Standard Test Method for
Kinetic Parameters for Thermally Unstable Materials by Differential Scanning Calorimetry Using the Kissinger Method[1]

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 and health practices and determine the applicability of regulatory limitations prior to use.*

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

E698 Test Method for Arrhenius Kinetic Constants 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

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

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

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

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, 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 at 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:

$$da/dt = k(T) f(\alpha) \tag{1}$$

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:

$$f_1(\alpha) = (1 - \alpha)^n \tag{2}$$

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

where:

n = nth reaction order (dimensionless), and
p = Avrami reaction order (dimensionless).

Note 1—There are a large number of conversion function expressions for $f(a)$ (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:

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

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:

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

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 $\ln[d (f (\alpha)) / d t]=0$, leads to Eq 6.

$$\ln[\beta / T_m^2] = \ln[Z R / E] - E/RT_m \tag{6}$$

where:

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

Note 2—The assumption of $\ln[d (f (\alpha)) / d t]=0$ holds strictly only for 1st order reaction but is considered a "reasonable" approximation for other nth 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).

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

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 [$f(\alpha)$]. 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 $\pm$ 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 $\pm$ 1μW, *(d)* a means of sustaining a *test chamber environment* of inert purge gas at a purge rate of 10 to 100 mL/min within $\pm$ 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 $\pm$ 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, Practice 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
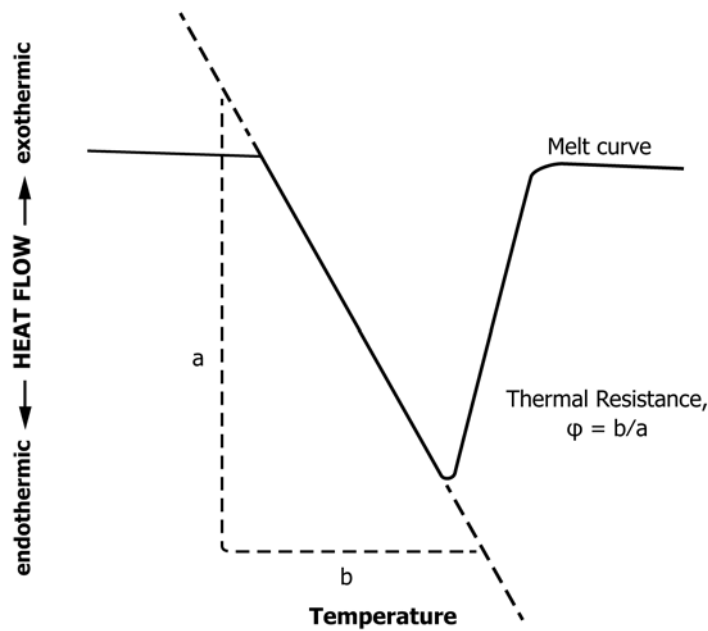
11.1 *Scouting Experiment:*

FIG. 1 Determination of Leading Edge Slope and Thermal Resistance

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 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.
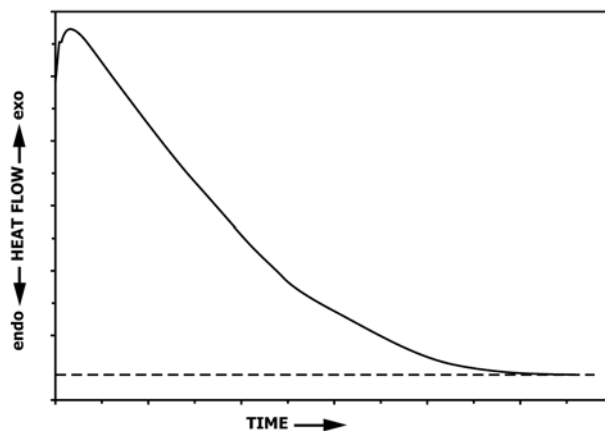

