



Designation: E3174 – 22

Standard Practice for Determination of Kinetic Reaction Model Using Differential Scanning Calorimetry¹

This standard is issued under the fixed designation E3174; 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 practice describes a procedure for determining the “model” of an exothermic reaction using differential scanning calorimetry. The procedure is typically performed on 1 mg to 3 mg specimen sizes over the temperature range from ambient to 600 °C.

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

1.3 *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.*

1.4 *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:²

- E473 Terminology Relating to Thermal Analysis and Rheology
- E537 Test Method for Thermal Stability of Chemicals by Differential Scanning Calorimetry
- E698 Test Method for Kinetic Parameters for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method
- E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

¹ This practice 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 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.

- E968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters
- E1142 Terminology Relating to Thermophysical Properties
- E2070 Test Methods for Kinetic Parameters by Differential Scanning Calorimetry Using Isothermal Methods
- E2890 Test Method for Determination of Kinetic Parameters and Reaction Order for Thermally Unstable Materials by Differential Scanning Calorimetry Using the Kissinger and Farjas Methods
- E3142 Test Method for Thermal Lag of Thermal Analysis Apparatus

3. Terminology

3.1 *Definitions*—Technical terms used in this standard are provided in Terminologies E473 and E1142 including: calorimeter, Celsius, derivative, differential scanning calorimeter, extrapolated onset, Kelvin, reaction, reaction order, and temperature.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *autocatalytic, n*—a chemical reaction where one or more reaction products are a catalyst for the same reaction.

3.2.1.1 *Discussion*—An example of an autocatalytic model is:

$$d\alpha/dt = \alpha^m k(1 - \alpha)^n \quad (1)$$

where:

- α = the fraction reacted,
- t = time,
- k = the rate constant, and
- m and n = the reaction orders.

3.2.2 *autocatalytic model, n*—a kinetic model used to describe an autocatalytic reaction.

3.2.3 *exotherm, n*—in thermal analysis, the thermal record of a transition where heat is evolved by the specimen.

3.2.4 *model, kinetic, n*—a mathematical construct used to describe the rates of a chemical reaction.

3.2.5 *nth order, n*—a kinetic model in which the rate of reaction ($d\alpha/dt$) is proportional to the power of the current concentration of the reactant(s).

3.2.5.1 *Discussion*—An example of an n th order model is:

$$d\alpha/dt = k(1 - \alpha)^n \quad (2)$$

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

where:

- α = the fraction reacted,
- t = time,
- k = the rate constant, and
- n = the reaction order.

3.2.6 *rate constant (k), n*—a coefficient of proportionality relating the rate of a chemical reaction at a given temperature to a function of the reactant's concentration.

4. Summary of Practice

4.1 A scouting experiment is conducted at a constant heating rate to determine the overall exothermic profile of the chemical reaction. From this thermal curve, the temperature of maximum rate and the extrapolated onset (test) temperature are determined.

4.2 A fresh test specimen is heated at a slow rate through a small fraction of its reaction exotherm. The test specimen is then rapidly cooled to a temperature where the reaction rate goes to “zero” thereby “quenching” the reaction. The test specimen is again heated at a slow rate through the whole of the reaction exotherm. The shift or non-shift of the temperature of maximum rate indicates the reaction model.

5. Significance and Use

5.1 Information concerning the reaction model aids in the selection of the appropriate method (and test method) for evaluation of kinetic parameters. n th order reaction may be treated by isoconversion methods such as Test Methods E698 and E2890. Autocatalytic reactions are treated by Test Methods E2070.

5.2 This practice may be used in research, forensic analysis, trouble shooting, product evaluation, and hazard potential evaluation.

6. Apparatus

6.1 A *Differential Scanning Calorimeter (DSC)* consisting of:

6.1.1 A *test chamber* consisting of:

6.1.1.1 A *furnace* or *furnaces* to provide a uniform controlled heating of a test specimen and reference at a constant rate of 5 °C/min (± 1 %) from ambient temperature to 600 °C.

6.1.1.2 A *temperature sensor* to provide an indication of the specimen temperature readable to ± 0.1 °C.

6.1.1.3 A *differential sensor* to provide an indication of the difference in heat flow between the specimen and reference material to within ± 10 μ W.

