CRITICAL CONSIDERATIONS ON THE ISOCONVERSIONAL METHODS
III. On the evaluation of the activation energy from non-isothermal data

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Abstract

The differential and integral isoconversional methods for evaluation the activation energy, described in the first note of this series, were applied for:

    a) simulated data for two successive reactions;
    b) dehydration of calcium oxalate monohydrate.

It was shown that for these systems the activation energy depends on the conversion degree as well as on the method of evaluation.

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

Introduction

In the first note of this series [1] the differential and integral isoconversional methods for the evaluation of the activation energy from non-isothermal data were critically analyzed. It was shown that if the activation energy depends on the conversion degree, the differential method (Friedman's method) gives values of the activation energy, which differ from those obtained using an integral isoconversional method. This statement is going to be verified for:

    a) simulated data for two successive reactions;
    b) dehydration of calcium oxalate monohydrate.

Simulated data for two successive reactions

Let us consider that solid compound A undergoes two successive decompositions:

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

$$B(s) \xrightarrow{k_1} C(s) + \nu_2 G_2(g) \tag{II}$$

where B and C are solid compounds and G_1 and G_2 are gaseous products.

We assume that the rate constants, k_1 and k_2, are expressed by Arrhenius equation with the following activation parameters: E_1=58.5 kJ mol^{-1}; A_1=9·10^2 s^{-1}; E_2=125.4 kJ mol^{-1}; A_2=5·10^8 s^{-1} (the indexes 1 and 2 refer to the reaction I and reaction II, respectively; E is the activation energy and A is the pre-exponential factor). The kinetic analysis of this sequence of successive reactions for isothermal conditions was performed in the note II from this series. For non-isothermal linear heating with the rate β, the corresponding kinetic equations have the forms:

$$\beta \frac{d\alpha_1}{dT} = k_1(1-\alpha_1) \tag{1}$$

$$\beta \frac{d\alpha_2}{dT} = k_2(\alpha_1-\alpha_2) \tag{2}$$

where α_1 and α_2 are the values of the conversion degree for reactions I and II, respectively.

The solution of the Eq. (1) can be written in the form:

$$\alpha_1 - 1 = (\alpha_1(T_0)-1)\exp\left\{ -\frac{A_1}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E_1}{RT} \right) dT \right\} \tag{3}$$

The integral in the right hand side of relation (3) cannot be expressed in analytical form. In order to obtain numeric approximations we used IMT (Iri , Moriguki and Takasawa) rule [3]. The temperature range was comprised between T_0=300 K and T=800 K. The obtained results are in a very good agreement with those obtained by using the values of temperature integral tabulated by Zsakó [4].

Once the function $\alpha_1(T)$ was determined, the relation (2) can be written as the following linear differential equation:

$$\frac{d\alpha_2}{dT} + \frac{A_2\alpha_2}{\beta}\exp\left(-\frac{E_2}{RT} \right) = \frac{A_2\alpha_1}{\beta}\exp\left(-\frac{E_2}{RT} \right) \tag{4}$$

The solution of this equation with a given initial condition can be expressed by means of the variation of constants (Duhamel's formula; see for example [5]). The resulting formula involved two successive indefinite integrals, which cannot be expressed in a closed form and, consequently, is of little help in this case. On the other hand, the application of direct integration methods for initial value problems of ordinary differential equations (as Runge–Kutta methods) fails to give the solution due to instability associated with the large values of the quantity $A_2/\beta \exp(-E_2/RT)$. In order to overcome these difficulties we used the Rosenbrock's generalization of the Runge–Kutta scheme [6]. We have used also an automatic stepsize adjustment algo-