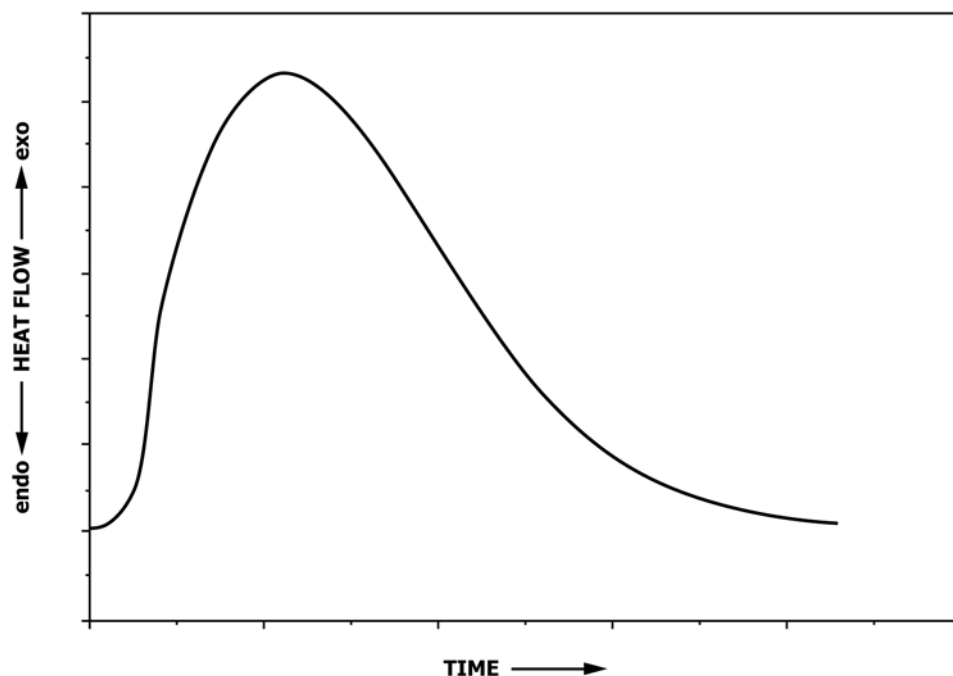**FIG. 2 Heat Flow Curve for an *n*th Order Reaction**

FIG. 3 Heat Flow Curve for an Accelerating Reaction

11.3 *Procedure for Measuring Kinetic Parameters:*

11.3.1 Weigh 1 to 5 mg of the test specimen to a precision of ± 10 µg into a tarred sample container and hermetically seal the container. Weigh the specimen and container to ± 10 µg. 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 $T_s = T_o − (10 \quad \min × β)$ 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 that 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 (σ(ln[Z])), the
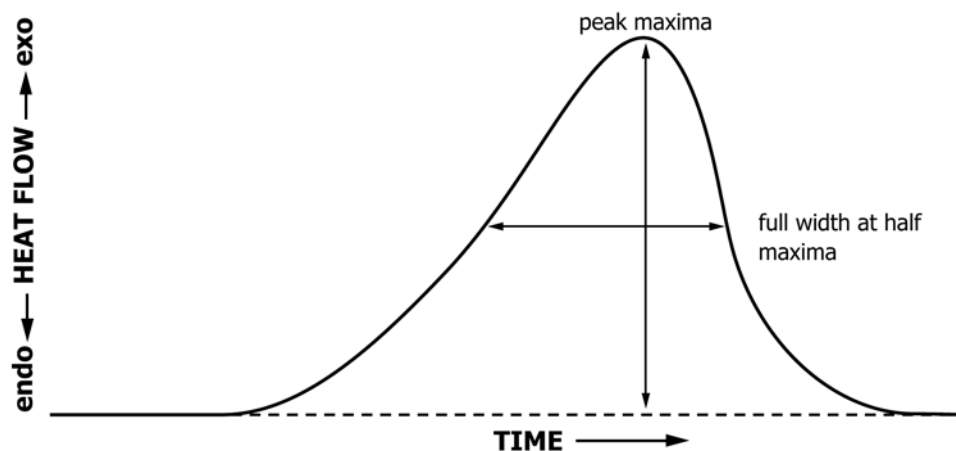
FIG. 4 Determination of the Time at Full-Width-at-Half-Maximum

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.

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).

$$\varphi = \Delta T / \Delta q = 1/S \qquad (8)$$

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.

$$T_m = T + \varphi \ q_{max} \qquad (9)$$

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.