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

NOTE 1—Typically 99+ % pure nitrogen, argon, or helium are employed.

6.1.3 A *temperature controller*, capable of executing a specific temperature program by operating the furnace(s) between selected temperature limits at a rate of 5 °C/min constant to ± 0.1 °C/min or at an isothermal temperature constant to ± 0.1 °C.

6.1.4 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.

6.1.5 *Containers (pans, crucibles, vials, etc.) and lids* that are inert to the specimen and reference materials and that are of suitable structure, shape and integrity to contain and seal the nominal 5-mg test specimen and reference.

6.2 A *balance*, with a capacity of at least 100 mg, to weigh specimens and/or containers to within ± 10 μ g.

6.3 A *cooling system*, to cool the chamber and the test specimen to ambient temperature at an initial rate of 50 °C/min or greater.

7. Hazards

7.1 This practice is applicable to thermally unstable materials, the potential hazards for which are unknown. This requires that caution be taken during sample preparation and testing. The user should avoid test specimens greater than 10 mg and be aware that sample size reduction techniques (such as grinding) that may cause localized heating.

7.2 Toxic or corrosive effluents, or both, may be released when heating the specimen that could be harmful to the user or the apparatus. Use of an exhaust system is recommended to remove such effluents.

8. Specimen Preparation

8.1 Specimens shall be representative of the sample being studied.

8.2 Specimen size shall be kept small to minimize temperature gradient within it. In general, a sample mass resulting in a maximum heat generation rate of less than 8 mW is satisfactory.

NOTE 2—A typical test specimen is 1 mg to 3 mg.

8.3 Specimens shall be placed in the containers so that good thermal contact is achieved between the specimen and container and sealed so that evolved gases are retained in the vicinity of the specimen.

8.4 Fig. 1 and Fig. 2 illustrate one acceptable specimen and container configuration.

8.5 The specimen container shall be inert (nonreactive) to the specimen or its reaction products.

8.6 The reference container is normally an empty container and lid.

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

9. Calibration

9.1 Perform any differential scanning calorimeter setup and calibration procedures described in the operations manual.

9.2 If not already performed, calibrate the temperature signal of the differential scanning calorimeter at 5 °C/min using Test Method E967 and the heat flow signal using Practice E968.