rithm based on Kaps and Rentrop work [7]. The code written in FORTRAN was based on fourth-order Rosenbrock formula. All the computations were performed in double precision.
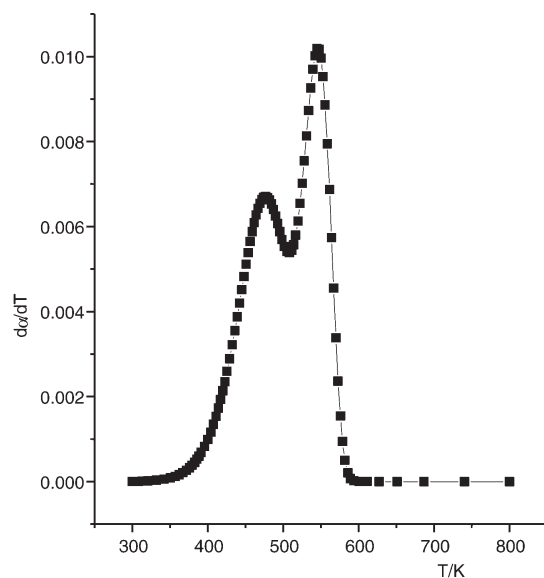
Fig. 1 The DTG curve obtained for two successive reactions ($\beta=1.00\cdot10^{-2}$ K s^{-1})
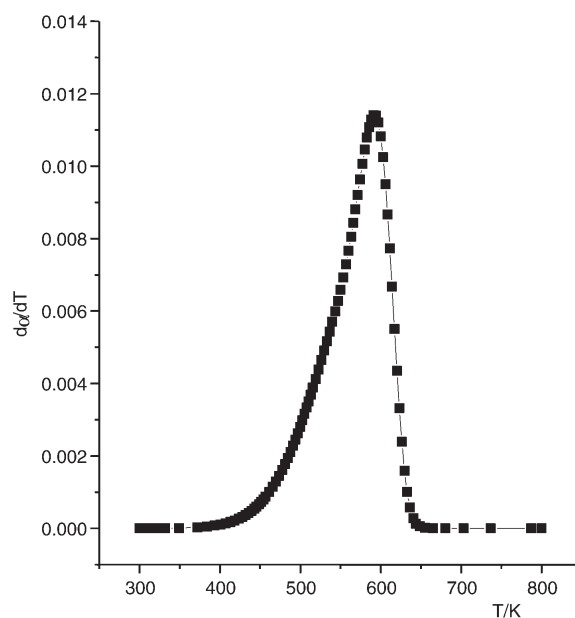
Fig. 2 The DTG curve obtained for two successive reactions ($\beta=1.00\cdot10^{-1}$ K s^{-1})

Like in note II from this series, we will consider the particular case $\nu_1 M_1 = \nu_2 M_2$, where M_1 is the molecular mass of the gaseous compound G_i. In this case the overall degree of conversion, α, is given by: $\alpha = (\alpha_1 + \alpha_2)/2$.

TG curves were calculated for 25 heating rates with values in the range $2.50 \cdot 10^{-3} - 3.33 \cdot 10^{-1}$ K s^{-1}. Through numeric differentiation of TG curves, the curves DTG (dα/dT $vs.$ T) were plotted. In such a way, it was shown that for $2.50 \cdot 10^{-3} \leq \beta \leq 1.67 \cdot 10^{-2}$ K s^{-1} the DTG curves exhibit two distinct maxima corresponding to the two reactions (Fig. 1) and for $3.75 \cdot 10^{-2} \leq \beta \leq 3.33 \cdot 10^{-1}$ K s^{-1} the DTG curves exhibit a single maximum (Fig. 2).

For $2.50 \cdot 10^{-3} \leq \beta \leq 1.67 \cdot 10^{-2}$ K s^{-1}, in order to evaluate the activation energy, Kissinger's method [8] was applied to the two DTG maxima. For the first maximum $E_K^{(1)} = 51.6 \pm 1.8$ kJ mol^{-1} and for the second one $E_K^{(2)} = 127.2 \pm 6.0$ kJ mol^{-1}. $E_K^{(1)}$ value is close to E_1 and $E_K^{(2)}$ value is close to E_2. Thus, in this range of heating rates, the two reactions (I and II) in [2] are separated in the DTG curves.