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

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 J/mol K).

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

$$\sigma E_K = \sigma m_K / R \qquad (12)$$

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.

$$\ln[Z] = b_k + \ln[-m_K] \qquad (13)$$

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

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.

12.6.2 Prepare a display of $\ln[t_{FWHM}]$ on the ordinate versus $1/T_m$ on the abscissa for each of the values determined in 12.6.1.

Note 12—This display should demonstrate linearity. Otherwise, this determination of Farjas activation energy and reaction order is not applicable.

12.6.3 Using a least squares (linear regression) method (see Practice E1970) determine the slope (m_F) and intercept (b_F), standard deviation of the slope (σm_F), and standard deviation of the intercept (σb_F) for the straight-line where $Y=\ln(t_{FWHM})$ and $X=1/T_m$.

12.6.4 Determine and report the Farjas activation energy (E_F) and standard deviation of the Farjas activation energy (σE_F) using Eq 15 and 16.

$$E_F = m_F R \quad (15)$$

$$\sigma E_F = \sigma m_F / R \quad (16)$$

12.7 *Determination of the Reaction Order:*

12.7.1 Determine the value of t' from the value of $\ln[Z]$ obtained in 12.5, the value of b_F obtained from 12.6 and Eq 17. Determine its standard deviation (σ_t) using Eq 18.

$$t' = Z\exp[b_F] \quad (17)$$

12.7.2 From 11.2, determine if the reaction is *n*th order or accelerating. If *n*th order, go to 12.7.3. If the reaction is accelerating, go to 12.7.4.

12.7.3 For *n*th order reactions, determine and report the value of reaction order (n) and its standard deviation (σ_n) using Eq 19 and 20 **(3)**.

$$n = -0.39374 + (0.36063 \quad s \times t') + (0.08934 \quad s^2 \times t'^2) \quad (19)$$

$$\sigma_n = [0.36063 \quad s + (0.17868 \quad s^2] \times t')\sigma_t \quad (20)$$

12.7.4 For accelerating reactions, determine the value of the Avrami reaction order (p) and its standard deviation (σ_p) using Eq 21 and 22 **(3)**.

$$p = 2.44639 \quad s^{-1}/t' \quad (21)$$

$$\sigma_p = \sigma_t p/t' \quad (22)$$

13. Report

13.1 The report shall include the following:

13.1.1 Identification of the sample by name or composition, source, and other qualities (such as history).

13.1.2 Description of the apparatus used to make the measurement as well as the container type used. Report the thermal resistance.

13.1.3 Description of test conditions such as specimen environment, degree of confinement, composition of the atmosphere, and whether the atmosphere is static, self-generated, or dynamic through or over the specimen.

13.1.4 The values determined for Kissinger activation energy (E_K), Farjas activation energy (E_F), logarithm of the pre-exponential factor ($\ln[Z]$), reaction type (wth order or autocatalytic), reaction order (n or p), and their respective standard deviations.

13.1.5 The specific dated version of this test method used.

14. Precision and Bias

14.1 An interlaboratory study (ILS) was conducted in the year 2000 with participation by eight laboratories using six instrument models from three manufacturers. Each laboratory characterized trityl azide (azidotriphenylmethane) at five heating rates. The ILS results were treated by Practices E691 and E1970. The results of this interlaboratory study are available from ASTM Headquarters.[4]

14.2 *Precision:*

14.2.1 Intralaboratory 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).

14.2.2 The pooled repeatability relative standard deviation for the Kissinger activation energy (E_K) was 4.2 %.

14.2.3 The pooled repeatability relative standard deviation for logarithm of the pre-exponential factor was 4.3 %.

14.2.4 Interlaboratory 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).

14.2.5 The relative reproducibility standard deviation for Kissinger activation energy was 4.6 %.

14.2.6 The relative reproducibility standard deviation for the logarithm of the pre-exponential factor was 6.1 %.

14.3 *Bias:*

14.3.1 Bias is the difference between a test result and an accepted reference value.

14.3.2 The values obtained in this interlaboratory test are $E_K=141.2\pm8.8$ kJ/mol and $\ln[Z, s^{-1}]=29.4\pm2.2$.

14.3.3 These values may be compared with the values obtain in Test Method E698 for the same set of experimental data of $E=145.5\pm11$ kJ/mol and $\ln[Z, s^{-1}]=31.0\pm3.2$ with an assumed value of $n=1$.

