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Standard Test Method for Kinetic Parameters for Thermally Unstable Materials by Differential Scanning Calorimetry Using the Kissinger Method¹

This standard is issued under the fixed designation E2890; 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 of Arrhenius activation energy and pre-exponential factor using the Kissinger variable heating rate iso-conversion method (**1**, **2**)² and activation energy and reaction order by the Farjas method (**3**) for thermally unstable materials. The test method is applicable to the temperature range from 300 to 900 K (27 to 627°C).

1.2 Both n th order and accelerating reactions are addressed by this method over the range of $0.5 < n < 4$ and $1 < p < 4$ where n is the n th order reaction order and p is the Avrami reaction order (**4**). Reaction orders n and p are determined by the Farjas method (**3**).

1.3 This test method uses the same experimental conditions as Test Method E698. The Flynn/Wall/Ozawa data treatment of Test Method E698 may be simultaneously applied to these experimental results.

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 There is no ISO equivalent to 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *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 Recom-*

mendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:³

- E473 Terminology Relating to Thermal Analysis and Rheology
- E537 Test Method for The Thermal Stability of Chemicals by Differential Scanning Calorimetry
- E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
- E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers
- E968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters
- E698 Test Method for Kinetic Parameters for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method
- 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
- E1970 Practice for Statistical Treatment of Thermoanalytical Data
- E2041 Test Method for Estimating Kinetic Parameters by Differential Scanning Calorimeter Using the Borchardt and Daniels Method
- E2161 Terminology Relating to Performance Validation in Thermal Analysis and Rheology

3. Terminology

3.1 Technical terms used in this test method are defined in Terminologies E473, E1142, and E2161. Referenced terms include *Arrhenius equation*, *baseline*, *calibration*, *Celsius*,

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 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.

differential scanning calorimeter, endotherm, enthalpy, figure-of-merit, first-deviation-from baseline, full-width-at-half-maximum, Kelvin, onset point, peak, peak value, relative standard deviation, standard deviation, thermal analysis, and thermal curve.

4. Summary of Test Method

4.1 A series of test specimens are heated at a minimum of four different linear rates in a differential scanning calorimeter through a region of exothermic reaction behavior. The rate of heat evolution, created by a chemical reaction, is proportional to the rate of reaction and is measured as a function of temperature and time.

4.2 The temperature corresponding to the maximum rate of reaction (measured at the heat flow maximum of the exothermic reaction peak) is recorded at each linear heating rate. This observed temperature is corrected for instrument thermal resistance. Activation energy and pre-exponential factor are derived from the linear regression of the natural logarithm of the heating rate, normalized to the square of the absolute temperature, versus the reciprocal absolute temperature of heat flow at the peak maximum. The approach is known as the Kissinger method (1, 2).

4.3 A reaction type is determined for the specimen from the shape of the reaction exotherm under isothermal temperature conditions.

4.4 Once a reaction type is determined kinetic parameters of order (either n or p) are determined using the shape of the reaction exotherm measured by the time at full-width-at-half-maximum (t_{FWHM}). This approach is known as the Farjas method (3). The activation energy and reaction order are derived from the linear regression of the natural logarithm of the time at full-width-at-half-maximum versus the reciprocal of absolute temperature at maximum reaction rate (heat flow).

5. Basis of Methodology

5.1 For reactions that are exothermic in nature, the rate of heat evolution is proportional to the rate of the reaction. Differential scanning calorimetry measures the heat flow as the dependent experimental parameter versus temperature (or time) as the independent parameter.

5.2 Reactions may be modeled with a number of suitable equations of the form:

$$da/dt = k(T) f(\alpha) \quad (1)$$

where:

da/dt = reaction rate (s^{-1}),
 α = fraction reacted or conversion (dimensionless),
 $k(T)$ = specific rate constant at temperature T , and
 $f(\alpha)$ = conversion function (dimensionless).

