INTERNATIONAL STANDARD

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Plastics — Thermogravimetry (TG) of polymers —

Part 3:
Determination of the activation energy using the Ozawa-Friedman plot and analysis of the reaction kinetics

Plastiques — Thermogravimétrie (TG) des polymères —

Partie 3: Détermination de l'énergie d'activation à l'aide du graphique d'Ozawa-Friedman et analyse cinétique de la réaction

Reference number
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Foreword

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The committee responsible for this document is ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

ISO 11358 consists of the following parts, under the general title *Plastics — Thermogravimetry (TG) of polymers*:

- *Part 1: General principles*
- *Part 2: Determination of activation energy*
- *Part 3: Determination of the activation energy using the Ozawa-Friedman plot and the reaction kinetic analysis*

Introduction

Controlled rate thermogravimetry (CRTG) is used to study the decomposition of polymers. The Ozawa-Friedman method is typically applied to the analysis of data obtained by CRTG and also to that obtained by the combined use of isothermal thermogravimetry (iso–TG) with conventional linear heating rate thermogravimetry (LHTG), i.e. using a constant heating rate.

INTERNATIONAL STANDARD **ISO 11358-3:2013(E)**

Plastics — Thermogravimetry (TG) of polymers —

Part 3:
Determination of the activation energy using the Ozawa-Friedman plot and analysis of the reaction kinetics

1 Scope

This International Standard specifies an analysis method for determining the activation energy using the Ozawa-Friedman plot. It also specifies the preparation of master plots for verification of the reaction kinetics determined by thermogravimetry.

The Ozawa-Friedman plot (logarithm of the rate of mass loss versus the reciprocal of absolute temperature at a given mass loss) is a derivative method that can be applied to data obtained by any mode of temperature change in thermal analysis; e.g. isothermal, constant heating rate, sample-controlled thermal analysis, temperature jump, and repeated temperature scanning.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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*

ISO 11358-2, *Plastics — Thermogravimetry (TG) of polymers — Part 2: Determination of activation energy*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11358-1, ISO 11358-2 and the following apply.

3.1
conversion

$C = (m_\mathrm{t} - m_\mathrm{i})/(m_\mathrm{f} - m_\mathrm{i})$

where

m_i is the initial quantity, in mg;

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

m_f is the final quantity, in mg.

See ISO 11358-1 and ISO 11358-2.

Note 1 to entry: It is also referred to as the mass loss fraction.

3.2

generalized time

***t*$_{\text{gen}}$**

$$t_{\text{gen}} = \int_0^t \exp\left(-\frac{E_{\text{a}}}{RT}\right) dt$$

where

E_{a} is the activation energy, expressed in kJ/mol;

R is the gas constant, expressed as 8.314 J/(mol K);

T is the absolute temperature, expressed in Kelvin;

t is time, expressed in minutes.

3.3

generalized rate of conversion

***dC/dt*$_{\text{gen}}$**

$$\frac{dC}{dt_{\text{gen}}} = \exp\left(\frac{E_{\text{a}}}{RT}\right)\frac{dC}{dt}$$

3.4

master curve

plot that can be used to evaluate the results and investigate the reaction kinetics models

Note 1 to entry: Examples of master curves are conversion versus the generalized time, conversion versus the generalized rate of conversion, generalized time versus the generalized rate of conversion.

4 Principle

Test specimens are heated using any temperature profile and the change in mass is measured as a function of temperature and time. At a given conversion, the logarithm of the rate of conversion is plotted versus the reciprocal of the absolute temperature, and the activation energy is calculated from the slope of the straight line fit to the data thus obtained.

At least two of the master curves enable verification of the reaction kinetics analysis.

5 Apparatus

The apparatus shall be in accordance with ISO 11358-1.

6 Test specimens

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).

7 Mass and temperature calibration

7.1 Mass calibration

The procedure of mass calibration is given in ISO 11358-1.

7.2 Temperature calibration

The procedure of temperature calibration is given in ISO 11358-1.

