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DIFFERENTIAL NON-LINEAR ISOCONVERSIONAL PROCEDURE FOR EVALUATING THE ACTIVATION ENERGY OF NON-ISOTHERMAL REACTIONS

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Abstract

A differential isoconversional non-linear procedure for evaluating activation energy from non-isothermal data is suggested. This procedure was applied to model reactions (simulations) and to the dehydration of $CaC_2O_4 \cdot H_2O$. The results were compared with those obtained by other isoconversional methods.

Keywords: activation energy, isoconversional methods, non-isothermal kinetics

Introduction

The kinetics of heterogeneous condensed phase reactions is usually described by the Eq. (1):

$$\frac{d\alpha}{dt} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \quad (1)$$

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

From Eq. (1) it follows that the kinetic triplet (A, E, $f(\alpha)$) gives the kinetic description of a certain reaction.

If the experiment is performed in non-isothermal conditions with a constant heating rate (β=dT/dt=*const.*), Eq. (1) turns in:

$$\beta\frac{d\alpha}{dT} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \quad (2)$$

Starting with this equation, various procedures for evaluating the kinetic triplet from non-isothermal data were developed [1]. A classification of these methods was proposed in [2]. In some recent papers [3–5], it was shown that the application of dif-

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ferent methods to the same non-isothermal data leads to different values of the kinetic parameters. On the other hand, it was shown [6–17] that several various kinetic models may relatively correctly describe a thermogravimetric curve. In many cases large differences can be noted among the activation parameters derived from each kinetic model. Consequently, kinetic analysis of the non-isothermal data has been subject of numerous criticisms.

Recently, the progresses made in the area of kinetic analysis of solid state reactions have been mirrored in the results of the ICTAC Kinetics Project [18–22]. The participants at this project applied a variety of computational methods to evaluate the kinetic parameters that characterize some heterogeneous reactions. It was concluded that the isoconversional and multiheating rate methods were particularly successful in correctly describing the multi-step kinetics. Among the isoconversional methods (Friedman (FR) [23], Flynn–Wall–Ozawa (FWO) [24, 25], Kissinger–Akahira–Sunose (KAS) [26], Li–Tang (LT) [27, 28], integral non-linear procedures given by Vyazovkin [29–31]), we will focus below on the integral non-linear procedure (NL-INT) suggested by Vyazovkin and Dollimore [29]. According to this non-linear procedure, for a set of n experiments carried out at different heating rates, the activation energy can be determined at any particular value of α by finding the value of E_α for which the function:

$$S_{\mathrm{INT}} \equiv \sum_{\mathrm{i}}^{\mathrm{n}} \sum_{\mathrm{j} \neq \mathrm{i}}^{\mathrm{n}} \frac{I(E_\alpha, T_{\alpha,\mathrm{i}})\beta_{\mathrm{j}}}{I(E_\alpha, T_{\alpha,\mathrm{j}})\beta_{\mathrm{i}}} \tag{3}$$

is minimum.

In this equation:

$$I(E_\alpha, T_\alpha) = \int_0^{T_\alpha} \left[\exp\left(-\frac{E}{RT}\right)\right] \mathrm{d}T \tag{4}$$

The values of $I(E_\alpha, T_\alpha)$ may be found by numerical integration as well as by means of an accurate approximation (e.g. Senum–Yang approximation [32]). By changing T variable with t, NL-INT procedure allows one to account for temperature deviations in a sample caused by overheating or cooling [30].

In order to derive the above minimum condition, it was assumed that the activation parameters (E and A) do not depend on α, which is equivalent with assumption of the activation parameters independence on the integration limits. On the other hand, it was pointed out [3–5] that when E depends on α, some important differences between E values determined by differential isoconversional method suggested by Friedman (E_{FR}) and those determined by FWO, KAS and LT integral isoconversional methods exist. The reason for these differences is the use of integral methods that assume constant values of E and A in cases when the activation parameters depend on α. It is expected that the NL-INT procedure [29], applied in the cases when the activation energy depends on α, leads to E values different from E_{FR} values. Indeed, in a very recent paper [33] Vyazovkin put in evidence such differences. In order to eliminate them, Vyazovkin [33] suggested a modified integral isoconversional method (MNL-INT) in which the constancy of E_α is assumed for only a small segment $\Delta\alpha$ and the integral (4) with the limits $T_{\alpha-\Delta\alpha}$ and T_α ($t_{\alpha-\Delta\alpha}$ and t_α, in [33]) is evaluated numerically from the non-isothermal data by using trapezoidal rule. This procedure leads to E_α values practically equal with those obtained by Friedman method.