Commonly used functions include:

$$f_1(\alpha) = (1 - \alpha)^n \quad (2)$$

$$f_2(\alpha) = p(1 - \alpha)[-\ln(1 - \alpha)]^{(p-1)/p} \quad (3)$$

where:

n = n th reaction order (dimensionless), and

p = Avrami reaction order (dimensionless).

NOTE 1—There are a large number of conversion function expressions for $f(\alpha)$ (5). Those described here are the more common ones but are not the only functions suitable for this method. Eq 2 is known as the Law of Mass Action (6) while Eq 3 is the Avrami equation (4).

5.3 The Arrhenius equation (7) describes how the reaction rate changes as a function of temperature:

$$k(T) = Ze^{-E/RT} \quad (4)$$

where:

Z = pre-exponential factor (s^{-1}),
 E = activation energy ($J mol^{-1}$),
 T = absolute temperature (K),
 R = gas constant ($8.314 J mol^{-1} K^{-1}$), and
 e = natural logarithm base (2.7182818).

5.4 Eq 1 and Eq 4 may be combined to yield the general rate equation:

$$da/dt = f(\alpha)Ze^{-E/RT} \quad (5)$$

5.5 As the temperature increases, the rate of reaction will increase until a maximum is reached and then the rate declines back to “zero” as the reactant is consumed. When the rate of reaction is displayed as a function of increasing temperature, the shape of this response is called a “peak”. The mathematical derivative of the reaction rate at the peak maximum equals zero. Taking the derivative of Eq 5 over time at the maximum point for the heating with constant rate β , then casting in logarithmic form and assuming that $\ln[d(f(\alpha))/dt]=0$, leads to Eq 6.

$$\ln[\beta/T_m^2] = \ln[Z R/E] - E/RT_m \quad (6)$$

where:

β = heating rate ($K s^{-1}$), and
 T_m = temperature at peak maximum (K).

NOTE 2—The assumption of $\ln[d(f(\alpha))/dt]=0$ holds strictly only for 1st order reaction but is considered a “reasonable” approximation for other n th order or Avrami reactions.

5.6 Eq 6 is of the form $Y=mX+b$. If $\ln[\beta/T_m^2]$ is set equal to Y and $1/T_m$ is set equal to X , then a display of Y versus X yields a slope (m_K) equal to $-E_K/R$ and an intercept (b_K) equal to $\ln[ZR/E_K]$ where Z and E_K are the pre-exponential factor and the activation energy, respectively, determined by the Kissinger method.

5.7 The shape of the reaction exothermic peak may be characterized by the time at full-width-at-half-maximum (t_{fwhm}) (3).

$$\ln[t_{FWHM}] = E_F/RT_m + \ln[t'/Z] \quad (7)$$

where:

t_{fwhm} = the full-width-at-half-maximum time (s), and
 t' = an arbitrary function (s^{-1}).

5.8 Eq 7 is of the form $Y=mX+b$. If $\ln[t_{FWHM}]$ is set equal to Y and $1/T_m$ is set equal to X , then a display of Y versus X yields a slope (m_F) equal to E_F/R and an intercept (b_F) equal to $\ln[t'/Z]$ where E_F is the activation energy determined by the Farjas method.

5.9 The reaction order, n or p , is determined through an empirical relationship based on t' .

6. Significance and Use

6.1 This test method is useful for research and development, quality assurance, regulatory compliance and specification-based acceptance.

6.2 The kinetic parameters determined by this method may be used to calculate thermal hazard figures-of-merit according to Practice E1231.

7. Interferences

7.1 This test method assumes a single reaction mechanism constant over the reaction conversion temperature range of the material under evaluation. Some overall reactions of interest are known to include a series of competing reaction mechanisms that lead to changes in reaction order with conversion (8). This method addresses the reaction only at a single conversion value at the maximum reaction rate—often about 0.7.