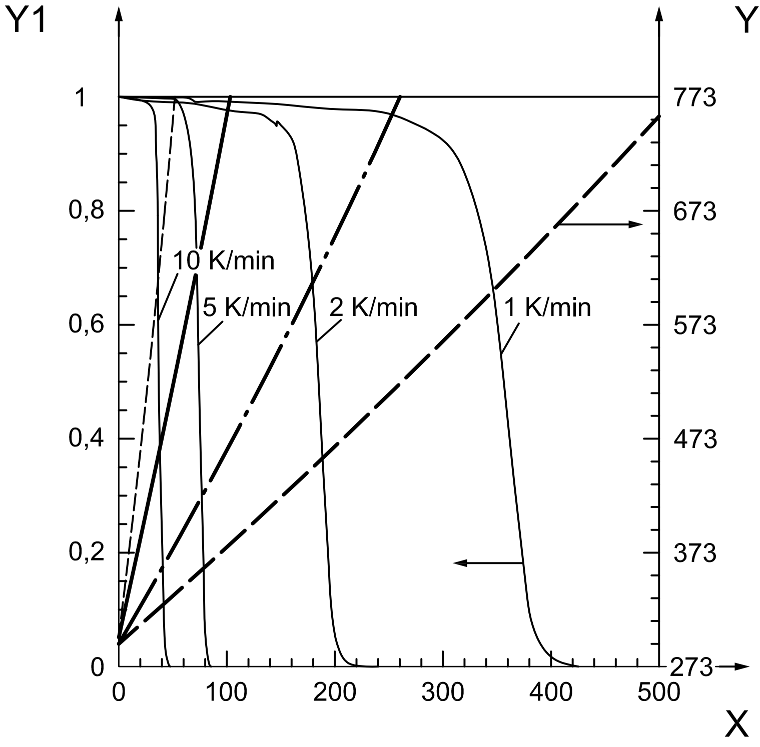
8 Procedure

8.1 General

The determination of the rate of conversion *dC/dt* is necessary for the analysis in this International Standard. The rate of conversion versus absolute temperature shall be determined.

See ISO 11358-1 and ISO 11358-2.

Perform tests using either an isothermal run, constant rate heating and cooling, sample mass controlled rate thermal analysis, temperature jump, repeated temperature scanning, or any combination of the above, using specimens of similar mass (±1 %). For examples of linear heating rate thermogravimetry (LHTG) and sample mass controlled rate thermogravimetry (CRTG), see Figures 1a and 1b, respectively.



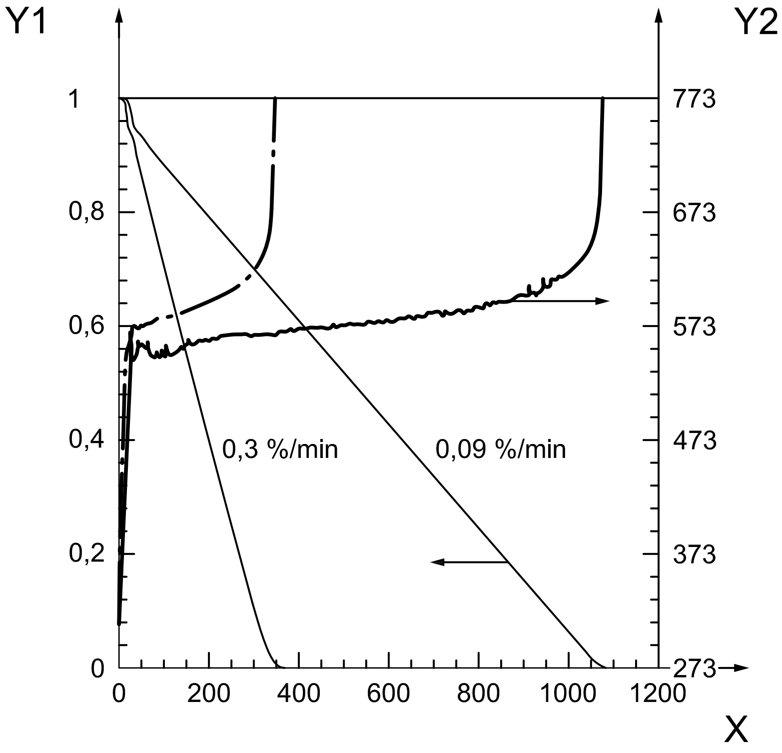
Key

X t/min

Y1 (1 – C)

