

# An integral method to determine variation in activation energy with extent of conversion

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## Abstract

This paper proposes an integral method that uses local heating rates to evaluate the activation energy dependence on the extent of conversion. The method leads to consistent results with those from a differential isoconversional technique while regular integral isoconversional technique results in systematic errors in the activation energy with the extent of conversion. The method is validated from (1) simulated thermal analysis curves for a single reaction model, (2) simulated thermal analysis curves involving in two parallel reactions, and (3) non-isothermal dehydration of calcium oxalate monohydrate.

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## 1. Introduction

Model-free isoconversional methods are the most reliable methods for the calculation of activation energies of thermally activated reactions. A large number of isoconversional methods have been proposed. Isoconversional techniques make it possible to estimate the activation energy of a process as a function of the extent of conversion,  $\alpha$ . Analysis of the activation energy dependence on  $\alpha$  provides important clues about reaction mechanism [1–5]. It is noteworthy [1,6,7] that, if the activation energy depends on  $\alpha$ , the differential method suggested by Friedman [8] gives values of the activation energy which differ from those obtained with integral isoconversional methods such as FWO [9,10], Li–Tang [11], KAS [12] and Vyazovkin methods [13,14]. The reason is that integral isoconversional techniques assume constant values of  $E$  and  $A$  even when the kinetic parameters depend on the extent of conversion. This assumption obviously introduces some systematic error, if  $E$  and  $A$  vary with  $\alpha$ . This systematic error does not appear in the Friedman method, and the systematic

error of an integral isoconversional method can be estimated by comparing it against the Friedman method. Because the Friedman method employs instantaneous rate values, it is sensitive to experimental noise and tends to be numerically unstable [15], especially when the rate is estimated by numerical differentiation of experimental data. This comparison is therefore more effectively performed on smoothed data that do not contain experimental noise.

Improved methods have recently been proposed to eliminate this systematic error. Vyazovkin [16] suggested a modified integral non-linear isoconversional procedure (MNL-INT), in which the constancy of activation energy  $E_\alpha$  is assumed for only a small segment,  $\Delta\alpha$ . When the segment  $\Delta\alpha$  is small enough, this procedure leads to  $E_\alpha$  values practically equal to those obtained by the Friedman technique.

Budrugaec [17] proposed a differential non-linear isoconversional procedure (NL-DIF) to evaluate the activation energy from non-isothermal data. This procedure also uses the minimum condition used in MNL-INT procedure when  $\Delta\alpha \rightarrow 0$ . When the activation parameters change with  $\alpha$ ,  $E_\alpha$  evaluated by the NL-DIF method is equal to that by the Friedman and MNL-INT procedures.

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Both NL-DIF and MNL-INT procedures make use of numerical iterations to find  $E_\alpha$  values that satisfy the minimum condition suggested by Vyazovkin [13]. This paper presents a local linear integral isoconversional procedure (LL-INT) for evaluation of activation energy dependence under non-isothermal conditions. The result is in agreement with that of Friedman method performed on simulated data that do not contain experimental noise.

## 2. Theoretical considerations and calculation procedure

The relationship between rate of reaction and extent of reaction is generally expressed in the form:

$$d\alpha/dt = A \exp(-E/RT) f(\alpha) \quad (1)$$

where  $\alpha$  is the extent of conversion,  $t$  the time,  $T$  the temperature,  $A$  the pre-exponential factor,  $E$  the activation energy,  $R$  the gas constant and  $f(\alpha)$  the differential reaction kinetic model, in which  $A$ ,  $E$ ,  $f(\alpha)$  are called the kinetic triplet of a reaction. A non-isothermal solid-state reaction with a programmed linear heating rate  $\beta$  is considered. As in all isoconversional methods, it is assumed that the reaction model is independent of the heating rate, but both the activation energy  $E$  and pre-exponential factor  $A$  are dependent on the conversion  $\alpha$ . The local heating rate [18,19] may deviate from  $\beta$ , however, for only a small segment  $[\alpha - \Delta\alpha, \alpha + \Delta\alpha]$ ,  $\beta_\alpha$ ,  $E_\alpha$  and  $A_\alpha$  may be assumed constant. Integrating Eq. (1) with the limits  $T_{\alpha - \Delta\alpha}$  and  $T_{\alpha + \Delta\alpha}$ , one gets