Like other procedures to evaluate E in which the approximation of the temperature integral over a large range of temperature is avoided by integrating the rate equation (Eq. (2)) over a small ranges of variables [34–38], MNL-INT procedure involves: a) the suitable choice of $\Delta\alpha$ that leads to correct values of E; b) the precise evaluation of $T_{\alpha-\Delta\alpha}$ and T_α (or $t_{\alpha-\Delta\alpha}$ and t_α); c) the attribution of α value corresponding to calculated E, when the activation energy depends on α. Obviously, for $\Delta\alpha \to 0$, all these methods [34–38] lead to E values practically equal with those obtained by Friedman method.

In this paper, a differential non-linear isoconversional procedure (NL-DIF) to evaluate the activation energy from non-isothermal data will be suggested. It will be pointed out that the minimum condition used in our procedure also results from the minimum condition used in MNL-INT procedure [33] when $\Delta\alpha \to 0$. The suggested procedure will be applied for some non-isothermal data and the obtained values of the activation energy will be compared with those evaluated by means of NL-INT and MNL-INT methods as well as by the linear isoconversional methods (FR, FWO, KAS and LT).

Differential isoconversional non-linear method (NL-DIF method)

Like in all isoconversional methods [23–31, 33] we assume that the reaction model ($f(\alpha)$) is independent of the heating rate.

The derivation of the minimum condition which grounds NL-DIF method is similar to that given by Vyazovkin and Dollimore [29] for the corresponding minimum condition which grounds NL-INT method.

Equation (2) can be written for a given conversion and a set of experiments performed under different heating rates β_i (i=1,…, n) as:

$$\beta_1\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_1\left[\exp\left(\frac{E_\alpha}{RT_{\alpha,1}}\right)\right]=\beta_2\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_2\left[\exp\left(\frac{E_\alpha}{RT_{\alpha,2}}\right)\right]=\ldots=\beta_n\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_n\left[\exp\left(\frac{E_\alpha}{RT_{\alpha,n}}\right)\right] \quad (5)$$

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

$$\sum_{i}^{n}\sum_{j\neq i}^{n}\frac{\beta_i\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_i\left[\exp\left(\frac{E_\alpha}{RT_{\alpha,i}}\right)\right]}{\beta_j\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_j\left[\exp\left(\frac{E_\alpha}{RT_{\alpha,j}}\right)\right]}=n(n-1) \quad (6)$$

Since $T_{\alpha,\,\mathrm{i}}$ and $\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\mathrm{i}}$ (I=1,…, n) are measured with some experimental errors, Eq. (6) can only be satisfied as an approximate equality. Consequently, Eq. (6) can be represented as the following condition of minimum:

$$\left|\sum_{\mathrm{i}}^{\mathrm{n}}\sum_{\mathrm{j}\neq\mathrm{i}}^{\mathrm{n}}\frac{\beta_{\mathrm{i}}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\mathrm{i}}\left[\exp\left(\frac{E_{\alpha}}{RT_{\alpha,\mathrm{i}}}\right)\right]}{\beta_{\mathrm{j}}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\mathrm{j}}\left[\exp\left(\frac{E_{\alpha}}{RT_{\alpha,\mathrm{j}}}\right)\right]}-n(n-1)\right|=\mathrm{min.} \tag{7}$$

or the equivalent form:

$$S_{\mathrm{D}}\equiv\sum_{\mathrm{i}}^{\mathrm{n}}\sum_{\mathrm{j}\neq\mathrm{i}}^{\mathrm{n}}\frac{\beta_{\mathrm{i}}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\mathrm{i}}\left[\exp\left(\frac{E_{\alpha}}{RT_{\alpha,\mathrm{i}}}\right)\right]}{\beta_{\mathrm{j}}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\mathrm{j}}\left[\exp\left(\frac{E_{\alpha}}{RT_{\alpha,\mathrm{j}}}\right)\right]}=\mathrm{min.} \tag{8}$$

By substituting experimental values of T_{α}, β and $\mathrm{d}\alpha/\mathrm{d}T$ into Eq. (8) and varying E_{α} to reach the minimum, gives the value of the activation energy at a given degree of conversion.

