INTERNATIONAL STANDARD

ISO 11358-2

Third edition
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Plastics — Thermogravimetry (TG) of polymers —

Part 2: Determination of activation energy

Plastiques — Thermogravimétrie (TG) des polymères —

Partie 2: Détermination de l'énergie d'activation

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

This third edition cancels and replaces the second edition (ISO 11358-2:2014), which has been technically revised.

The main changes compared to the previous edition are as follows:

— the designation of rate of conversion has been changed in order to match that used in ISO 11358-3;

— the purge gas requirements have been changed with a reference to ISO 11358-1.

A list of all parts in the ISO 11358 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Plastics — Thermogravimetry (TG) of polymers —

Part 2: Determination of activation energy

1 Scope

This document specifies a method for the determination of the activation energy, E_a, in the Arrhenius formula for the decomposition of polymers using a thermogravimetric technique. The method is applicable only if the reaction proceeds by a single mechanism. It is applicable to multistage reactions if they consist of clearly separated single-stage steps.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 11358-1, *Plastics — Thermogravimetry (TG) of polymers — Part 1: General principles*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11358-1 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
Arrhenius formula
formula representing the temperature dependence of the rate constant of a reaction

Note 1 to entry: The rate constant, k, of a reaction is expressed by the Arrhenius formula, as follows:

$$k = A \cdot \exp^{(-E_a/\mathrm{RT})}$$

where

R is the gas constant (= 8,314 J · K^{-1} · mol^{-1});

T is the absolute temperature, in kelvins (K);

A is the pre-exponential factor, in reciprocal seconds (s^{-1});

E_a is the activation energy, in J · mol^{-1};

k is the rate of reaction (= $dC/\mathrm{d}t$), in reciprocal seconds (s^{-1}).

3.2
activation energy
E_a
energy, above that of the ground state, which must be added to an atomic or a molecular system to allow a particular process to take place

Note 1 to entry: It is expressed in $J \cdot mol^{-1}$.

3.3
degree of conversion
C
quantity of products present at a particular time and temperature during a reaction compared with the final quantity of the products

Note 1 to entry: It is given by the formula:

$$C = (m_i - m_t)/(m_i - m_f)$$

where

m_i is the initial quantity, in milligrams;

m_t is the quantity at a particular time and temperature, in milligrams;

m_f in the final quantity, in milligrams.

Note 2 to entry: When multistage reactions occur, the degree of conversion is calculated separately for each stage.

Note 3 to entry: The degree of conversion is dimensionless and varies in value from 0 to 1.

4 Principle

Test specimens are heated at several different heating rates and the change in mass measured as a function of temperature. The temperatures corresponding to given degrees of conversion are determined for each heating rate. For a given degree of conversion, the logarithm of the heating rate is plotted against the reciprocal of the absolute temperature, and the activation energy is calculated from the slope of the straight line thus obtained.

5 Apparatus

According to ISO 11358-1.

6 Mass and temperature calibration

6.1 Mass calibration

According to ISO 11358-1.

6.2 Temperature calibration

According to ISO 11358-1.

7 Test specimens

The test specimens shall be in the form of powder, pellets, flakes, filaments or film. The test specimens shall be prepared by cutting the material, as necessary, to a size appropriate for the apparatus (see

ISO 11358-1). Particles of small size, i.e. of high surface-area-to-volume ratio, are preferred. Grinding in a liquid-nitrogen mill may be used to decrease the particle size.

8 Procedure

8.1 General

See ISO 11358-1.

Perform the procedure at three or more heating rates, using specimens of identical mass (±1 %). The lowest and highest heating rates shall differ by a factor of at least 5.

In order to improve the accuracy of the determination, record the mass of an empty crucible subjected to the same test conditions of atmosphere, gas flow, and heating rate as used in the run with the specimen. If there is a mass change during the run with the empty crucible (which is usually ascribed to buoyancy), subtract the curve obtained with the empty crucible from that obtained with the test specimen to obtain a corrected thermogravimetric curve for the specimen. This procedure shall be repeated for all heating rates. Corrected curves shall be used for the analysis of the results.

It is preferable to use specimens less than 10 mg in size and heating rates of less than 20 $K \cdot min^{-1}$. For specimens greater than 10 mg and heating rates greater than 20 $K \cdot min^{-1}$, the specimen temperature might not follow the required temperature profile.

8.2 Non-oxidative reactions

When required, an inert gas atmosphere (e.g. nitrogen) shall be maintained during the determination to prevent oxidation of the specimen. Purity requirements shall be in accordance with ISO 11358-1.

8.3 Oxidative reactions

An oxidative gas atmosphere (oxygen or air) shall be used when testing polymers that undergo oxidation reactions. The water content of purge gas shall be in accordance with ISO 11358-1. Additional details of the type and purity of the gas used shall be included in the test report.