$$g(\alpha)|_{\alpha - \Delta\alpha}^{\alpha + \Delta\alpha} = \frac{A_\alpha}{\beta_\alpha} \int_{T_{\alpha - \Delta\alpha}}^{T_{\alpha + \Delta\alpha}} \exp(-E_\alpha/RT) dT \quad (2)$$

where  $g(\alpha)$  is the integral reaction kinetic model. Let  $P(x) = \int_0^x \exp(-1/x) dx$ , in which  $x = RT/E$ . Taylor series of the function  $P(x + \delta)$  and  $P(x - \delta)$  around the point  $x$  is developed to calculate the integral:

$$P(x + \delta) = \sum_{n=0}^{\infty} (P^{(n)}(x)/n!) \delta^n \quad (3)$$

$$P(x - \delta) = \sum_{n=0}^{\infty} (P^{(n)}(x)/n!) (-1)^n \delta^n \quad (4)$$

In Eqs. (3) and (4),

$$P^{(1)}(x) = \exp(-1/x), \quad P^{(2)}(x) = x^{-2} \exp(-1/x),$$

$$P^{(3)}(x) = x^{-4} (1 - 2x) \exp(-1/x)$$

Eq. (3) being subtracted from Eq. (4), one obtains

$$\begin{aligned} P(x + \delta) - P(x - \delta) \\ = 2\delta \exp(-1/x) + (1/3)\delta^3 x^{-4} (1 - 2x) \exp(-1/x) + \dots \end{aligned} \quad (5)$$

If  $\delta$  is small enough, taking the first two terms from Eq. (5), we obtain

$$P(x)|_{x-\delta}^{x+\delta} = 2\delta \exp(-x) [1 + (1/6)\delta^2 x^{-4} (1 - 2x)] \quad (6)$$

let  $\delta = kx$ , in which  $k$  denotes a small deviation from  $x$ . Eq. (6) becomes

$$P(x)|_{x-\delta}^{x+\delta} = 2\delta \exp(-x) [1 + (k/x)^2 (1 - 2x)/6] \quad (7)$$

In Eq. (7), the term  $(k/x)^2 (1 - 2x)/6$  can be considered as a correction term with respect to the approximation developed previously [20–22]. That is

$$P(x)|_{x-\delta}^{x+\delta} = 2\delta \exp(-x) \quad (8)$$

If the segment  $[\alpha - \Delta\alpha, \alpha + \Delta\alpha]$  is small enough,  $T_{\alpha + \Delta\alpha} + T_{\alpha - \Delta\alpha} \approx 2T_\alpha$ . Taking into account the fact that  $\delta = R(T_{\alpha + \Delta\alpha} - T_{\alpha - \Delta\alpha})/2E_\alpha$ ,  $k = (T_{\alpha + \Delta\alpha} - T_{\alpha - \Delta\alpha})/2T_\alpha$  Eq. (7) takes the following form:

$$\begin{aligned} \int_{T_{\alpha - \Delta\alpha}}^{T_{\alpha + \Delta\alpha}} \exp(-E_\alpha/RT) dT \\ = (T_{\alpha + \Delta\alpha} - T_{\alpha - \Delta\alpha})(1 + a) \exp(-E_\alpha/RT_\alpha), \\ \alpha = (1/24)[E_\alpha(T_{\alpha + \Delta\alpha} - T_{\alpha - \Delta\alpha}/RT_\alpha^2)]^2 (1 - 2RT_\alpha/E_\alpha) \end{aligned} \quad (9)$$

