



Application of the golden section search algorithm in the nonlinear isoconversional calculations to the determination of the activation energy from nonisothermal kinetic conversion data

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ABSTRACT

In this study, the golden section search algorithm in the nonlinear isoconversional calculations to be used for the determination of the activation energy from nonisothermal kinetic conversion data has been introduced. The technique has been applied to two simulated processes (one corresponds to a constant activation energy process, and the other corresponds to a varying activation energy process) and cellulose pyrolysis. The results have shown that the golden section search algorithm is capable of providing the valid activation energy values.

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1. Introduction

The kinetics of thermally stimulated solid-state reactions is usually described by the following equation [1]:

$$\frac{d\alpha}{dt} = A e^{-E/RT} f(\alpha) \quad (1)$$

where α is the degree of conversion, t is the time, $f(\alpha)$ is the differential conversion function related on the reaction mechanism, A is the pre-exponential factor, E is the activation energy, R is the universal gas constant, T is the absolute temperature, and t is the time.

Some solid-state reactions are commonly studied using linear heating program [2]

$$\beta = dT/dt \quad (2)$$

where β is the heating rate.

Substituting Equation (2) into Equation (1), we can obtain the equation that describes the progress of reaction under non-isothermal conditions:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \quad (3)$$

Integration of Equation (3) over small segments of variables (concretely over segments of the degree of conversion and temperature) leads to

$$g(\alpha, \alpha - \Delta\alpha) = \int_{\alpha - \Delta\alpha}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A_{\alpha}}{\beta} \int_{T_{\alpha - \Delta\alpha}}^{T_{\alpha}} e^{-E_{\alpha}/RT} dT \quad (4)$$

where the subscript α designates a given value of the degree of conversion.

Using a general assumption that the reaction model is independent on the heating rate, Equation (4) can be written for a given degree of conversion and kinetic data at different heating rates β_i ($i = 1, \dots, n$) as

$$\begin{aligned} \frac{A_{\alpha}}{\beta_1} \int_{T_{\alpha - \Delta\alpha,1}}^{T_{\alpha,1}} e^{-E_{\alpha}/RT} dT &= \frac{A_{\alpha}}{\beta_2} \int_{T_{\alpha - \Delta\alpha,2}}^{T_{\alpha,2}} e^{-E_{\alpha}/RT} dT = \dots \\ &= \frac{A_{\alpha}}{\beta_n} \int_{T_{\alpha - \Delta\alpha,n}}^{T_{\alpha,n}} e^{-E_{\alpha}/RT} dT \end{aligned} \quad (5)$$

It follows from the strict fulfillment of Equation (5) that:

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$$\sum_{j \neq i}^n \sum_i^n \frac{\frac{1}{\beta_i} \int_{T_{\alpha-\Delta\alpha,i}}^{T_{\alpha,i}} e^{-E_\alpha/RT} dT}{\frac{1}{\beta_j} \int_{T_{\alpha-\Delta\alpha,j}}^{T_{\alpha,j}} e^{-E_\alpha/RT} dT} = n(n-1) \quad (6)$$

Since $T_{\alpha,i}$ are measured with some experimental errors, Equation (6) can only be satisfied as an approximate equality. Consequently, Equation (6) can be represented as the following condition of minimum:

$$\text{O.F.} = \sum_{j \neq i}^n \sum_i^n \frac{\frac{1}{\beta_i} \int_{T_{\alpha-\Delta\alpha,i}}^{T_{\alpha,i}} e^{-E_\alpha/RT} dT}{\frac{1}{\beta_j} \int_{T_{\alpha-\Delta\alpha,j}}^{T_{\alpha,j}} e^{-E_\alpha/RT} dT} = \min \quad (7)$$

By substituting experimental values of T_α and β into Equation (7) and varying E_α to reach the minimum gives the activation energy value at a given degree of conversion.

The isoconversional method for the determination of the activation energy dependent on the degree of conversion described previously was originally developed by Vyazovkin [3], which is further referred as the Vyazovkin method.

The integral in Equation (7) is the temperature integral, which does not have an exact analytical solution. Many approximations have been proposed [4,5]. In this study, the accurate approximation proposed by Örfão [6] was used:

$$\int_0^T e^{-E/RT} dT = \frac{E e^{-u}}{R u} \frac{0.9999936u^3 + 7.5739391u^2 + 12.4648922u + 3.6907232}{u^4 + 9.5733223u^3 + 25.6329561u^2 + 21.0996531u + 3.9584969} \quad (8)$$

$$u = \frac{E}{RT} \quad (9)$$

Equation (7) cannot be expressed in an explicit form and its analytical derivatives with respect to E_α cannot be obtained. The optimal value of E_α that minimizes Equation (7) cannot be evaluated by means of those optimization methods which require derivatives of the objective function. Therefore, some methods that do not use derivatives are preferred.

The aim of this paper is to show the application of golden section search algorithm to the determination of the activation energy as a function of conversion.

2. Golden section search algorithm

The golden section search is a technique for finding the extremum (minimum and maximum) of a function by successively narrowing the range of values inside which the extremum is known to exist [7]. The technique derives its name from the fact that the algorithm maintains the function values for triples of points whose distances form a golden ratio $\rho = (\sqrt{5} + 1)/2 \approx 1.618$. The golden section search algorithm, which only uses function evaluations, is among the most efficient region elimination methods to optimize functions of a single variable, provided upper and lower bounds are defined [8].

Fig. 1 shows a single step in the golden section search algorithm for finding a minimum. The x parameter represents the horizontal axis, and $f(x)$ represents the vertical axis. The golden section search starts with three points x_A , x_B , and x_C , which satisfy the following conditions: (1) $(x_C - x_B)/(x_C - x_A) = (1/\rho)$, (2) $f(x_A) \geq f(x_B) \leq f(x_C)$. If the $f(x)$ function is single-troughed, we can then be sure that the minimum lies between x_A and x_C . The next step in the minimization process is to “probe” the function by evaluating it at a new value of x , namely x_D . It is most efficient to choose x_D somewhere inside the largest interval. From Fig. 1, it is clear that if the function yields f_{D1} then a minimum lies between x_A and x_D and the new triplet of points will be x_A , x_B , and x_D . However if the function yields the value f_{D2} then a minimum lies between x_B and x_C , and the new triplet of points will be x_B , x_D , and x_C .

Below is a simple program coded in Mathematica to run the golden section search algorithm:

```

x̄A = 50;
x̄C = 350;
ϵ = 10-3;
σ = N[ $\frac{\sqrt{5}-1}{2}$ ];
xB = x̄C - σ * (x̄C - x̄A);
xD = x̄A + x̄C - xB;
fC = OF[x̄C];
fD = OF[xD];
Print[{x̄A, x̄C, x̄C - x̄A}]
While[x̄C - x̄A > ϵ,
  If[N[fC] > N[fD],
    {xB = xB, xB = xD, xD = x̄A + σ * (x̄C - x̄A), fC = fD, fD = OF[xD], Print[{x̄A, x̄C, x̄C - x̄A}]},
    {x̄C = xD, xD = xB, xB = x̄C - σ * (x̄C - x̄A), fD = fC, fC = OF[xB], Print[{x̄A, x̄C, x̄C - x̄A}]}
  ]
]
Print[ $\frac{x̄A + x̄C}{2}$ ]

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