Y2 T/K

Figure 1a — Example of linear heating rate thermogravimetry (LHTG) measurements of PMMA



Key

X t/min

Y1 (1 – C)

Y2 T/K

NOTE The units of %/min indicate the percentage weight loss per minute of the mass controlled rate.

Figure 1b — Example of sample mass controlled rate thermogravimetry (CRTG) measurements of PMMA

Preferably, the specimen mass should be between 1 mg and 10 mg and the temperature scanning rate between 2 K min^{-1} and 10 K min^{-1}.

Determine the rate of conversion (or rate of change of mass loss fraction with time) at a given conversion (or given mass loss fraction).

8.2 Non-oxidative reactions

The procedure of non-oxidative reactions is given in ISO 11358-2.

8.3 Oxidative reactions

The procedure of oxidative reactions is given in ISO 11358-2.

9 Expression of results

9.1 Graphical presentation

For a given conversion (or mass loss fraction), present the thermogravimetry data in the form of a plot of the logarithm of the rate of conversion (or rate of change of mass loss fraction with time) versus the reciprocal of the absolute temperature, i.e. the Ozawa-Friedman plot, see Figure 2.

9.2 Determination of activation energy

The conversion (or the mass loss fraction) is not directly related to the quantity of reacted pieces, for example as in the random scission of the main chain of polymers. Generally, the rate formulae are as follows:

$$C = f(\alpha) \tag{1}$$

and

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E_\mathrm{a}}{RT}\right)g(\alpha) \tag{2}$$

where

α is the reacted fraction at time t;

$f(\alpha)$ is an arbitrary function;

A is the pre-exponential factor;

$g(\alpha)$ is a function describing the reaction mechanism.

By taking the logarithm of both sides of Formula (2) then

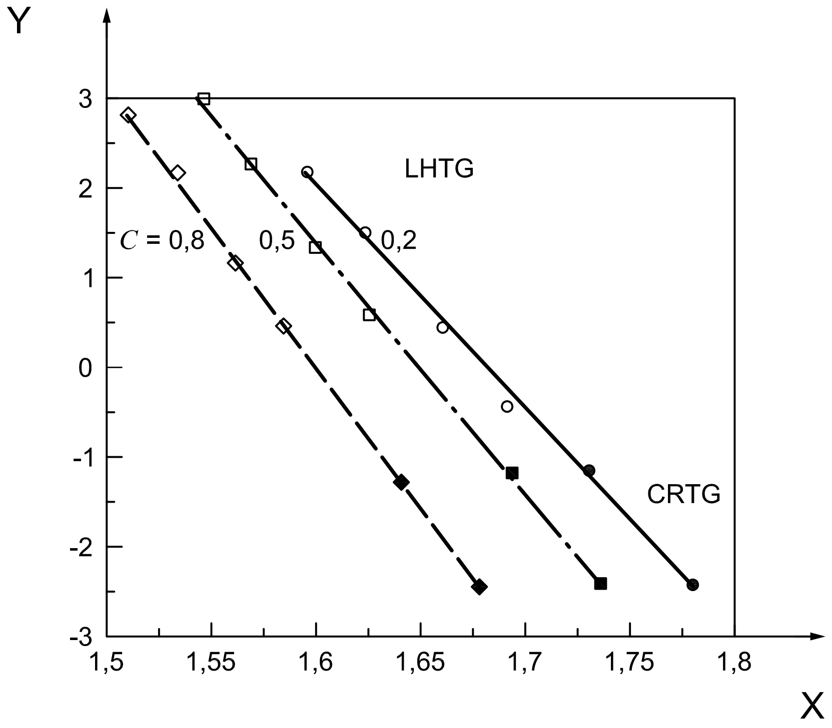
$$ln\left(\frac{d\alpha}{dt}\right) = ln\left\{Ag(\alpha)\right\} - \frac{E_\mathrm{a}}{RT} \tag{3}$$

