL/min.

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

6.1.1.5 *Temperature Controller*, capable of executing a specific temperature program by operating the furnace(s) between selected temperature limits (ambient temperature to 600°C) at a heating rate between 2 and 20°C/min constant to within  $\pm 0.1^\circ\text{C}/\text{min}$ .

6.1.1.6 *Recording Device*, capable of recording and displaying any portion (including signal noise) of the differential heat flow on the ordinate as a function of temperature or time on the abscissa.

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

6.3 *Balance*, with a capacity of 100 mg or greater to weigh specimens and containers, or both, to a sensitivity of  $\pm 1$   $\mu\text{g}$ .

## 7. Safety Precautions

7.1 The use of this test method for materials of unknown potential hazards requires that precautions be taken during the sample preparation and testing.

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

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

## 8. Calibration

8.1 Perform any calibration procedures recommended by the apparatus manufacturer as described in the Operations Manual.

8.2 Calibrate the temperature signal to within  $\pm 2^\circ\text{C}$  using Practice E967.

8.3 Calibrate the heat flow signal to within  $\pm 0.5$  % using Practice E968.

8.4 Calibrate the elapsed time signal, or ascertain its accuracy, to within  $\pm 0.5$  % using Test Method E1860.

## 9. Procedure

9.1 Into a tared sample container, weigh to within  $\pm 1$   $\mu\text{g}$ , 1 to 2 mg of the test specimen. Record this mass as  $M$  in mg. Close the sample. Weigh the sealed container to within  $\pm 1$   $\mu\text{g}$  and recorded this mass as  $N$  in mg.

NOTE 2—Because of the reactive nature of the materials examined by this method, small specimen sizes shall be used unless the approximate reactivity of the test specimen is known. Other specimen sizes may be used but shall be reported. Make sure that the specimen is homogenous and represents the sample.

NOTE 3—Some substances may have non-reactive components mixed with the thermally reactive material. An example would be reinforcing fibers mixed with a thermally-curing polymer. A specification of the fraction of inert material in the mixture may accompany these materials. The user should be aware that such specifications involve tolerances so that the actual fraction of inert material may vary within these tolerances from lot to lot. In such cases, the actual fraction of inert material must be taken into account.

NOTE 4—For highly reactive materials, the selection of sample containers can be particularly important. The material from which the container is constructed may catalyze the reaction or react with the sample material. Sealed containers may cause an autocatalytic effect or possibly a pressure effect. In open containers loss of material, and thereby loss of heat, could be an issue. Excessive pressurization of a sample container can be avoided by using vented containers, however, vented or unsealed containers may cause the measured heat of reaction to be much smaller than the true value. see 12.4 for an example of such an effect.

9.2 Heat the test specimen at a controlled rate of  $10 \pm 0.1^\circ\text{C}/\text{min}$  from ambient until the thermal curve returns to baseline following the exothermic event. If the upper limit of temperature for this method, 600°C, is reached before the thermal curve returns to baseline, then this method is not applicable.

NOTE 5—Other heating rates may be used but shall be reported.

9.3 Cool the test specimen to ambient temperature upon completion of the experiment.

9.4 Reweigh the sample container. Compare this mass of the sealed sample container weight with  $N$  determined in 9.1. Report any specimen weight loss observed.

9.5 Construct a line connecting the baseline before the exothermic reaction to that after the reaction (see Fig. 1).

NOTE 6—For highly energetic reactions, a significant change may occur in the baseline prior to and following the exothermic reaction, due to a significant change in the heat capacity of the reacted material in the sample container. Such an instance might be handled by the construction of a baseline that is not a straight line. If a nonlinear baseline (for example, a sigmoidal baseline) is used it should be stated in the report and an example of the constructed baseline and the thermal curve should be included also.

9.6 Integrate the area, as a function of time, bounded by the thermal curve and the baseline constructed in 9.5. Record this area as the heat of the reaction ( $A$ ) in mJ.

NOTE 7—The area bounded by the thermal curve and the constructed baseline gives the heat of the reaction. Instrument software is most often used to integrate this area. Although such software packages display thermal curves as in Fig. 1, they calculate the bound area on a basis of time. If older instruments without these software packages are used, or if manual checks are performed on newer instruments, then the manual integration must be performed with the abscissa presented as a time (seconds) coordinate.

NOTE 8—The amount of material should be chosen such that the maximum heat flow is less than 8 mW. This requirement reduces the potential of obtaining adiabatic heating of the sample. Adiabatic heating of the sample results in “leaning” peaks, an example of which is shown in Fig. 2 (adapted from Figure 11 of Jones (1996)).<sup>3</sup> For highly energetic materials, it might be impossible to satisfy simultaneously the direction of 9.1 (using 1 to 2 mg of the test specimen) and the condition of this note (maximum heat flow less than 8 mW). If heat flow is larger than 8 mW and the peak is not “leaning”, it should not be necessary to reduce sample mass. Or, in other words, when both directions cannot be met

simultaneously, sample mass need be reduced only if the observe peak leans.