7.2 Method precision is enhanced with the selection of the appropriate conversion function [$f(a)$]. The shape of the thermal curve, as described in 11.2, may confirm the selection of the n th order or accelerating reaction models.

7.2.1 Typically n th reactions include many (but not all) decomposition reactions or those where one of the participating species is in excess.

7.2.2 Typical accelerating (Avrami) reactions include thermoset cure, crystallization, and some pyrotechnic reactions.

7.3 Since this method uses milligram quantities of material, it is essential for the test specimens to be homogeneous and representative of the larger sample from which they are taken.

7.4 A critical literature evaluation of kinetic methods reports that the Kissinger method is the most accurate method for determining activation energy in many cases (9).

8. Apparatus

8.1 *Differential Scanning Calorimeter (DSC)*—The essential instrumentation required to provide the minimum differential scanning calorimetric capability for this method includes (a) a furnace(s) to provide uniform controlled heating or cooling of a specimen and reference to a constant temperature or at a constant rate over the range of 300 K to 900 K, (b) a temperature sensor to provide a measurement of the specimen temperature to ± 0.01 K, (c) differential sensors to detect a heat flow difference between the specimen and reference with a range of 100 mW readable to $\pm 1\mu\text{W}$, (d) a means of sustaining a test chamber environment of inert purge gas at a purge rate of 10 to 100 mL/min within ± 5 mL/min, (e) a temperature controller, capable of executing a specific temperature program by operating the furnace(s) between selected temperature limits over the range of ambient to 900 K (627°C) at a rate of 0.1 to 20 K/min constant to 1 % or at an isothermal temperature constant to 0.1 K, (f) a data collection device, to provide a means of acquiring, storing, and displaying measured or calculated signals or both. The minimum output signals required are heat flow, temperature, and time.

8.2 *Containers* (pans, crucibles, vials, lids, closures, seals, etc.) that are inert to the specimen and reference materials (if

any) and that are of suitable structural shape and integrity to contain the specimen (even under internal pressure developed during the reaction) and reference in accordance with the specific requirements of this test method.

NOTE 3—Many users find glass, gold or gold coated hermetically sealed containers of low headspace volume advantageous for testing with high energy materials. The selected container shall meet the necessary internal pressure rating to withstand internal pressure buildup.

8.3 A means, tool or device to close, encapsulate or seal the container of choice.

8.4 *Analytical Balance* with a capacity of at least 100 mg to weigh specimens or containers, or both to ± 10 μg .

8.5 Auxiliary instrumentation considered useful but not essential for conducting this method would include *cooling capability* to hasten cooling to ambient temperature conditions at the end of the test.

9. Hazards

9.1 This test method is used to determine the properties of thermally reactive materials. The user of this test method shall use the smallest quantity of material (typically a few milligrams) needed to obtain the desired analytical results.

9.2 Special precautions shall be taken to protect personnel and equipment when the apparatus in use requires the insertion of specimens into a heated furnace. Typical special precautions include adequate shielding, ventilation of equipment and face and hand protection for users. A safety analysis prior to testing is recommended.

10. Calibration and Standardization

10.1 Perform any calibration procedures recommended by the manufacturer as described in the operator's manual to ensure that the apparatus is calibrated at each heating rate used.

10.2 Calibrate the heat flow signal using 99.99+ % indium, Practice E968, and the same type of specimen container to be used in the subsequent test for kinetic parameters.

10.3 Calibrate the temperature signal using 99.99+ % indium, Test Method E967, and the same type of specimen container and heating rates to be used in the subsequent test for kinetic parameters.

10.4 Calibrate the elapsed time signal using Test Method E1860.

10.5 Determine the thermal resistance (ϕ) from the leading edge slope ($S = \Delta q / \Delta T$) in (mW/K) of the indium melting endotherm as shown in Fig. 1 and 12.1.