When plotted for fixed values of α, with various conversion rate values determined for different experimental temperature control profiles, the slope of the plot of $ln\left(\frac{d\alpha}{dt}\right)$ versus $\frac{1}{T}$ has the value $-E_\mathrm{a}/R$ and is used to determine the activation energy E_a, as the first term in the right side of Formula (3) is constant.

As an example, the experimental data presented in Figures 1a and 1b have been analysed, assuming an nth order type reaction and thus $C = f(\alpha) = \alpha$ (Annex A), the results of which are presented in Table 1 and Figure 2.

Table 1 — The rate of conversion *dC/dt* and the estimated activation energy E_a at different conversion levels, determined from the controlled rate thermogravimetry (CRTG) data presented in Figure 1b

	1000/T (K^{-1})	ln(dC/dt (% min^{-1})) at C = 0,2	1000/T (K^{-1})	ln(dC/dt (% min^{-1})) at C = 0,5	1000/T (K^{-1})	ln(dC/dt (% min^{-1})) at C = 0,8
CRTG, 0,09 %/min	1,779	−2,425	1,735	−2,411	1,677	−2,448
CRTG, 0,3 %/min	1,731	−1,161	1,693	−1,183	1,641	−1,288
Activation Energy (kJmol^{-1})						
Ozawa-Friedman plot		207,3		232,8		261,9



Key

X 1 000/T K^{-1}

Y ln (dC/dt / % min^{-1})

Figure 2 — Ozawa-Friedman plot of the LHTG data determined from Figure 1a (open symbols), and CRTG data from Table 1 (closed symbols) at conversion values of 0,2, 0,5 and 0,8

9.3 Master curves

Given Formulae (1) and (2), the assumed models of the method, then

$$\frac{dC}{dt}=\frac{df(\alpha)}{d\alpha}\frac{d\alpha}{dt}=\frac{df(\alpha)}{d\alpha}A\exp(\frac{-E_a}{RT})g(\alpha) \tag{4}$$

Thus, using the generalized rate of conversion in 3.3,

$$\frac{dC}{dt_{\text{gen}}}=Ag(\alpha)\frac{df(\alpha)}{d\alpha} \tag{5}$$

The master curve, the plot of

$$\frac{dC}{dt_{\text{gen}}}=\exp\left(\frac{E_a}{RT}\right)\frac{dC}{dt} \tag{6}$$

can be used to demonstrate how consistent the reaction being analysed is with the assumed models of Formulae (1) and (2).

