Designation: E2890 – 21

Standard Test Method for Determination of Kinetic Parameters and Reaction Order for Thermally Unstable Materials by Differential Scanning Calorimetry Using the Kissinger and Farjas Methods[1]

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 K to 900 K (27 °C 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 *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.*

1.6 *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:*[3]

E473 Terminology Relating to Thermal Analysis and Rheology

E537 Test Method for 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 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

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

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

[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.

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

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

where:

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

NOTE 2—The assumption of $\ln[d(f(\alpha))/dt] = 0$ 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.

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'.