11. Procedure

11.1 Scouting Experiment:

11.1.1 Using a 1 to 5 mg test specimen, weighed to a precision of ± 0.1 mg, perform a scouting experiment using Test Method E537 to determine the temperature of first-deviation-from baseline (T_o) and the heat of reaction (ΔH).

11.2 Determination of Reaction Type:

11.2.1 Weigh into a specimen container 1 to 5 mg of the test specimen, with a precision of ± 0.1 mg, and hermetically seal the container. DO NOT load the test specimen into the

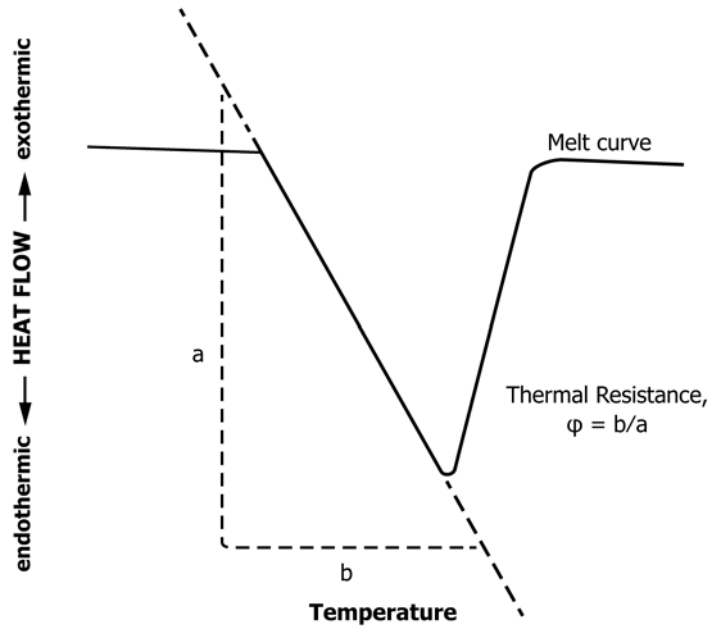


FIG. 1 Determination of Leading Edge Slope and Thermal Resistance

apparatus. Load an empty specimen container into the reference chamber. Close the *DSC* chamber and prepare the apparatus for an experimental run.

11.2.2 Select an isothermal test temperature corresponding to 10 % peak area (ΔH) from the scouting experiment performed in 11.1. Equilibrate the apparatus for 1 min at this test temperature.

11.2.3 Initiate the experiment, recording heat flow as a function of time.

11.2.4 Open the *DSC* sample chamber and quickly load the test specimen container into the apparatus. Immediately close the sample chamber. Record the thermal curve for 20 min or until the exothermic event is complete and the rate of heat flow approaches zero. (**Warning**—Burn hazard. The sample chamber, heat shield and covers present a burn hazard to the operator. Exercise great care in this operation. Protective safety

equipment (such as heat resistant gloves and face shield) shall be used to ensure the safety of the operator.)

11.2.5 Evaluate the shape of the resultant thermal curve and determine whether the reaction is *n*th order or autocatalytic. An *n*th order reaction is likely when the heat flow curve reaches a maximum within seconds after the specimen is loaded into the apparatus then slowly returns to baseline heat flow as shown in Fig. 2. An accelerating reaction is likely when heat flow builds to a maximum (after tens of seconds) and then decays, as shown in Fig. 3.

11.3 Procedure for Measuring Kinetic Parameters:

11.3.1 Weigh 1 to 5 mg of the test specimen to a precision of $\pm 10 \mu\text{g}$ into a tarred sample container and hermetically seal the container. Weigh the specimen and container to $\pm 10 \mu\text{g}$.