Equations (7) and (8) can be adapted to an arbitrary variation of temperature as well as to isothermal conditions by replacing $\beta(\mathrm{d}\alpha/\mathrm{d}T)$ with $\mathrm{d}\alpha/\mathrm{d}t$.

We will point out below that the minimum condition (8) also results from the minimum condition used in MNL-INT method [33].

For small segment $\Delta\alpha$, the temperature integral (4) can be approximated using the average theorem:

$$I(E_{\alpha},T_{\alpha})=\int_{T_{\alpha-\Delta\alpha}}^{T_{\alpha}}\left[\exp\left(-\frac{E_{\alpha}}{RT}\right)\right]\mathrm{d}T\approx\Delta T\exp\left(-\frac{E_{\alpha}}{RT_{\xi}}\right) \tag{9}$$

where $T_{\alpha-\Delta a}<T_{\xi}<T_{\alpha}$ and $\Delta T=T_{\alpha}-T_{\alpha-\Delta\alpha}$.

Consequently:

$$\frac{I(E_{\alpha},T_{\alpha})}{\beta}=\frac{\Delta\alpha}{\frac{\Delta\alpha}{\Delta T}\beta\left[\exp\left(\frac{E_{\alpha}}{RT_{\xi}}\right)\right]} \tag{10}$$

$\Delta\alpha$ having the same value for all considered heating rates, it results:

$$\beta_1\left(\frac{\Delta\alpha}{\Delta T}\right)_1\left[\exp\left(\frac{E_\alpha}{RT_{\alpha,\xi 1}}\right)\right]=\beta_2\left(\frac{\Delta\alpha}{\Delta T}\right)_2\left[\exp\left(\frac{E_\alpha}{RT_{\alpha,\xi 2}}\right)\right]= \\ ...=\beta_n\left(\frac{\Delta\alpha}{\Delta T}\right)_n\left[\exp\left(\frac{E_\alpha}{RT_{\alpha,\xi n}}\right)\right] \tag{11}$$

For $\Delta\alpha \rightarrow 0$: $T_{\alpha,\,\xi i} \rightarrow T_{\alpha,\,i}$ and Eq. (11) turns into Eq. (5) that grounds the NL-DIF method.

NL-DIF procedure corresponds to the differential linear method given by Friedman (FR) and to MNL-INT procedure. Consequently, it is expected that, when the activation parameters change with α, E evaluated by NL-DIF method to be equal with those by FR method and MNL-INT procedure, but different from those evaluated by integral isoconversional methods (FWO, KAS, LT, NL-INT).

Simulations

Firstly, NL-DIF procedure will be checked for two sets of non-isothermal simulated data corresponding to a single reaction and two consecutive reactions. Obviously, unlike the experimental data, these data are not affected by noises and, therefore, are suitable for the verification of the suggested procedure.

Simulated thermogravimetric curves for a single reaction

The data were simulated for $f(\alpha)=1-\alpha$; $E=58.5$ kJ mol^{-1}; $A=900$ s^{-1} and the following heating rates: 0.5, 0.9, 5, 10 and 15 K min^{-1}.

The values of the activation energy obtained by means of all isoconversional methods (FR, FWO, KAS, LT, NL-INT, MNL-INT and NL-INT) are practically equal to E value used for simulation and, obviously do not depend on the conversion degree. The straight lines corresponding to the linear methods (FR, FWO, KAS and LT) exhibit a correlation coefficient $|r|\geq 0.99940$. We suggest that for non-linear procedures, $e=1-|S-n(n-1)|/n(n-1)$ is a measure of the accuracy in E_α evaluation (S is the double sum involved in the corresponding non-linear procedure). For all considered non-linear procedures, it was obtained $e\geq 0.99921$.

Simulated thermogravimetric curves for two consecutive reactions

A strong variation of the apparent activation energy with α may be observed for a process that involves two consecutive decomposition steps:

$$\mathbf{A}(s) \xrightarrow{k_1} \mathbf{B}(s) + \nu_1\mathbf{G_1}(g) \tag{I}$$

$$\mathbf{B}(\mathrm{s}) \xrightarrow{k_2} \mathbf{C}(s) + \nu_2\mathbf{G_2}(g) \tag{II}$$

where **A, B** and **C** are solid compounds and $\mathbf{G_1}$ and $\mathbf{G_2}$ are gaseous products.

