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An iterative model-free method to determine the activation energy of heterogeneous processes under arbitrary temperature programs

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ABSTRACT

A new iterative model-free (isoconversional) method with integration over a given range of conversion for the determination of the activation energy using non-isothermal data recorded at arbitrary temperature programs has been suggested. The advantages of applying this method in comparison with differential linear and nonlinear methods and advanced nonlinear method are put in evidence. The applicability of the suggested method was checked for simulated data for a single-step process, thermal decomposition of calcium carbonate, and thermal degradation of high density polyethylene.

1. Introduction

The importance of the isoconversional (model-free) methods in the evaluation of the kinetic parameters of heterogeneous processes was put in evidence and critical analyzed in several recent papers (see for example Refs. [1–15]). The most of the suggested model-free methods are applicable for data recorded in isothermal or constant heating rate conditions. Nevertheless, one of these conditions is not always met in some practical situations. Vyazovkin [15–17] mentioned that the constant heating rate program could be disturbed as a result of thermal effects of reactions, which occur during the heating of the investigated sample. In an isothermal experiment, the constant temperatures are reached by rapid heating of the sample, and in such a case the decomposition or thermo-oxidation of the sample could began during heating from the room temperature to the desired constant temperature.

The linear differential method suggested by Friedman [18] (FR method) and nonlinear differential method suggested by Budrugeac [19] (NL-DIF method) can be applied to handle data obtained under arbitrary variation of temperature. However, these methods involve the evaluation of the local reaction rates, which are sensitive to inherent noises and tend to be numerically unstable [20]. The corresponding errors could be reduced by smoothing of the experimental data. A substantially diminishing of these errors is obtained by using the advanced nonlinear isoconversional method (A-NL) suggested by Vyazovkin [15–17], which could be also used for data obtained under arbitrary temperature programs. In this method, the value of the activation energy, E_α, corresponding to the conversion degree α results by minimizing the function:

$$\Phi(E_\alpha) = \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \tag{1}$$

where

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_\alpha-\Delta\alpha}^{t_\alpha} \exp\left[-\frac{E_\alpha}{RT_i(t)}\right] dt \tag{2}$$

and E is the activation energy, T is the temperature, t is the time, R is the gas constant, $\Delta\alpha$ has a small value, and subscripts i and j refer to used α vs. t curves.

In comparison with FR method, this method exhibits a higher accuracy, but a longer time-consuming.

In this paper, the iterative integral isoconversional method recently suggested for constant heating rates [21], will be modified for handle data obtained under arbitrary temperature programs.

2. Iterative isoconversional method applicable for arbitrary variations of temperature

As all model-free methods, the suggested method has the origin in the single-step kinetic equation:

$$\frac{d\alpha}{dt} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{3}$$

where A is the pre-exponential factor and $f(\alpha)$ is the differential conversion function.

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Nomenclature

α	conversion degree
β	heating rate
t	time
T	temperature
E	activation energy
A	Arrhenius pre-exponential factor
$f(\alpha)$	differential conversion function (differential reaction model)
$g(\alpha)$	integral conversion function (integral reaction model)
R_I^*	see Eq. (5)
R_I	see Eq. (8)

Superscripts

(1), (2), (i) and ($i+1$) the number of iteration

Let us consider an arbitrary temperature program $T = T(t)$. The integration of Eq. (3) for the limits $\alpha_1(T_1(t_1))$ and $\alpha_2(T_2(t_2))$ leads to:

$$\int_{\alpha_1}^{\alpha_2} \frac{d\alpha}{f(\alpha)} = g(\alpha_2) - g(\alpha_1) = A \int_{t_1}^{t_2} \left[\exp\left(-\frac{E}{RT(t)}\right) dt \right] \tag{4}$$

where $g(\alpha)$ is the integral conversion function that is assumed independent on the variation of temperature.

Eq. (4) can be written as:

$$\ln(t_2 - t_1) + \ln R_I^* = \ln \frac{g(\alpha_2) - g(\alpha_1)}{A} + \frac{E}{RT_2} \tag{5}$$

where

$$R_I^* = \frac{\int_{t_1}^{t_2} [\exp(-E/RT(t))] dt}{(t_2 - t_1)[\exp(-E/RT_2)]}.$$

According to relation (5):

$$E = R \frac{d\ \ln(t_2 - t_1)}{d(1/T_2)} + R \frac{d \ln\ R_I^*}{d(1/T_2)} \tag{6}$$

Similar with other isoconversional methods, the procedure that will be given below needs the data recorded for several different temperature programs. In order to evaluate the activation energy for a given pair α_1 and α_2 by using Eq. (6), the following iterative procedure is proposed:

I. For $R_I^* = \text{const.}$, by plotting $\ln(t_2 - t_1)$ vs. $(1/T_2)$ activation energy $E^{(1)}$ is obtained from the slope of this line.
II. $E^{(1)}$ being introducing in the expression of R_I^*, the value of $E^{(2)}$ is evaluated from the slope of the straight line $(\ln(t_2 - t_1) + \ln R_I^*)$ vs. $(1/T_2)$.
III. Let $E^{(2)}$ replace $E^{(1)}$ and repeat step II until $|(E^{(i^*1)} - E^{(i)})| \leq 0.1\ \text{kJ mol}^{-1}$.