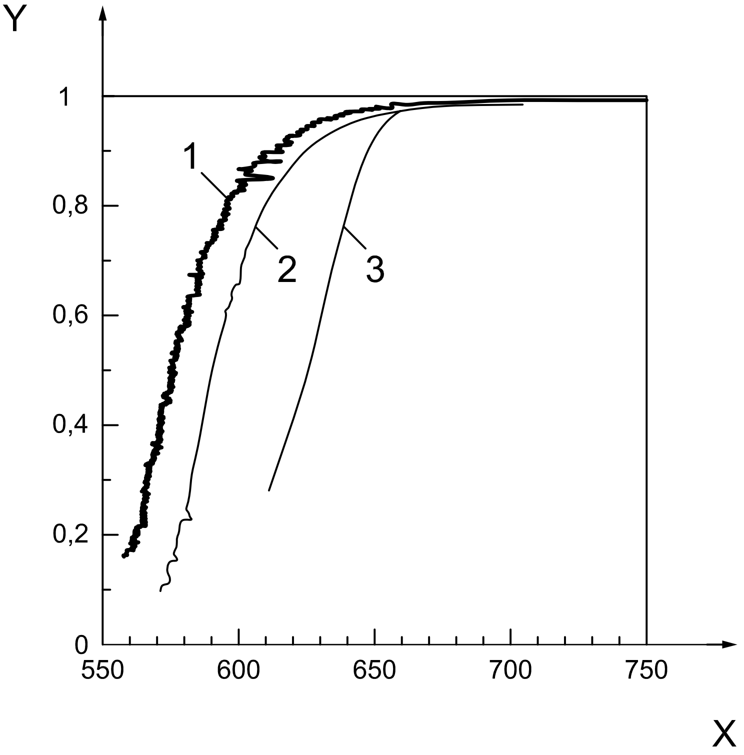
Similarly, other relations between C, t_{gen} and dC/dt_{gen} can be derived. According to Formula (6) and Formula (A.7) in Annex A, the generalized rate of conversion dC/dt_{gen} has the following relationship to the experimental kinetic data via the generalized rate of the reacted fraction $d\alpha/dt_{gen}$ for an n^{th} order reaction where $C = f(\alpha) = \alpha$, as shown in Table A.1:

$$\frac{dC/dt_{gen}}{\left(dC/dt_{gen}\right)_{C=0,5}} = \frac{d\alpha/dt_{gen}}{\left(d\alpha/dt_{gen}\right)_{C=0,5}} = \frac{d\alpha/dt}{\left(d\alpha/dt\right)_{C=0,5}} \cdot \frac{\exp\left(E_a/RT\right)}{\exp\left(E_a/RT_{0,5}\right)} \tag{7}$$

where

$T_{0,5}$ is the reaction temperature at $C = 0,5$.

For calculating the experimental values of $(dC/dt_{gen})/(dC/dt_{gen})_{C=0,5}$, the experimental kinetic data have to be used, e.g. Figure 3.



Key

X T / K

Y Conversion C

1 CRTG 0,09 %/min

2 CRTG 0,3 %/min

3 LHTG 2 K/min

Figure 3 — Experimental conversion curves of CRTG (0,3 %/min and 0,09 %/min) and LHTG (2 K/min) of PMMA plotted as a function of temperature

Furthermore, master curves can be used to help identify the reaction mechanism model, $g(\alpha)$, and the relation between the conversion and the reaction species, $f(\alpha)$, by fitting theoretical models to the experimental data, and revising the model as necessary to achieve a good fit of experimental data with theoretical values.

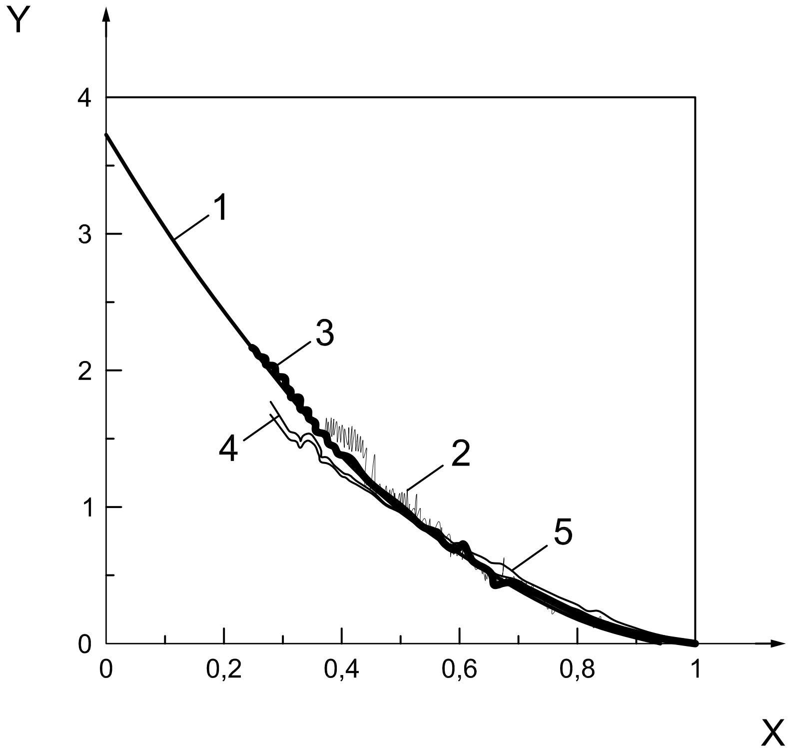
In the case of $C = f(\alpha) = \alpha$, Formula (5) gives