14.3.4 These values may be compared to values obtained in Test Method E2041 of $E=165\pm17$ kJ/mol and $\ln[Z, s^{-1}]=13.1\pm1.4$ with a measured value of $n=1.32\pm0.30$.

15. Keywords

15.1 activation energy; arrhenius kinetic parameters; differential scanning calorimetry; hazard potential; kinetics; pre-exponential factor; thermal analysis; thermal hazard; thermal stability

APPENDIX

(Nonmandatory Information)

X1. EXAMPLE CALCULATIONS

Note X1.1—Retain all available digits during intermediate calculations. Rounding shall take place only at the expression of the final results.

X1.1 Example Calculation of Thermal Resistance

X1.1.1 A set of experimental data including $\Delta T = 0.153$ K, $\Delta q = 3.437$ mW are explored using Eq 8.

$$\varphi = \Delta T / \Delta q = 0.153 \text{ K}/-3.437 \text{ mW} = 1/S = -1/22.46 \text{ mW/K}$$
$$= -0.04452 \text{ K/mW}$$

X1.2 Example Calculation of Corrected Peak Temperature

X1.2.1 A set of experimental data including $T = 491.55$ K, $q = 1.545$ mW and $\varphi = -0.04452$ mW/K are explored using Eq 9.

$$T_m = T + \varphi q = 491.55 \text{ K} + (-0.04452 \text{ K}/\text{mW})1.545 \text{ mW}$$
$$= 491.55 - 0.069 \text{ K}$$
$$T_m = 491.48 \text{ K}$$

X1.3 Example Calculation of the Heating Rate

X1.3.1 A set of experimental data including $T_i = 399.35$ K, $T_f = 482.65$ K, $t_i = 0.00$ min and $t_f = 33.34$ min is explored using Eq 10.

$$\beta = (T_f - T_i)/(t_f - t_i)$$
$$= (482.65 \text{ K} - 399.35 \text{ K})/(33.45 \text{ min} - 0.00 \text{ min})$$
$$= 83.30 \text{ K}/33.45 \text{ min} = 2.490 \text{ K/min}$$

X1.4 Example Calculation of Kissinger Activation Energy and Logarithm Pre-Exponential Factor

X1.4.1 A set of experimental data including heating rate (β) and corrected temperature T_m are provided in Table X1.1.

X1.4.2 Values for $\ln[\beta/T_m^2]$ and $1/T_m$ are calculated for each set of experimental data as indicated and are added to Table X1.1.

X1.4.3 Prepare a display of $\ln[\beta/T_m^2]$ on the ordinate (Y-axis) versus $1/T_m$ on the abscissa (X-axis) as in Fig. X1.1.

X1.4.4 Determining the linear regression line to the data points yields $b_K = 4.4944$ and $m_K = -23670$ K as is shown in Fig. X1.1.

Note X1.2—Determination of the least-squares best-fit straight (linear regression)line is described in Practice E1970. Alternatively, many statistical calculators or computer programs will provide these results.

X1.4.5 Using Eq 11 and the value of $R = 8.314$ J mol^{-1} K^{-1}, the Kissinger activation energy is determined.

$$E_K = -m_K R = -(-23670 \text{ K}) \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \text{kJ}/1000 \text{ J}$$
$$= 196.8 \text{ kJ mol}^{-1}$$

X1.5 Example Calculation of Pre-Exponential Factor

X1.5.1 Using Eq 13 and the value for b_K and m_K from X1.4.4, determine the logarithm pre-exponential factor.

$$\ln[Z] = b_K + \ln[-m_K] = 4.4944 + \ln[-(-23670)] = 4.4944$$
$$+ 10.0720 = 14.5664 \text{ with } Z \text{ in s}^{-1}$$

Taking the antilog, $Z = 2.119 \times 10^6$ s^{-1}

X1.6 Example Calculation of Standard Deviation of Kissinger Activation Energy

X1.6.1 A set of experimental data including $\ln[\beta/T_m^2]$ and $1/T_m$ are provided in Table X1.2.