For $3.75 \cdot 10^{-2} \leq \beta \leq 3.33 \cdot 10^{-1}$ K s^{-1}, reactions I and II are not separated in the DTG curves. For this range of heating rates we shall analyze the consequences of expressing the reaction rate through relation (2) [1] in which E and A are the apparent activation parameters. Firstly, let us notice that the Kissinger [8] activation energy value corresponding to the DTG maxima, $E_K = 104.2 \pm 2.2$ kJ mol^{-1}, lies between E_1 and E_2. The use of Kissinger's method requires a good constancy of the conversion degree at the top of the DTG peak [9]. As shown in Table 1, unlike the case of single reaction (simulated for $E = 125.4$ kJ mol^{-1}; $A = 5 \cdot 10^8$ s^{-1} and $f(\alpha) = 1 - \alpha$, and 15 heating rates in the range $4.17 \cdot 10^{-3} - 3.67 \cdot 10^{-1}$ K s^{-1}), for two successive reactions an important variation of α_{max} when a relative wide range of heating rates was used, can be noticed. A similar result was recently reported by Sbirrazzuoli $et\ al.$ [10] who analyzed a complex process consisting in two parallel reactions in the framework of the $reaction\ order$ model.

Table 1 Peak temperatures (T_{max}) and values of the corresponding degree of conversion (α_{max}) for various heating rates (β) on simulated TG curves

Single reaction*			Two successive reactions		
β/K s^{-1}	T_{max}/K	α_{max}	β/K s^{-1}	T_{max}/K	α_{max}
$4.17 \cdot 10^{-3}$	531.9	0.62	$3.75 \cdot 10^{-2}$	571.0	0.77
$8.33 \cdot 10^{-3}$	543.4	0.60	$5.00 \cdot 10^{-2}$	575.0	0.73
$2.50 \cdot 10^{-2}$	563.6	0.59	$1.00 \cdot 10^{-1}$	592.0	0.71
$5.00 \cdot 10^{-2}$	578.8	0.62	$1.67 \cdot 10^{-1}$	605.6	0.69
$1.00 \cdot 10^{-1}$	592.2	0.60	$2.50 \cdot 10^{-1}$	617.9	0.67
$1.67 \cdot 10^{-1}$	604.2	0.61	$3.33 \cdot 10^{-1}$	626.6	0.66
$2.33 \cdot 10^{-1}$	611.6	0.60			
$3.67 \cdot 10^{-1}$	621.7	0.60			

*Simulated data for: $E = 125.4$ kJ mol^{-1}; $A = 5 \cdot 10^8$ s^{-1}; $f(\alpha) = 1 - \alpha$

For $3.75 \cdot 10^{-2} \leq \beta \leq 3.33 \cdot 10^{-1}$ K s^{-1} and $0.05 \leq \alpha \leq 0.80$, values of E_{FR}, E_{FWO}, corrected using Flynn's procedure [1] (four iterations), E_V and E_{LT} were calculated (indexes *FR*, *FWO*, *V* and *LT* refer to the isoconversional methods suggested by Friedman; Flynn, Wall and Ozawa; Vyazovkin and Li and Tang, respectively; the corresponding relations which ground these methods are given and discussed in the note I from this series [1]). For all isoconversional straight lines, the correlation coefficients higher than 0.996 were obtained. As shown in Fig. 3, the values E_{FWO} equal practically E_V, but are lower than E_{FR}. The lowest values of the activation energy are obtained by Li and Tang method. Figure 4 shows the dependence of the deviations of the activation energy obtained by integral methods with respect to E_{FR} ($e\%$), on the degree of conversion. As one can see, $e\%$ exhibits a minimum ($\approx$–22% for E_{FWO} and E_V; $\approx$–27% for E_{LT}) for α=0.50. For $0.25 \leq \alpha \leq 0.70$, for all integral methods, $|e\%|>10\%$, i.e. the deviations of E_{FWO}, E_V and E_{LT} with respect E_{FR} higher than the usually admitted errors on activation energy evaluation.