The rate constants, k_1 and k_2, are expressed by Arrhenius equation:

$$k_i = A_i \exp\left(-\frac{E_i}{RT}\right) \tag{12}$$

where $i=1$ for reaction I and $i=2$ for reaction II.

Both successive reactions are characterized by a value of the reaction order that equals one. The following values of the activation parameters are going to be considered: $E_1=58.5$ kJ mol^{-1}; $A_1=9\cdot10^2$ s^{-1}; $E_2=125.4$ kJ mol^{-1}; $A_1=5\cdot10^8$ s^{-1}.

The system of differential kinetic equations is then [39]:

$$\begin{aligned} \beta\frac{d\alpha_1}{dT} &= k_1(1-\alpha_1) \\ \beta\frac{d\alpha_2}{dT} &= k_2(1-\alpha_2) \end{aligned} \tag{13}$$

where α_1 and α_2 are respectively the values of the degree of conversion for reactions I and II (α_i is the ratio between the mass of the gaseous product at a given moment and the maximum mass of this product which can be evolved in reaction).

The numeric method for solving this equations system is given in [40].

The particular case $\nu_1 M_1=\nu_2 M_2$, where M_i is the molecular mass of the gaseous product G_i, and for which the total degree of conversion, α, is given by: $\alpha=(\alpha_1+\alpha_2)/2$ will be considered.

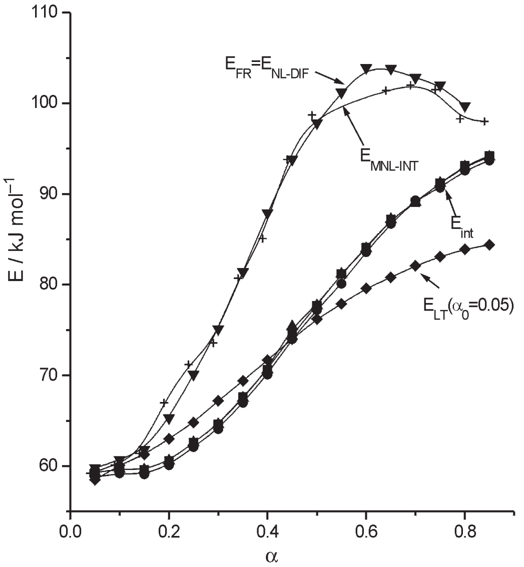

Fig. 1 Dependence of the apparent activation energy evaluated by means of isoconversional methods on the conversion degree, for simulated two consecutive reactions. $E_{int}=E$ evaluated by FWO, KAS and NL-INT methods; $E_{FR}=E$ evaluated by Friedman method; $E_{NL-DIF}=E$ evaluated by NL-DIF method; $E_{LT}(\alpha_0=0.05)=E$ evaluated by LT method for the inferior limit of integration $\alpha_0=0.05$; $E_{MNL-INT}=E$ evaluated by MNL-INT procedure

The thermogravimetric curves were calculated for 25 heating rates with values in the range 0.15–20 K min^{-1}. Through numeric differentiation of thermogravimetric curves, the curves $d\alpha/dT$ *vs.* T were plotted. In such way, it was shown that for 0.15 K $\text{min}^{-1} \leq \beta \leq$ 2 K min^{-1} the $d\alpha/dT$ *vs.* T curves exhibit two distinct maxima corresponding to the two reactions and for 2.25 K $\text{min}^{-1} \leq \beta \leq 20$ K min^{-1}, each $d\alpha/dT$ *vs.* T curve exhibit a single maximum. For this last range of β, reactions I and II are not separated in curves. Consequently, for this range of heating rates, the values of the apparent activation energy were determined by means of the isoconversional methods. The obtained dependencies are displayed in Fig. 1, from which one can see:

- the used differential methods (FR and NL-DIF) as well as MNL-INT procedure lead to practically the same values of E which are considerable higher than those obtained by means of the integral methods (FWO, KAS, NL-INT); the absolute maximum relative deviation of E_{int} with respect to $E_{\text{NL-DIF}} \equiv E_{\text{FR}} \approx E_{\text{MNL-INT}}$ is≈21%);
- except E_{LT}, all the considered integral methods (FWO, KAS, NL-INT) give practically the equal values of the apparent activation energy (the differences between E_{LT} and E_{int} can be explained by the dependence of E_{LT} on α_0, when E changes with α [41]).