$$\frac{dC}{dt_{\mathrm{gen}}} = Ag(\alpha) \tag{8}$$

Using the conversion of α = 0,5 as a reference value, the following formula is derived from Formula (2) and (7):

$$\frac{d\alpha / dt_{\mathrm{gen}}}{\left(d\alpha / dt_{\mathrm{gen}}\right)_{\alpha=0,5}} = \frac{g(\alpha)}{g(0,5)} \tag{9}$$

Formula (9) states that, at a given conversion α, the experimentally determined $(d\alpha/dt_{\mathrm{gen}})/(d\alpha/dt_{\mathrm{gen}})_{\alpha = 0,5}$ and the theoretically calculated $g(\alpha)/g(0,5)$ are equivalent when an appropriate function $g(\alpha)$ for describing the reaction process under investigation is applied. Figure 4 compares the theoretical plot of $g(\alpha)/g(0,5)$ versus α with the experimental master plots of $(d\alpha/dt_{\mathrm{gen}})/(d\alpha/dt_{\mathrm{gen}})_{\alpha = 0,5}$ versus α calculated using the experimental data of Figure 3. In this case an n$^{\mathrm{th}}$ order reaction with a reaction order n = 1,9 has been assumed and used to generate the theoretical plot and provides a good fit to the experimental master plot data as shown in Figure 4.



Key

X α

Y $(d\alpha/dt_{\mathrm{gen}})/(d\alpha/dt_{\mathrm{gen}})_{\alpha = 0,5}$

1 $g(\alpha)/g(0,5)$

2 CRTG 0,09 %/min

3 CRTG 0,3 %/min

4 LHTG 2 °K/min

5 LHTG 5 °K/min

NOTE It was assumed that $C = \alpha$ as for an n$^{\mathrm{th}}$ order reaction as listed in Table A.1 and thus $dC/dt_{\mathrm{gen}} = d\alpha/dt_{\mathrm{gen}}$.

Figure 4 — A comparison of the experimental master plots of $(d\alpha/dt_{\mathrm{gen}})/(d\alpha/dt_{\mathrm{gen}})_{\alpha = 0,5}$ versus α with the theoretical master curves $g(\alpha)/g(0,5)$ versus α for the thermal decomposition of PMMA

10 Precision

The standard deviations of the estimated activation energy E_a and the generalized rate of conversion dC/dt_{gen} are reported for the specific case analysed to be less than 5 %.[4]

11 Test report

The test report shall include the following information:

a) a reference to this part of ISO 11358 (i.e. ISO 11358-3);

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

c) the form and dimensions 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 pan size, mass and material of construction;

g) the atmosphere and gas–flow rate used;

h) the details of the temperature profile used;

i) the standard reference material(s) used for temperature calibration;

j) the activation energy, determined from a linear slope in the plot of the logarithm of the rate of mass loss versus the reciprocal absolute temperature at a given mass loss, and the mass loss (see Figure 1);

k) the reaction order determined with a fitting function of the kinetics, if required (see Table 1).

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

m) the date of the determination.