From a comparison of the results shown in Fig. 3 with those shown in Fig. 3 – note II [2], it turns out that at the analysis of isothermal data as well as the non-isothermal ones, E values obtained with the help of a differential method are higher than those obtained using an integral method. We will focus on E values obtained through a differential method using isothermal as well as non-isothermal data. One has to notice that E_{dif} values, obtained from isothermal data (Fig. 3 – note II [2]), differ from E_{FR}, obtained from non-isothermal data. This result is probably due to the bending of the isoconversional lines. In order to verify this last statement, E_{FR} and E_{dif}
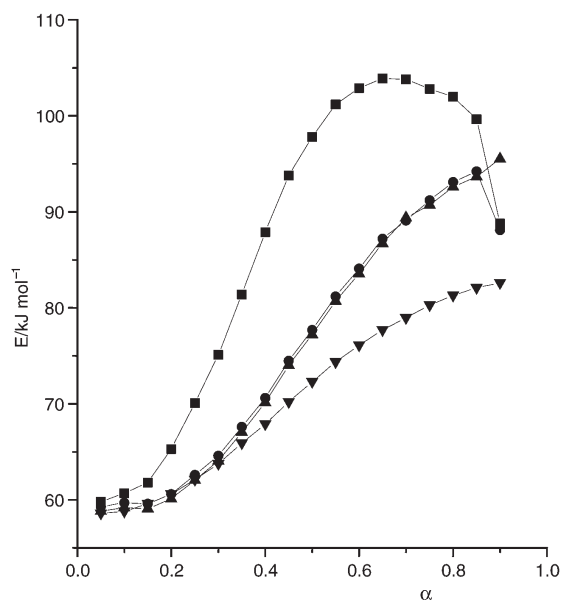
Fig. 3 Dependences *E vs.* α for simulated TG curves corresponding to two successive reactions ($3.75 \cdot 10^{-2} \leq \beta \leq 3.33 \cdot 10^{-1}$ K s^{-1}) $\blacksquare - E_{FR}$; $\bullet - E_{FWO}$; $\blacktriangle - E_V$; $\blacktriangledown - E_{LT}$

were evaluated for relative narrow temperature ranges (40 K). The obtained results are shown in Table 2. For the same pair (α, ΔT), the values E_{FR} and E_{dif} are close. Besides, for the α value which allowed to consider several temperature ranges, the increasing or decreasing sense of change of activation energy with ΔT is the same for E_{FR} as well as for E_{dif}. Even the non-realistic values of the apparent activation energy ($E>125.4$ kJ mol^{-1}) are obtained for E_{FR} as well as for E_{dif}, if the same values of the pair (α, ΔT) are used.

Table 2 Dependence of E_{FR} and E_{dif} on the temperature range for which the straight lines $\ln\beta(d\alpha/dt)$ *vs.* $1/T$ (non-isothermal data) and $\ln(d\alpha/dt)$ *vs.* $1/T$ (isothermal data) were plotted