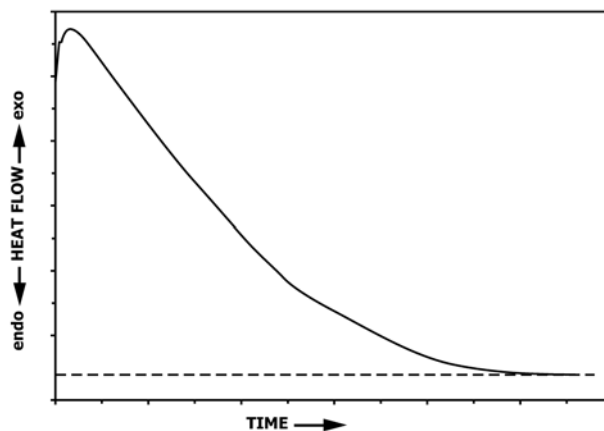


FIG. 2 Heat Flow Curve for an *n*th Order Reaction

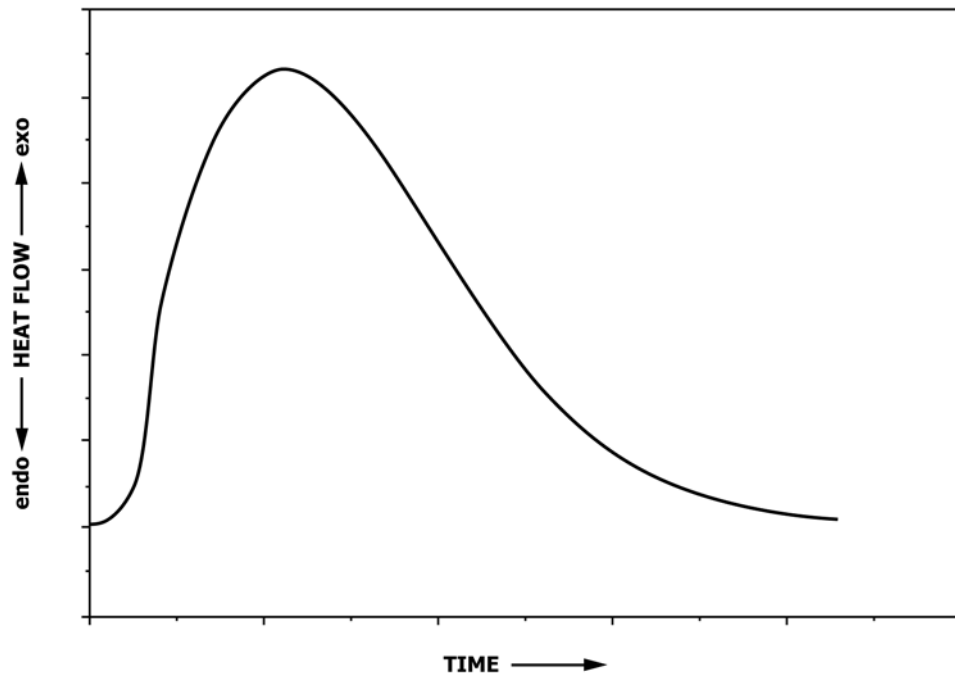


FIG. 3 Heat Flow Curve for an Accelerating Reaction

Load the test specimen into the apparatus. Prepare an equivalent empty, sealed specimen container for use as the reference container. Close the DSC sample chamber and prepare the apparatus for an experimental run.

11.3.2 Equilibrate the specimen for 1 min at a temperature (T_s); that is, 10 min below the first-deviation-from-baseline temperature (T_o) observed in 11.1.

NOTE 4—Starting temperature $T_s = T_o - (10 \text{ min} \times \beta)$ where β is the selected heating rate in K/min.

11.3.3 Heat the test specimen at a rate of 1 K min^{-1} to a temperature 10 min higher than the completion of the exothermic reaction as indicated by the return to baseline. Record the heat flow, time, and sample temperature throughout this region.

NOTE 5—If the heat flow at peak maximum is greater than 8 mW, discard the result and re-examine the material using a smaller specimen size. Specimens with heat flow greater than 8 mW may not be uniform in temperature and may produce erroneous results.

NOTE 6—Other heating rates may be used but shall have a maximum heat flow of less than 8 mW and shall be reported.