9 Expression of results

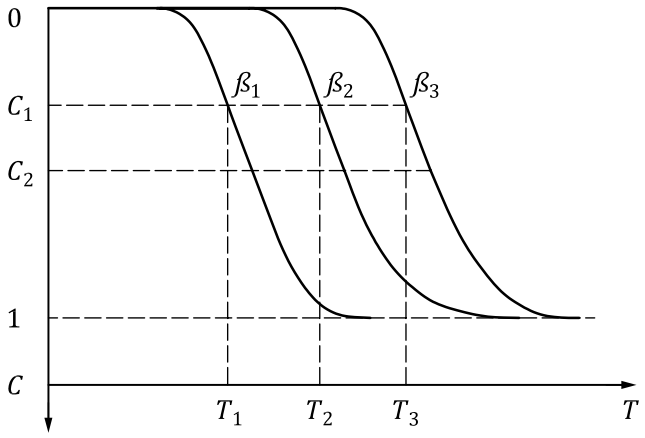
9.1 Graphical presentation

Present the thermogravimetry data obtained in the form of a mass change or percentage mass change versus temperature curve. Determine specific temperatures from the TG curve using the procedures described in ISO 11358-1.

9.2 Determination of activation energy

Check that the final mass reached at the end of each measurement run is constant, thereby indicating completion of the reaction, and that the percentage change in mass from the start of the run to the end of the run for each of the heating rates is also the same.

For a given degree of conversion, C, determine, from the TG curves, the absolute temperatures for each of the heating rates, β. Repeat for other degrees of conversion. Typical curves are shown in Figure 1.



Key

T	absolute temperature, in K
C	degree of conversion
$\beta_1<\beta_2<\beta_3$	heating rates

Figure 1 — Determination of absolute temperature for a given degree of conversion and heating rate

The approximate relationship given by Formula (1) was derived by Ozawa and later by Flynn and Wall (see References [1] and [2]) and is used to determine the activation energy, E_a.

$$\log\beta + 0{,}456\ 7\left(E_a / RT\right) = z \tag{1}$$

where

E_a is the activation energy;

R is the gas constant (R = 8,314 J · K^{-1} · mol^{-1});

z is the constant.

For heating rates β_1, β_2, β_3, …, and temperatures T_1, T_2, T_3, …, Formula (2) is obtained for a given degree of conversion, C_1:

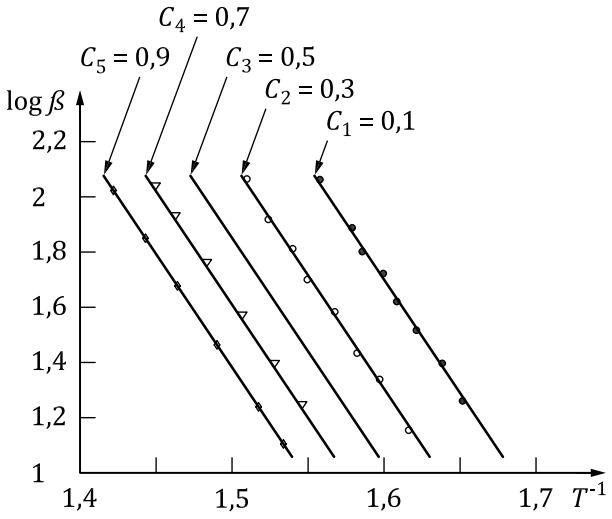
$$\log\beta_1 + 0{,}456\ 7\left(E_a / RT_1\right) = \log\beta_2 + 0{,}456\ 7\left(E_a / RT_2\right) = \log\beta_3 + 0{,}456\ 7\left(E_a / RT_3\right) \tag{2}$$

Plotting the logarithm of the heating rate, $\log\beta$, against the reciprocal of the absolute temperature, T^{-1}, for each degree of conversion C gives a series of straight-line curves (see Figure 2), and the activation energy, E_a, is calculated from the slope ($-0{,}456\ 7E_a/R$) in each case.

NOTE 1 This method is not suitable for very high degrees of conversion.

NOTE 2 This method is not reliable when the value of E_a varies widely from one degree of conversion to another and/or the log β versus T^{-1} relationship is not linear.

NOTE 3 Some thermobalances provide evaluation programs for the determination of the activation energy based on dynamic and/or isothermal measurements. It is up to the user to decide whether these kinetic programs correspond with the method specified in this document.



Key

T^{-1} reciprocal of the absolute temperature, in $K^{-1} \cdot 10^{-3}$

logβ logarithm of the heating rate, in $K \cdot min^{-1}$

Figure 2 — Heating rate versus the reciprocal of the absolute temperature

10 Precision

See Reference [3].

11 Test report

The test report shall include the following information:

a) a reference to this document, i.e. ISO 11358-2:2021;

b) all details necessary for complete identification of the material analysed;

c) the form and dimensions (if applicable) of the test specimen;

d) the mass of the test specimen;

e) details of the conditioning of the specimen prior to the test;

f) the specimen crucible size and material of construction;

g) the atmosphere and gas-flow rate used;

h) the heating rates used;

i) the standard reference material used for temperature calibration;

j) the activation energy determined using the formula in Note 1 to entry of 3.1 or Formula (1);

k) any observations regarding equipment, test conditions, or test specimen behaviour;

l) the date of the determination.

Bibliography

[1] Ozawa T., A new method of analyzing thermogravimetric data. Bull. Chem. Soc. Jpn. 1965, **38** p. 1881

[2] Flynn J. H., Wall L. A., A quick, direct method for the determination of activation energy from thermogravimetric data. J. Polym. Sci. 1966, **4** p. 323

[3] Anderson H. L., Kemmler A., Hohne G.W.H., Keldt K., Strey R., Round robin test on the kinetic evaluation of a complex solid state reaction from 13 European laboratories — Part 1: Kinetics TG-analysis. Thermochim. Acta. 1999, **332** p. 33