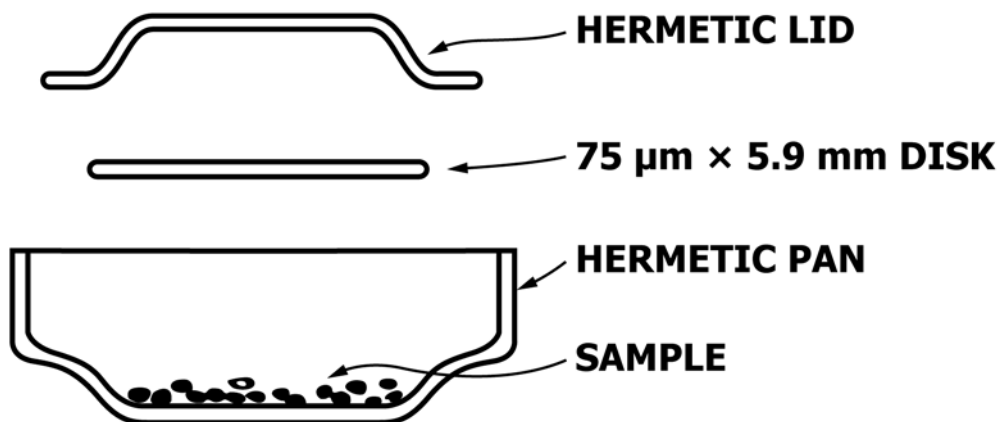


FIG. 1 Arrangement for Good Sample Contact with Container

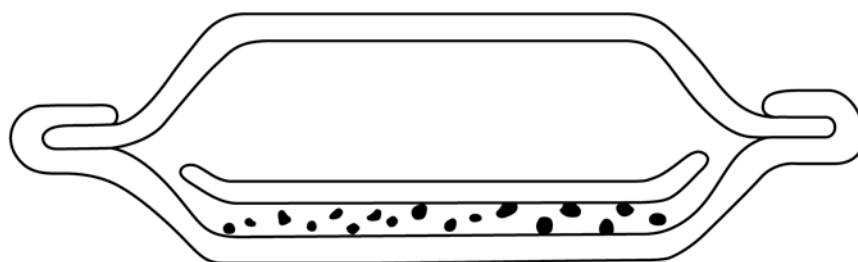


FIG. 2 Specimen Pan Sealed for Use

NOTE 3—Guide E3142 may be used to temperature calibrate at 5 °C/min apparatus previously calibrated at alternative heating rates.

10. Procedure—Scouting

10.1 Perform a scouting experiment to determine appropriate specimen mass (m_{\max}) and extrapolated onset temperature (T_o).

10.2 Weigh into a specimen container 5 mg or less of the test specimen. Record this mass as m_o . Seal the container.

10.3 Load the test specimen container and reference container into the differential scanning calorimeter and prepare it for operation.

10.4 Beginning at ambient temperature or, alternatively, at least 50 °C below the onset to the anticipated exothermic reaction onset, record the thermal curve, and heat the test specimen at 5 °C/min through its reaction exotherm until the reaction is complete as indicated by the heat flow returning to a constant value for a minimum of 2 min. Remove and discard the specimen and its container.

10.5 Prepare a display of the thermal curve with heat flow on the Y-axis and temperature on the X-axis (see Fig. 3).

10.6 Construct a baseline for the thermal curve by extrapolating forward the baseline before the appearance of the reaction exotherm.

10.7 Determine the heat flow (q) and temperature (T_{\max}) at the peak of the reaction exotherm measured from the extrapolated baseline of 10.6 (in Fig. 3, T_{\max} is identified as T_p).

10.8 Determine the maximum specimen size (m_{\max}) from Eq 3.

$$m_{\max} = 8 \text{ mW} \times m_o / q \quad (3)$$

NOTE 4—Eight milliwatts has been shown to be the maximum heat flow that does not produce specimen self-heating.^{3,4}

10.9 Using the thermal curve from 10.7, construct a tangent at the inflection point before the maximum heat flow rate on the leading edge of the exotherm. Extrapolate this tangent to the baseline constructed in 10.6. Determine the temperature corresponding to this intersection as the extrapolated onset temperature T_o .