All straight lines corresponding to use linear isoconversional procedures have $|r| \geq 0.9964$. The values of $e = 1 - |S - n(n-1)|/n(n-1)$ for used non-linear methods are higher than 0.9971.

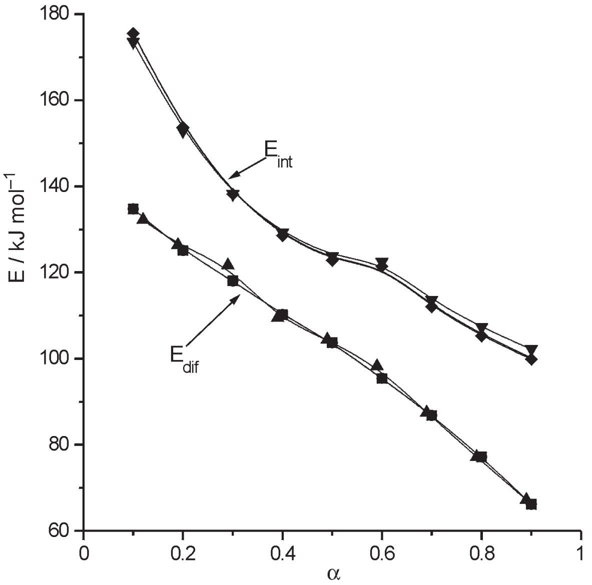

Fig. 2 Dependence of the apparent activation energy evaluated by means of isoconversional methods on the conversion degree, for dehydration of $CaC_2O_4 \cdot H_2O$. $E_{\text{int}} = E$ evaluated by FWO (▾), KAS (▾) and NL-INT (+ superposed on ◆) methods; $E_{\text{dif}} = E$ evaluated by FR (■), MNL-INT (▲) and NL-DIF (superposed on ■) methods

Experimental example: dehydration of $CaC_2O_4{\cdot}H_2O$

In this section, we test the suggested isoconversional procedure (NL-DIF) against experimental data corresponding to the dehydration of $CaC_2O_4{\cdot}H_2O$, to compare E values obtained by our procedure with those obtained by other isoconversional methods (FR, FWO, KAS, MNL-INT, NL-INT).

The thermogravimetric curves corresponding to the dehydration of $CaC_2O_4{\cdot}H_2O$ in static air atmosphere at the heating rates of 0.987, 2.353, 4.988 and 9.573 K min^{-1} were recorded with a DuPont 1090 thermal analyzer. The obtained results were reported previously by Urbanovici and Segal [37].

The dependence of the activation energy, obtained by means of isoconversional methods, on the conversion degree is shown in Fig. 2. For a given value of α, $E_{FR}=E_{MNL\text{-}INT}=E_{NL\text{-}DIF}<E_{FWO}=E_{KAS}=E_{NL\text{-}INT}$. In a very recent paper [33], Vyazovkin reported similar results ($E_{FR}=E_{MNL\text{-}INT}<E_{NL\text{-}INT}$). All straight lines corresponding to use linear isoconversional procedures have $|r|\geq 0.992$. The values of $e=1-|S-n(n-1)|/n(n-1)$ for used non-linear methods are higher than 0.991.

Conclusions

A differential isoconversional non-linear procedure (NL-DIF) to evaluate the activation energy from non-isothermal data has been suggested.

It was pointed out that the minimum condition that ground this procedure results from minimum condition used in MNL-INT procedure suggested by Vyazovkin, for $\Delta\alpha \rightarrow 0$.

If the activation energy does not change with the conversion degree, NL-DIF procedure leads to values of the activation energy, which are in good agreement with those obtained by means of other differential and integral isoconversional methods.

If the activation energy varies with the conversion degree, NL-DIF procedure leads to E values identical with those obtained by Friedman and MNL-INT methods, but which differ significantly from those evaluated by means of integral isoconversional methods.

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