X1.6.2 Using the values of m_K and b_K from X1.4.4, values for the best-fit values of Y are determined for each value of $1/T_m$ (Y $= m_K/T_m + b_K$) are added to Table X1.2 as (Y).

X1.6.3 The difference between the best-fit values of Y and actual values of $\ln[\beta/T_m^2]$ are determined as δY. These values are squared in $(\delta Y)^2$, added to Table X1.2, and summed as $\Sigma(\delta Y)^2$, here equal to 0.055415.

X1.6.4 The squared values of $1/T_m$ are entered as X^2 and summed as $\Sigma(X^2)$, here equal to 3.28969×10^{-6} K^{-2}.

X1.6.5 The values of $1/T_m$ are summed as ΣX here equal to 0.00362502 K^{-1}.

X1.6.6 Given the number of data sets $\eta = 4$, σY is given by Eq 11 of Practice E1970 as:

X1.6.7 Determine the value of D using Eq 14 from Practice E1970.

X1.6.8 The equation for σm_K is found using Eq. 12 of Practice E1970 and values from X1.6.6 and X1.6.7.

$$\sigma m_K = \sigma_Y [\eta/D]^{1/2} = 0.16646 [4/1.799 \times 10^{-8} \text{ K}^{-2}]^{1/2}$$
$$= 0.16646 [2.223 \times 10^8 \text{ K}^2]^{1/2} = 0.16646 \times 1.493$$
$$\times 10^4 \text{ K} = 2482 \text{ K}$$

X1.6.9 The value of σb_K is found using Eq. 13 of Practice E1970 and values from Table X1.1, X1.6.6 and X1.6.7.

TABLE X1.1 Data Table for Example Determination of Kissinger Activation Energy and Logarithm Pre-Exponential Factor

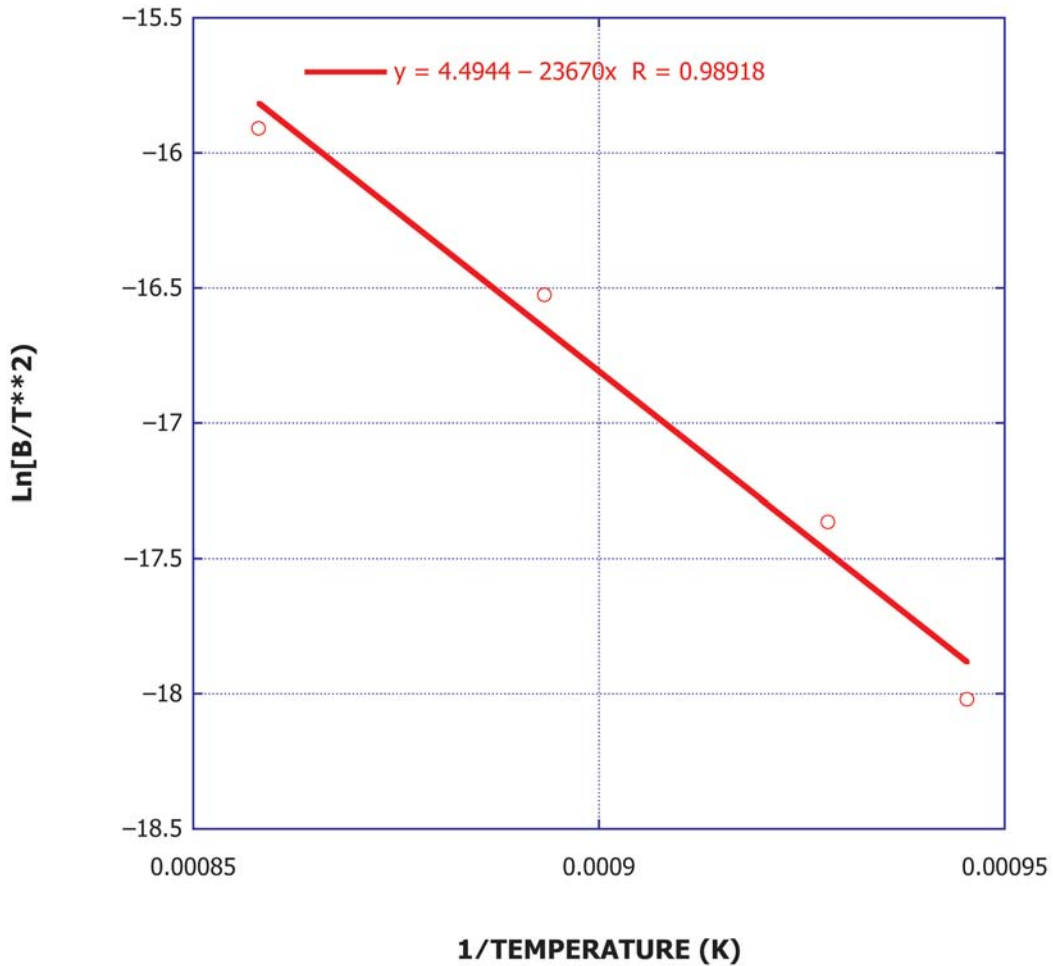| Heating Rate (K/min)	Heating Rate (K/s)	Temperature Corrected (K)	β/T_m^2 (K^{-1} s^{-1})	$\ln[\beta/T_m^2]$ (in K^{-1} s^{-1})	$1/T_m$ (K^{-1})
10.00	0.1667	1165.3	12.276×10^{-8}	-15.9130	0.00085815
5.00	0.0833	1119.5	6.647×10^{-8}	-16.5265	0.00089326
2.00	0.0333	1077.3	2.869×10^{-8}	-17.3667	0.00092825
1.00	0.0167	1057.8	1.492×10^{-8}	-18.0206	0.00094536