11.3.4 Cool the specimen container to ambient temperature and reweigh. Record and report any change in mass greater than 3 % as from the initial mass from 11.3.1.

11.3.5 Prepare a display of the heat flow on the ordinate (Y-axis) versus temperature on the abscissa (X-axis).

11.3.6 Construct a linear baseline under the reaction exotherm connecting a point on the baseline immediately before the reaction exotherm to a point on the baseline immediately after the reaction exotherm. Determine the temperature (T_i) and time (t_i) for the point on the baseline before the reaction and temperature (T_f) and time (t_f) for the point on the baseline after the reaction.

11.3.7 From the baseline, determine the temperature (T) value corresponding to the heat flow maximum of the reaction exotherm.

11.3.8 Correct the observed temperature (T) using Eq 9 and the thermal resistance (ϕ) value determined in 10.4 to determine T_m .

11.3.9 Determine the heating rate through the reaction using T_i , T_f , t_i , and t_f from 11.3.6 and Eq 10.

11.3.10 Display the reaction exotherm and baseline of 11.3.6 versus time on the X-axis.

NOTE 7—Modern differential scanning calorimeters may easily transform the thermal curve between temperature and time.

11.3.11 From the baseline, determine the heat flow (q_{max}) corresponding to the maximum of the reaction exotherm.

11.3.12 Determine the elapsed time between the leading and trailing edges of the reaction exothermic peak (t_{FWHM}) corresponding to the value of 0.5 of the maximum heat flow (q_{max}) as shown in Fig. 4.

11.3.13 Repeat steps 11.3.1 to 11.3.12 using at least three additional heating rates.

NOTE 8—A minimum of four determinations at heating rates typically between 1 and 10 K/min are recommended. Additional replicates or heating rates (up to eight) will improve precision of the determinations. Heating rates less than 1 K/min are more reliable for the determination of kinetic values.

11.4 Using the four (or more) results from 11.3.1 to 11.3.12, determine and report the Kissinger activation energy (E_K), and its standard deviation (σE_K), the logarithm of the pre-exponential factor ($\ln[Z]$), its standard deviation ($\sigma(\ln[Z])$), the Farjas activation energy (E_F), its standard deviation (σE_F), the reaction order (n or p) and its standard deviation (σ_n or σ_p) using the calculations of Section 12.

11.5 The values of E_K and E_F should be the same within the determined experimental error. If they are not, then the determination of E_F and/or reaction order n or p should be considered suspect.

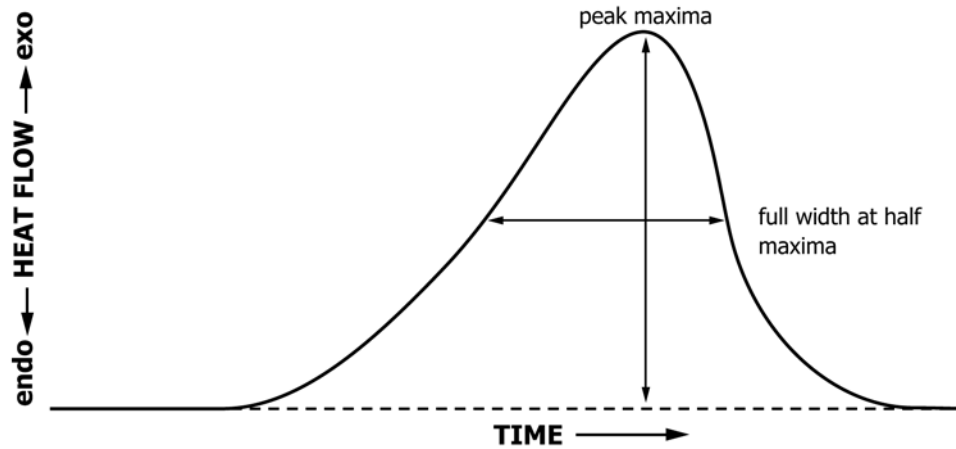


FIG. 4 Determination of the Time at Full-Width-at-Half-Maximum

12. Calculations

12.1 Determination of Thermal Resistance:

12.1.1 Prepare a display of the melting endotherm for the temperature calibration in 10.3 with heat flow on the ordinate (Y-axis) and temperature on the abscissa (X-axis) (see Fig. 1).