9.7 Construct a tangent to the leading edge of the exothermic peak at the point of maximum rate of change and extrapolate that tangent to the baseline constructed in 9.5. Record the intersection of the tangent with the baseline as the onset temperature ( $T_o$ ).

NOTE 9—In some cases, reactions may have induction periods or other effects that are manifested as exothermic deviations from the established baseline well before the onset temperature obtained by 9.7. Because of the importance of these effects for highly reactive materials, an additional onset temperature, the temperature of first deviation ( $T_f$ ), is to be reported also. The temperature of first deviation is the temperature for which the thermal curve first deviates from the established baseline. The temperature of first deviation is to be noted in the report.

NOTE 10—Peak temperatures from two different determinations are comparable only if the same conditions were used for both measurements, for example, sample mass and vent diameter.

9.8 Record the temperature at the maximum deflection from the baseline constructed in 9.5 as the peak temperature ( $T_p$ ).

## 10. Calculations

10.1 The normalized heat of reaction is calculated by dividing the heat of reaction ( $A$ ) from 9.6 by the specimen mass ( $M$ ) from 9.1:

$$H = A/M$$

10.2 Performing this test on a test specimen that is completely unreacted, produces, by 10.1, the total heat of reaction for this sample ( $H_t$ ).

10.3 The fraction of sample reacted is calculated by:

$$\text{fraction reacted} = (H_t - H) 100\% / H_t = (1 - H/H_t) 100\%$$

10.3.1 For a thermoset resin, the Degree of Cure ( $DC$ ) is the fraction reacted:

$$DC = \text{fraction reacted} = (H_t - H) 100\% / H_t = (1 - H/H_t) 100\%$$

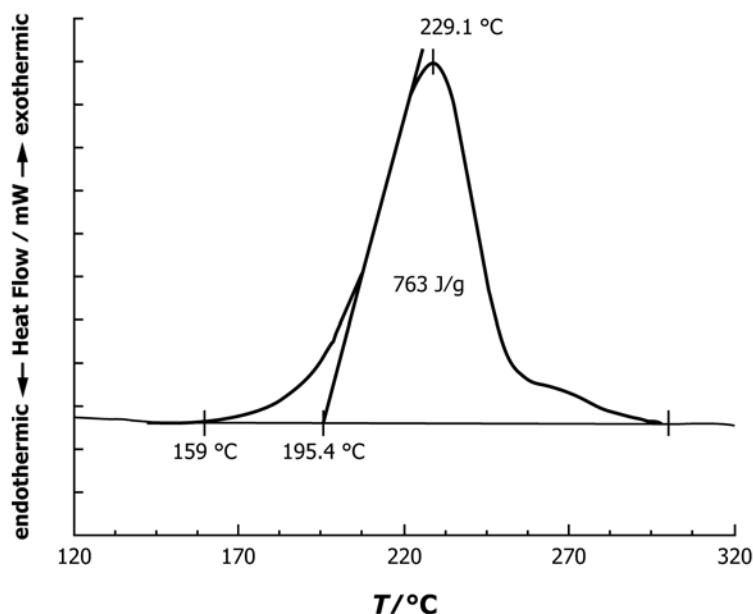


FIG. 1 Thermal Curve, Determination of Reported Values

<sup>3</sup> Jones, D.E.G., and Augsten R.A., “Evaluation of Systems for Use in DSC Measurements on Energetic Materials,” *Thermochimica Acta*, Vol 286, 1996, pp. 355–373.

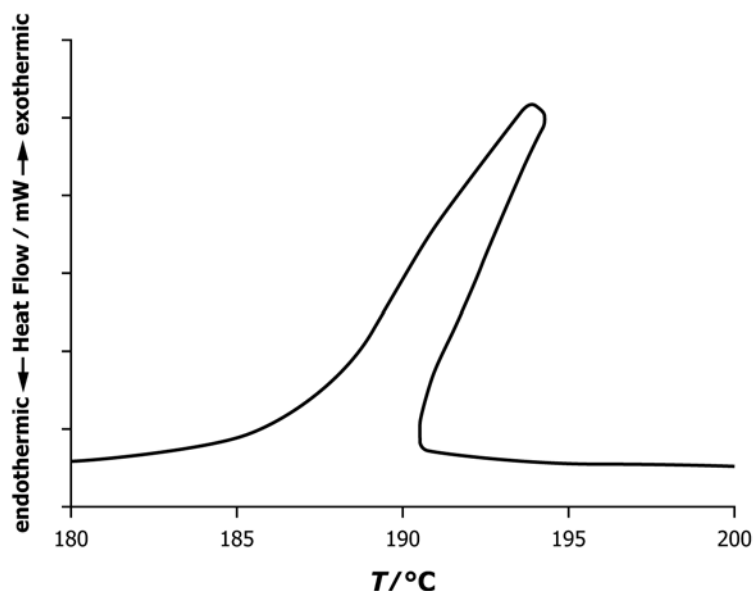


FIG. 2 Example of a Leaning Thermal Curve Resulting From Too Much Material in the Sample Pan