FIG. X1.1 Kissinger Data Line (β/T^2 in units of s^{-1} K^{-1})

TABLE X1.2 Data Table for Example Determination of Relative Standard Deviation for Kissinger Activation Energy and Logarithm Pre-Exponential Factor

ln[β/T_m^2] (in K^{-1} s^{-1})	1/T_m (K^{-1})	Y (in K^{-1} s^{-1})	δY (in K^{-1} s^{-1})	(δY)^2 (in K^{-2} s^{-2})	X^2 (K^{-2})
-15.9130	0.00085815	-15.8180	+0.0950	0.009025	7.3642 × 10^{-7}
-16.5265	0.00089326	-16.6491	-0.1226	0.015031	7.9791 × 10^{-7}
-17.3667	0.00092825	-17.4773	-0.1106	0.012232	8.6165 × 10^{-7}
-18.0206	0.00094536	-17.8823	+0.1383	0.019127	8.9371 × 10^{-7}
Σ	0.00362502			0.055415	32.8969 × 10^{-7}

$\sigma b_K = \sigma m_K R = 2483$ K $\times 8.314$ J/mol K $\times$ kJ/1000 J = 20.6 kJ/mol

X1.6.10 Determining the standard deviation of the Kissinger activation energy using Eq 12 and values from X1.4.4, X1.4.5 and X1.6.8.

X1.7 Example Calculation of the Standard Deviation of the Logarithm Pre-Exponential Factor

X1.7.1 From Eq 14 and data from X1.4.4, X1.6.8 and X1.6.9.

X1.8 Example Calculation of Farjas Activation Energy

X1.8.1 A set of experimental data including time at full-width-at-half-maximum (Δt_{FWHM}) and 1/T_m (from Table X1.2) are provided in Table X1.3.

TABLE X1.3 Data Table for Example Determination of Farjas Activation Energy and Reaction Order

Δt_{FWHM} (s)	(1/T_m) (K^{-1})	ln(Δt_{FWHM}) (in s)
841.8	0.00085815	6.73554
1588.2	0.00089326	7.37036
3684.8	0.00092825	8.21197
6976.1	0.00094536	8.85025

X1.8.2 Values for ln[Δt_{FWHM}] are calculated for each set of experimental data and added to Table X1.3.

X1.8.3 Prepare a display of ln[Δt_{FWHM}] on the ordinate (Y-axis) versus 1/T_m on the abscissa (X-axis) as in Fig. X1.2.