The integral included in R_I^* expression is numerically evaluated by using $T = T(t)$ with $t_1 \leq t \leq t_2$ corresponding to each used temperature program. The possible errors in E evaluation could be due to the accuracy of t_1 and t_2 reading and the precision of numerical integration performed for the assessment of R_I^*. These errors can be shortened by accuracy recording $T = T(t)$ curves with numerous experimental points.

Like the aforementioned FR, NL-DIF and A-NL methods, the suggested iterative procedure imposes no restrictions on the form of $T = T(t)$ and may be applied to the “time temperature–yield” data obtained by any experimental technique. Other advantages are that this iterative procedure can be applied for all ranges of $\alpha_1 - \alpha_2 = \Delta\alpha$, even small $\Delta\alpha$ ranges, and is smaller time-consuming than A-NL method.

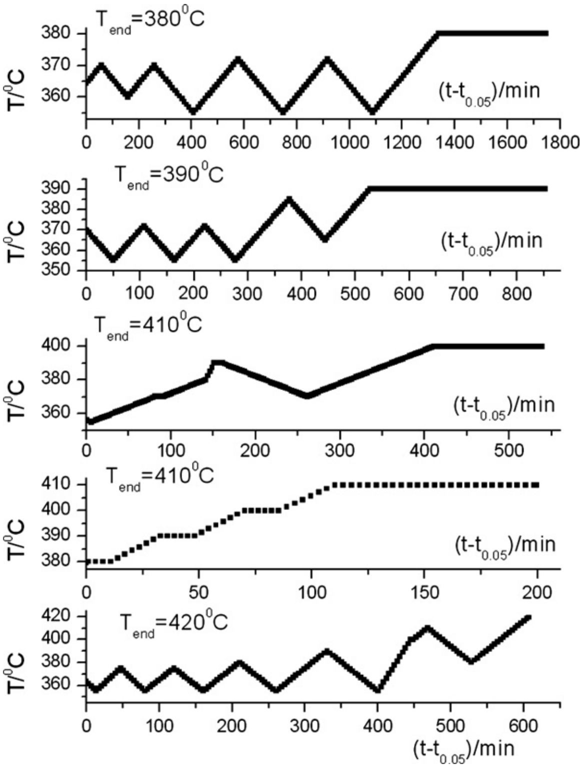

Fig. 1. The temperature programs used in simulations. $t_{0.05}$ is the time used in simulations.

If E does not depend on α, it is expected that the activation energy evaluated by iterative method is independent of $\Delta\alpha$. On the other hand, when E depends on α, it is expected that for a very small value of $\Delta\alpha$, E evaluated by iterative method to be close to that obtained by FR, NL-DIF and A-NL methods.

Of course, the aforementioned observations are also valid when the iterative method is applied for the data corresponding to most employed temperature programs, namely isothermal data and non-isothermal data recorded at constant heating rates.

For isothermal data $T_1 = T_2 = T$, and consequently $R_I^* = 1$. In such case Eq. (5) becomes:

$$\ln(t_2 - t_1) = \ln \frac{g(\alpha_2) - g(\alpha_1)}{A} + \frac{E}{RT} \tag{7}$$

For small values of $\Delta\alpha$, Eq. (7) allows evaluating the dependence of activation energy on the conversion degree from a series of isotherms.

For non-isothermal data with constant heating rate ($\beta = dT/dt = \text{const.}$), the change of variable t with T in Eq. (5) leads to:

$$\ln \frac{\beta}{T_2 - T_1} - \ln\ R_I = \ln \frac{A}{g(\alpha_2) - g(\alpha_1)} - \frac{E}{RT_2} \tag{8}$$

where

$$R_I = \frac{\int_{T_1}^{T_2} [\exp(-E/RT)] dT}{(T_2 - T_1)[\exp(-E/RT_2)]}.$$

The last equation was derived in a recent previous paper [21] in which its applicability in the evaluation of E vs. α by using non-isothermal data recorded at constant heating rates was pointed out.