11. Procedure—Model Determination

11.1 Weigh into a specimen container m_{\max} or less of the test specimen. Record this mass as m . Seal the container.

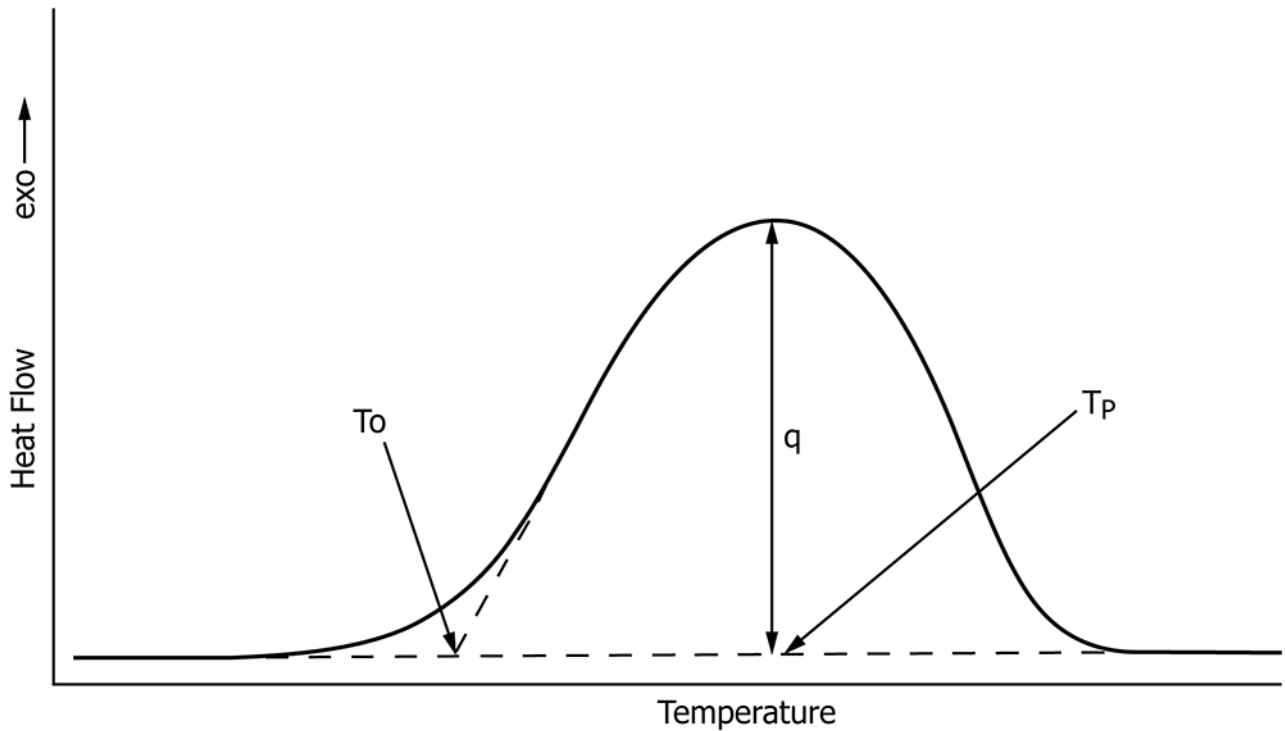
11.2 Load the test specimen container and reference container into the differential scanning calorimeter and prepare it for operation.

11.3 Beginning at ambient temperature or, alternatively, at least 50 °C below the onset to the anticipated exothermic reaction onset determined in 10.9, heat the test specimen at 5 °C/min to temperature T_o .

11.4 Immediately cool the test specimen at the maximum rate possible but at an initial rate greater than 50 °C/min to the initial temperature of 11.3.

³ Lyon, R. E., et al., "Thermokinetic Model of Sample Response in Nonisothermal Analysis," *Thermochimica Acta*, Vol 545, 2012, pp. 82–89.

⁴ Vyazovkin, S., "How Much is the Accuracy of Activation Energy Affected by Ignoring Thermal Inertia?," *International Journal of Chemical Kinetics*, Vol 52, 2020, pp. 23–27.



T_o = Extrapolated Onset temperature

T_p = Temperature at Peak Maximum

q = Peak heat flow

FIG. 3 Reaction Exotherm

11.5 While recording the thermal curve, immediately heat the test specimen at 5 °C/min through its reaction exotherm until the reaction is complete as indicated by the heat flow returning to a constant value for a minimum of 2 min. Remove and discard the specimen and its container.

11.6 Prepare a display of the thermal curve from 11.5 with heat flow on the Y-axis and temperature on the X-axis.

11.7 Construct a baseline for the thermal curve by extrapolating forward the baseline before the appearance of the reaction exotherm.

11.8 Determine the temperature (T_p) at the peak of the reaction exotherm measured from the extrapolated baseline of 10.7.

12. Interpretation of Results

12.1 Compare the values for T_{max} and T_p from 10.7 and 11.8. If T_p is approximately equal to or greater than T_{max} (that is, ± 3 °C), then the reaction under study is n th order. If the

value of T_p is less than T_{max} by more than 3 °C, then the reaction is autocatalytic.

NOTE 5—If in doubt whether the reaction is n th order or autocatalytic, treat the reaction as if it is autocatalytic. The kinetic equation for autocatalytic reactions reduces to that of n th order reaction as the exponent for the fraction reacted (α) in Eq 1 goes to zero.

NOTE 6—If the reaction model is determined to be n th order, then Test Method E2890, Section 12.5, may be used to estimate the value of n .

13. Report

13.1 Report the complete identification of the test material and its mass (m).

13.2 Report whether the model of the reaction is n th order or autocatalytic.

14. Keywords

14.1 autocatalytic; differential scanning calorimetry; DSC; kinetics