12.1.2 Determine the thermal resistance (ϕ) from the tangent to the point of greatest leading edge slope using Eq 8 (see Fig. 1).

$$\phi = \Delta T / \Delta q = 1/S \quad (8)$$

where:

ΔT = change in temperature (K),
 Δq = change in heat flow (mW),
 ϕ = thermal resistance (K/mW), and
 S = the leading edge slope (mW/K).

NOTE 9—The values of Δq and ϕ are negative due to the endothermic transition.

12.2 Correct Observed Peak Temperatures for Thermal Resistance:

12.2.1 Using the thermal curve obtained in 11.3, construct a linear baseline by connecting the two points before and after the reaction exotherm that first deviates from baseline. (See Fig. 4.)

12.2.2 Determine the maximum heat flow (q_{max}) on the reaction exotherm above the baseline.

12.2.3 Determine the temperature point (T) on the reaction exotherm that corresponds to the maximum heat flow above the baseline.

12.2.4 Correct the temperature point (T) using the thermal resistance from 12.1 and Eq 9 to determine T_m .

$$T_m = T + \phi q_{max} \quad (9)$$

NOTE 10—Since the value of ϕ is negative, the value for T_m will be less than T .

12.3 Determination of the Heating Rate (β) through the Reaction Exotherm:

12.3.1 Determine the heating rate (β) for each experiment in 11.3.1 to 11.3.12 using Eq 10.

$$\beta = (T_f - T_i) / (t_f - t_i) \quad (10)$$

12.4 Determination of Kissinger Activation Energy (E_K):

12.4.1 From the heating rate (β) experimental result from 11.3, and the corrected temperature from 12.2, determine the values for $\ln[\beta/T_m^2]$ and $1/T_m$ for each thermal (heating rate) curve obtained.

12.4.2 Prepare a display of $\ln[\beta/T_m^2]$ on the ordinate versus $1/T_m$ on the abscissa for each of the thermal curves in 11.3 corrected by 12.2.

NOTE 11—This display should demonstrate linearity. Otherwise Kissinger method is not applicable.

12.4.3 Using a least-squares (linear regression) method (see Practice E1970) determine the slope (m_K), intercept (b_K), standard deviation of the slope (σm_K) and the standard deviation of the intercept (σb_K) for the straight line where $Y = \ln(\beta / T_m^2)$ and $X = 1/T_m$.

12.4.4 Determine and report the Kissinger activation energy (E_K), and its standard deviation (σE_K) using Eq 11 and 12 and the gas constant ($R = 8.314 \text{ J/m o l K}$).

$$E_K = -m_K R \quad (11)$$

$$\sigma E_K = \sigma m_K R \quad (12)$$

12.5 Determination of the Pre-Exponential Factor (Z):

12.5.1 From the values of m_K and b_K experimental results from 12.4.3, determine and report the natural logarithm of the pre-exponential factor ($\ln[Z]$) and its standard deviation ($\sigma(\ln[Z])$) using Eq 13 and 14.

$$\ln[Z] = b_K + \ln[-m_K] \quad (13)$$

$$\sigma(\ln[Z]) = [\sigma b_K^2 + (\sigma m_K / m_K)^2]^{1/2} \quad (14)$$

12.6 Determination of Farjas Activation Energy (E_F):

12.6.1 From the time at full-width-at-half-maximum experimental values of 11.3, determine the values of $\ln[t_{FWHM}]$ and $1/T_m$ for each thermal curve.