## 11. Report

11.1 Report the following information:

11.1.1 The identification of the sample characterized.

11.1.2 The DSC apparatus by manufacturer and model number.

11.1.3 The heating rate, temperature range, purge gas type and rate and specimen container type and material used.

11.1.4 The extrapolated onset temperature ( $T_o$ ), the peak temperature ( $T_p$ ), the temperature of first deviation ( $T_f$ ), and the normalized heat of reaction ( $H$ ).

11.1.5 If appropriate or desired, report the fraction reacted or the degree of cure ( $DC$ ) of the reaction.

11.1.6 Any specimen weight loss observed.

11.1.7 The specific dated version of this method used.

## 12. Precision and Bias

12.1 The precision of this test method was determined in an interlaboratory investigation. The interlaboratory study was conducted in two part. The first part determined the precision of the test method and the second part examined interlaboratory differenced from confounding variables. the results of this interlaboratory study are on file at ASTM Headquarters.<sup>4</sup>

12.2 The first part of the interlaboratory study included 8 laboratories, each of which reported five replicates of the heat of reaction, the peak temperature, and the onset temperature for the thermal decomposition of 1-phenyl-1H-tetrazole-5-thiol. Three models of instrument were used among the eight laboratories. Two laboratories used high-pressure sample containers that showed little or no mass loss during the measurements. Five laboratories used hermetically sealed aluminum sample containers and one laboratory used Hastelloy sample

containers. The hermetically sealed containers sometimes leaked gaseous material during or after the measurement. A significant correlation of heat of reaction with mass loss was not observed. The following criteria should be used for judging the acceptability of measured results.

12.2.1 *Repeatability (Single Analyst)*—The coefficient of variation of results for the heat of reaction was 5.3 %, for the peak temperature was 0.94K, and for the onset temperature was 0.81 K, with 39 degrees of freedom for each. Two average heat of reaction values should be considered suspect (95 % confidence interval) if the heats of reaction differ by 14.8 %. Two average peak temperatures should be considered suspect (95 % confidence interval) if the temperatures differ by 2.6 K. Two average onset temperatures should be considered suspect (95 % confidence interval) if the temperatures differ by 2.3 K.

12.2.2 *Reproducibility*—The coefficient of variation of results fro the heat of reaction was 7.4 %, for the peak temperature was 1.68 K, and for the onset temperature was 1.87 K. Two average heat of reaction values should be considered suspect (95 % confidence interval) if the heat of reaction differ by 20.7 %. Two average peak temperatures should be considered suspect (95 % confidence interval) if the temperatures differ by 4.7 K. Two average onset temperatures should be considered suspect (95 % confidence interval) if the temperatures differ by 5.2 K.

12.3 *Bias*—Bias information is not yet available for this method.

12.4 The second part of the interlaboratory study examined the effect of different sample containers on the measured quantities for a self-accelerating decomposition reaction. This part of the interlaboratory test used a commercially available sample of 2-butanone peroxide. Six laboratories reported results; two of the laboratories reported results with two different types of sample containers, which thus yielded a total of eight independent determinations. Three types of sample

<sup>4</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1030. Contact ASTM Customer Service at service@astm.org.

containers were used. Two studies used gold-plated high-pressure containers; two studies used sealed glass vessels, which also provided a high pressure seal; and four studies used hermetically sealed aluminum pans. Replicate numbers ranged from 3 to 9 for the independent studies. The coefficient of variation for the measured heats of reaction from the four laboratories that used high-pressure sample containers was 5.0 %, which is consistent with the precision statement of 12.2.1 and 12.2.2. Hermetically sealed aluminum containers lost significant masses in all replicates from three of the four independent studies that used this sample containers. The failure of the sample container seals allowed gaseous material to escape during the measurements and these determinations showed heats of reaction that were significantly smaller, as much as 55 % smaller, than the average heat of reaction that was obtained when using the high-pressure vessels. Significant

differences of temperatures of first deviation,  $T_f$ , were observed and these differences depended on the material of construction of the sample containers. Gold-plated vessels showed values of  $T_f$  that were 50 °C lower than those observed using glass vessels. Aluminum containers showed values of  $T_f$  that were intermediate to those observed in the gold and glass containers. The interlaboratory study with this peroxide material demonstrated that large effects on measure property may be caused by the selection of sample container. It is important to recognize the possibility of such effects when interpreting data obtained with this method.

### 13. Keywords

13.1 degree of cure; differential scanning calorimetry; hazard potential; heat of reaction; thermal analysis; thermoset

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