ΔT/K	α	E_{FR}/kJ mol^{-1}	E_{dif}/kJ mol^{-1}	$\dfrac{E_{FR}-E_{dif}}{E_{dif}}\cdot 100$
473–513	0.05	59.9	58.8	1.9
473–513	0.10	60.6	59.4	2.0
473–513	0.20	62.2	60.9	2.1
513–553	0.20	65.2	65.0	0.3
473–513	0.30	64.1	64.4	−0.5
513–553	0.30	70.7	71.4	−1.0
553–593	0.30	80.1	77.8	3.0
473–513	0.40	71.0	72.9	−2.6
513–553	0.40	83.4	82.2	1.5
553–593	0.40	89.5	85.2	5.0
473–513	0.50	111.0	106.3	4.4
513–553	0.50	105.0	100.8	4.2
553–593	0.50	98.5	93.1	5.8
473–513	0.55	140.5	142.2	−1.2
513–553	0.55	120.2	112.7	6.7
553–593	0.55	103.9	97.3	6.8
513–553	0.60	127.6	123.7	3.1
553–593	0.60	109.8	101.4	8.3
513–553	0.65	130.8	130.6	0.2
553–593	0.65	113.4	105.5	7.5
513–553	0.70	126.5	131.3	−3.7
553–593	0.70	120.8	109.2	10.6
593–623	0.70	94.9	88.6	7.1

ΔT – temperature range for which the isoconversional straight lines were plotted in isothermal and non-isothermal conditions; α – degree of conversion; E_{FR} – activation energy evaluated using Friedman's method; E_{dif} – activation energy evaluated by help of the differential method from isothermal data
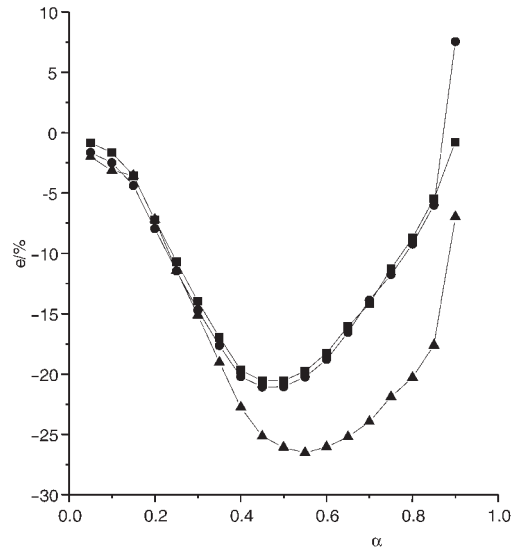
Fig. 4 The dependences $e\%$ *vs.* α for the data shown in Fig. 3

$$\blacksquare - e\%=\frac{E_{FWO}-E_{FR}}{E_{FR}}\cdot 100; \quad \bullet - e\%=\frac{E_V-E_{FR}}{E_{FR}}\cdot 100; \quad \blacktriangle - e\%=\frac{E_{LT}-E_{FR}}{E_{FR}}\cdot 100$$
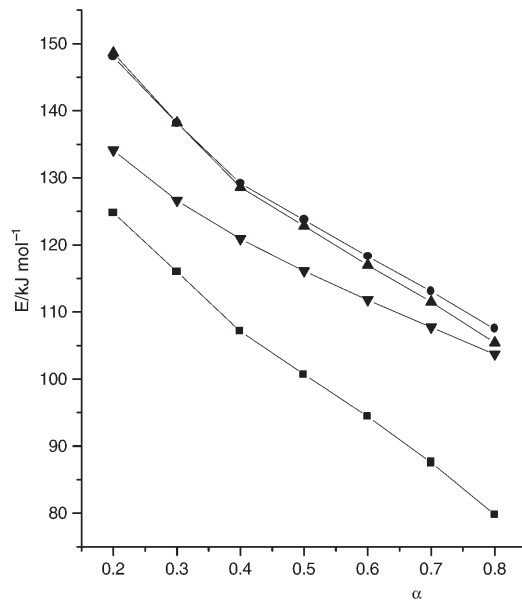

Fig. 5 Dependencies E *vs.* α for the dehydration of calcium oxalate monohydrate
$\blacksquare - E_{FR}; \bullet - E_{FWO}; \blacktriangle - E_V; \blacktriangledown - E_{LT}$

Dehydration of calcium oxalate monohydrate

Thermogravimetric data from [11] for heating rates of $1.645 \cdot 10^{-2}$, $3.921 \cdot 10^{-2}$, $8.313 \cdot 10^{-2}$ and $1.596 \cdot 10^{-1}$ K s^{-1} were used.