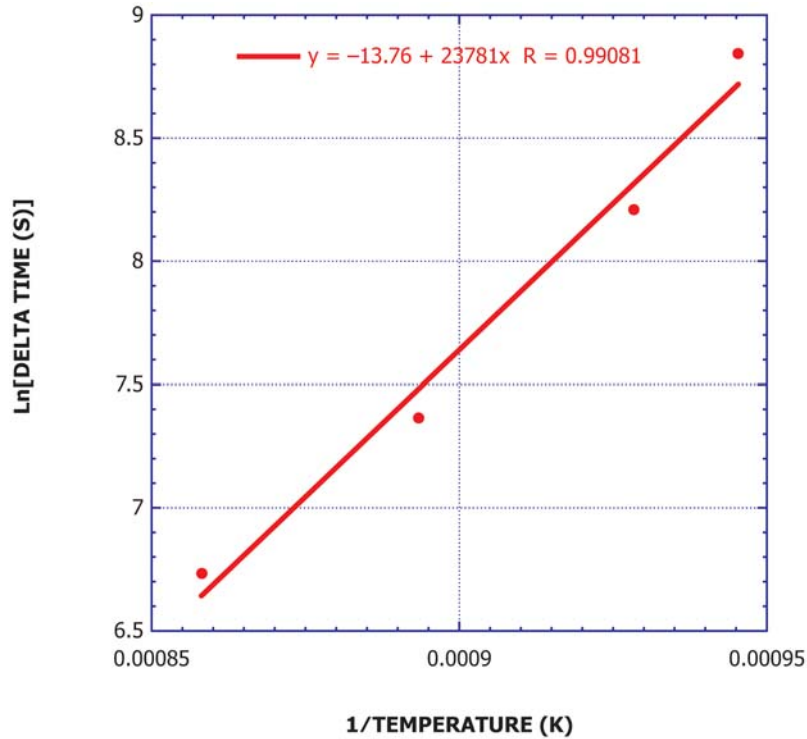X1.8.4 Determining the least squares best-fit straight (linear

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FIG. X1.2 Farjas Data Linear Regression Line (t_{FWHM} in units of s)

regression) line to the data points as in Fig. X1.2 yields $b_F = -13.760$ and the value of $m_F = 23781$ K.

NOTE X1.3—Determination of the least-squares best-fit straight (linear regression) line is described in Practice E1970. Alternatively, many statistical calculators or computer program will provide these results.

X1.8.5 Using Eq 15, the value from X1.8.4, and the value of $R = 8.314$ J mol^{-1} K^{-1}, the value of Farjas activation energy is calculated.

$$E_F = m_F R = 23781 \text{ K} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \text{kJ}/1000 \text{ J}$$
$$= 197.7 \text{ kJ mol}^{-1}$$

X1.9 Example Calculation of Reaction Order

X1.9.1 Using Eq 17 and the values from X1.5.1 and X1.8.4, the value of t' is calculated.

$$t' = Z\exp[b_F] = (2.119 \times 10^6 \text{ s}^{-1}) \times \exp[-13.760]$$
$$= (2.119 \times 10^6 \text{ s}^{-1}) \times 1.057 \times 10^{-6}$$
$$= 2.24 \text{ s}^{-1}$$

X1.9.2 Substituting this value into Eq 19.

$$n = -0.39374 + 0.36063 \text{s} t' + 0.08934 \text{s}^2 t'^2$$
$$= -0.39374 + 0.36063 \text{s} \times 2.24 \text{s}^{-1} + 0.08934 \text{s}^2 \times (2.24 \text{ s}^{-1})^2$$
$$= -0.39374 + 0.80781 + 0.44827 = 0.862$$

X1.10 Example Calculation of Relative Precision of the Farjas Activation Energy

X1.10.1 A set of experimental data including $\ln[\Delta t_{FWHM}]$ and $1/T_m$ are provided in Table X1.4.

X1.10.2 Using the values of m_F and b_F from X1.8.4, values for the best-fit values of Y are determined and added to Table X1.4 as Y values.