Annex A
(informative)

Mathematical background

In thermal analysis, the property P of the sample, for example the mass, or the rate of change of the property, dP/dt (or dP/dT) are recorded as a function of time t or temperature T. In order to estimate the kinetic parameters by this method, the property measured should be described only by the parameter, α. Thus the conversion, C, which is equal to $(P-P_0)/(P_\infty-P_0)$, (where P_0 and P_∞ are the property values before and after the reaction, respectively), is a function of α:

$$C=f\left(\alpha\right) \tag{A.1}$$

The parameter α is assumed to change following ordinary reaction kinetics:

$$\frac{d\alpha}{dt}=A\exp\left(-\frac{E_\mathrm{a}}{RT}\right)g\left(\alpha\right) \tag{A.2}$$

where

A, E_a and R are the pre-exponential factor, the activation energy and the gas constant, respectively.

Formula (A.2) is rearranged as:

$$\int_0^\alpha \frac{d\alpha}{g\left(\alpha\right)}=A\int_0^t \exp\left(-\frac{E_\mathrm{a}}{RT}\right)dt \tag{A.3}$$

or

$$G\left(\alpha\right)=At_\mathrm{gen} \tag{A.4}$$

where

$$G\left(\alpha\right)=\int_0^\alpha \frac{d\alpha}{g\left(\alpha\right)} \tag{A.5}$$

and t_gen is the generalized time defined as

$$t_\mathrm{gen}=\int\limits_0^t \exp\left(-\frac{E_\mathrm{a}}{RT}\right)dt \tag{A.6}$$

In principle, from Formulae (A.1) and (A.5) and given the functions $f(\alpha)$ and $g(\alpha)$, the relationship between P and At_gen can be derived. The relationship between C and At_gen is dependent only on the functions $f(\alpha)$ and $g(\alpha)$, i.e. the mechanism of the reaction and the relationship of P with α and can be theoretically derived.

Similar theoretical relationships of derivative type can also be derived:

$$\frac{dC}{dAt_\mathrm{gen}}=\frac{df\left(\alpha\right)}{d\alpha}\frac{d\alpha}{dAt_\mathrm{gen}}=\frac{df\left(\alpha\right)}{d\alpha}\frac{d\alpha}{dt}\frac{dt}{dAt_\mathrm{gen}}=g\left(\alpha\right)\frac{df\left(\alpha\right)}{d\alpha} \tag{A.7}$$

as

$$\frac{dAt_{\mathrm{gen}}}{dt} = A\exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \tag{A.8}$$

Thus, the theoretical relationship between dC/dAt_{gen} and C and between dC/dAt_{gen} and At_{gen} can be derived and depend only on the functions $f(\alpha)$ and $g(\alpha)$. For some typical cases, dC/dAt_{gen} is shown as a function of At_{gen} in Table A.1.

In the random degradation of high polymer, α is the fraction of bonds broken, and L is a measure of the least length of the polymer not volatilized. When the conversion follows a reaction of nth order, $C = \alpha$.

Table A.1 — Relationship between C, α and dC/dt_{gen} for typical reaction models

Type of reaction	$C = f(\alpha)$	$g(\alpha)$	$G(\alpha)$	$d\alpha/dAt_{\text{gen}}$	dC/dAt_{gen}
n$^{\text{th}}$ order	A	$\left(1-C\right)^{n}$	$\frac{1}{n-1}\left\{\left(1-C\right)^{1-n}-1\right\}$	$\left(1-C\right)^{n}$	$\left\{1+\left(n-1\right)At_{\text{gen}}\right\}^{n/\left(1-n\right)}$
1st order	A	$1-C$	$-ln\left(1-C\right)$	$1-C$	$\exp\left(-At_{\text{gen}}\right)$
Random scission	$\left(1-x\right)^{L-1}\left\{1+\left(L-1\right)\alpha\right\}$	$1-\alpha$	$-ln\left(1-\alpha\right)$	$-L\left(L-1\right)\left(1-\alpha\right)^{L-1}\alpha$	$L\left(L-1\right)\exp\left\{-\left(L-1\right)At_{\text{gen}}\right\}\left\{1-\exp\left(-At_{\text{gen}}\right)\right\}$

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