The activation energy was evaluated by means of the three previously mentioned isoconversional methods. In order to apply Friedman's method, $d\alpha/dt$ values were evaluated numerically. The correct values of E_{FWO} were calculated using the first procedure suggested by Flynn [1] (three iterations). For all the isoconversional straight lines, values of the correlation coefficient of the linear regression higher than 0.997 were obtained. As shown in Fig. 5, E_{FWO} values equal practically E_V values but E values obtained with the help of integral methods are higher than those obtained using Friedman's method. The activation energy decreases progressively with the degree of conversion. This decrease was explained by Vyazovkin and Linert [12] through the complex mechanism of decomposition of $CaC_2O_4 \cdot H_2O$. According to these authors, this process manifest itself kinetically as a change from a reversible dehydration to an irreversible one when the temperature is increased.
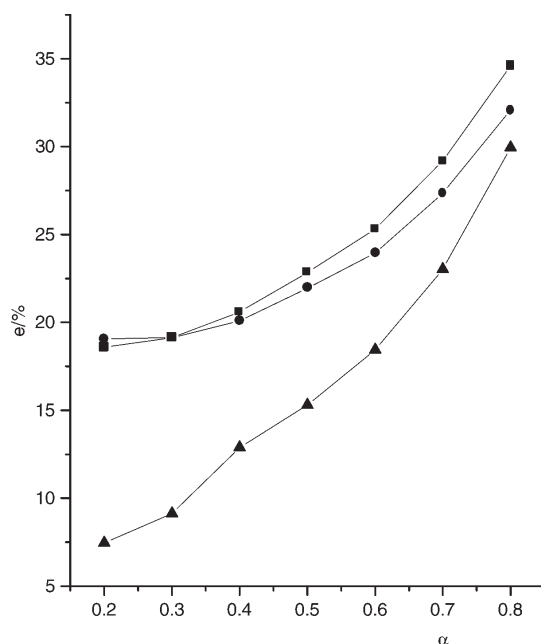

Fig. 6 The dependencies $e\%$ *vs.* α for the data shown in Fig. 5

$$\blacksquare - e\% = \frac{E_{FWO} - E_{FR}}{E_{FR}} \cdot 100; \quad \bullet - e\% = \frac{E_V - E_{FR}}{E_{FR}} \cdot 100; \quad \blacktriangle - e\% = \frac{E_{LT} - E_{FR}}{E_{FR}} \cdot 100$$

Figure 6 shows the dependence of the deviations of the activation energy values obtained by integral methods with respect to E_{FR} ($e\%$), on the degree of conversion. As one

can see, for all integral methods, e% increases with α. The deviations higher than 10% are higher than the usually admitted error in the activation energy evaluation.

Conclusions

1. The differential and integral isoconversional methods to evaluate the activation energy from non-isothermal data were applied for:

- simulated data for two successive reactions;
- dehydration of calcium oxalate monohydrate.

2. For the two used data, the apparent activation energy values, no matter the applied method, depend on the conversion degree.

3. The values of the apparent activation energy obtained by different methods, applied to the same non-isothermal data, are different.

4. The integral methods (Flynn–Wall–Ozawa, Vyazovkin, and Li and Tang methods) are based on the integration of the rate equation for constant activation parameters. That is the reason for we consider that for activation parameters dependent on conversion degree, only the differential isoconversional method (Friedman's method) is suitable.

5. The use of the differential method, for isothermal and non-isothermal data corresponding to two successive reactions, showed that, in both cases the activation energy values depend on the temperature range. For the same temperature range and activation parameters used for simulation, a good agreement between the values of apparent activation energy obtained from isothermal and non-isothermal data was put in evidence.

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