X1.10.3 The difference between the best-fit values of Y and the actual values of $\ln[\Delta t_{FWHM}]$ are determined as δY and added to Table X1.4. These values are square in $(\delta Y)^2$ and the squares are summed as $\Sigma(\delta Y)^2$ here equal to 0.047427.

X1.10.4 The squared values of $1/T_m$ are entered as X^2 and summed as $\Sigma(X^2)$, here equal to 3.28969×10^{-6} K^{-2}.

TABLE X1.4 Data Table for Example Calculation of Relative Standard Deviation for Farjas Activation Energy and Reaction Order

$\ln[\Delta t_{FWHM}]$	$1/T_m$ (K^{-1})	Y	δY	$(\delta Y)^2$	X^2 (K^{-2})
6.73554	0.00085815	6.64767	-0.08787	0.007721	7.3642×10^{-7}
7.37036	0.00089326	7.48262	+0.11226	0.012602	7.9791×10^{-7}
8.21197	0.00092825	8.31471	+0.10274	0.010556	8.6165×10^{-7}
8.85025	0.00094536	8.72161	-0.12864	0.016548	8.9371×10^{-7}
Σ	0.00362502			0.047427	32.8969×10^{-7}

X1.10.5 The values of $1/T_m$ are summed as ΣX here equal to 0.00362502.

X1.10.6 Given the number of data sets $\eta = 4$, σ_Y is given by Eq 11 of Practice E1970 as:

X1.10.7 The value D from Eq 14 in Practice E1970 is determined in X1.6.7.

X1.10.8 The value of σm_F is found using values from X1.6.7 and X1.10.6 in Eq 12 of Practice E1970.

$$\sigma m_F = \sigma Y [\eta / D]^{1/2} = 0.15399 [4 / 1.799 \times 10^{-8}]^{1/2}$$
$$= 0.15399 [2.223 \times 10^8]^{1/2}$$
$$= 0.15399 \times 1.4910 \times 10^4 = 2296$$

X1.10.9 The value of σb_F is found using Eq. 13 from Practice E1970.

$$\sigma b_F = \sigma Y [\Sigma X^2 / D]^{1/2} = 0.15399 [3.28969 \times 10^{-6} / 1.799 \times 10^{-8}]^{1/2}$$
$$= 0.15399 [182.86]^{1/2} = 0.15399 \times 13.523 = 2.082$$

X1.10.10 Using value of E_F, σm_F, and m_F from X1.8.5, X1.10.8 and X1.8.4, and Eq 17, determine the standard deviation of Farjas activation energy (σE_F) is determined.

$$\sigma E_F = E_F \sigma m_F / m_F = 197.7 \text{ kJ/mol} \times (2296 \text{ K} / 23781 \text{ K})$$
$$= 19.1 \text{ J/mol}$$

X1.11 Example Calculation of the Relative Precision of the Reaction Order

X1.11.1 Using the value of σb_F from X1.10.9, b_F from X1.8.4, $\ln[Z]$ from X1.5.1, $\sigma \ln[Z]$ from X1.7.1, and Eq 18, determine the standard deviation of the Farjas value (σ_t).

X1.11.2 Using the value of σ_t from X1.11.1, the value of t' from X1.9.1, and Eq 20, determine the standard deviation of the reaction order (σ_n).

$$\sigma_n = [0.36063 \text{ s} + 0.17868 \text{ s}^2 t']\sigma_t$$
$$= [0.36063 \text{ s} + 0.17868 \text{ s}^2 \times 2.24 \text{ s}^{-1}] \times 0.4844 \text{ s}^{-1}$$
$$= [0.36063 \text{ s} + 0.4002 \text{ s}] \times 0.4844 \text{ s}^{-1} = [0.76083] \times 0.4844$$
$$= 0.37$$

X1.12 Gather and Compare Results for Reasonableness

X1.12.1 Gather and compare results for reasonableness.

$E_K = 197 \pm 21$ kJ/mol	(RSD = $\pm$ 11 %)
$E_F = 198 \pm 19$ kJ/mol	(RSD = $\pm$ 16 %)
$\ln[Z, s^{-1}] = 14.6 \pm 2.3$	(RSD = $\pm$ 16 %)
$n = 0.86 \pm 0.37$	(RSD = $\pm$ 49 %)

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