Rearranging Eq. (9), and taking the logarithms of both sides, one gets Eq. (10):

$$\begin{aligned} \ln((\beta_\alpha/(T_{\alpha + \Delta\alpha} - T_{\alpha - \Delta\alpha}))(1/(1 + a))) \\ = \ln A_\alpha - \ln[g(\alpha)]_{\alpha - \Delta\alpha}^{\alpha + \Delta\alpha} - E_\alpha/RT_\alpha \end{aligned} \quad (10)$$

Eq. (10) is the basis of local linear integral isoconversional method (LL-INT). According to the isoconversional principle, the reaction rate at a constant conversion depends only on the reaction temperature. Also, values of  $\ln A_\alpha - \ln[g(\alpha)]_{\alpha - \Delta\alpha}^{\alpha + \Delta\alpha}$  will be the same as  $\alpha$  and  $\Delta\alpha$ . To solve Eq. (10), the following iterative procedure is proposed.

- I. For  $a = 0$ , plotting  $\ln(\beta_\alpha/(T_{\alpha + \Delta\alpha} - T_{\alpha - \Delta\alpha}))$  versus  $1/RT_\alpha$ , activation energy  $E_\alpha^{(1)}$  is obtained from the slope of the line.
- II.  $E_\alpha^{(1)}$  being introduced into Eq. (10), the value of  $a$  is calculated. Plotting  $\ln((\beta_\alpha/(T_{\alpha + \Delta\alpha} - T_{\alpha - \Delta\alpha}))(1/(1 + a)))$  versus  $1/RT_\alpha$ , activation energy  $E_\alpha^{(2)}$  is obtained from the slope of the line.
- III. Let  $E_\alpha^{(2)}$  replace  $E_\alpha^{(1)}$  and repeat procedure II until

$$|E_\alpha^{(1)} - E_\alpha^{(2)}| < \varepsilon \quad (11)$$

where  $\varepsilon$  is preset as the iteration accuracy, which was 0.001 kJ/mol for the calculations in this paper. The value of final  $E_\alpha$  is determined. If the segment  $[\alpha - \Delta\alpha, \alpha + \Delta\alpha]$  is small enough, i.e.  $\Delta\alpha \rightarrow 0$ , this method will lead to  $E$  values practically equal to those obtained by the differential isoconversional method.

The inaccuracy in approximations for temperature integral is one of the main sources of error involving the isoconversional methods [23]. The values of  $P(x)$  over small intervals

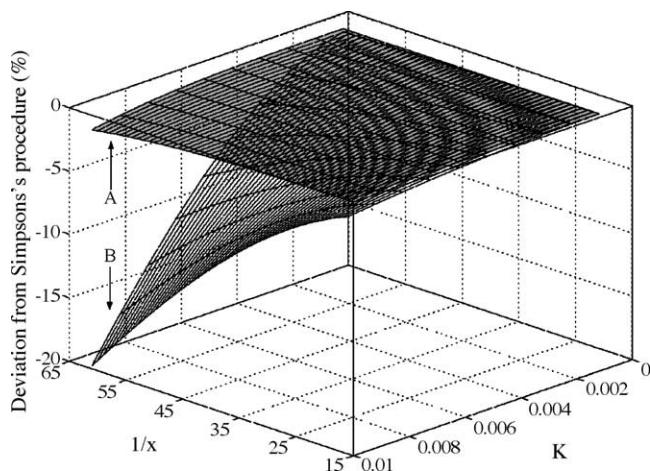


Fig. 1. Surface plot of the percent deviation of Eqs. (7) and (8) (plots A and B refer to Eqs. (7) and (8), respectively) from numerical results of the integral interval  $P(x)|_{x-\delta}^{x+\delta}$ , in which  $\delta = kx$ .

were calculated with Simpson's rule. The relative percent errors associated with the use of the approximate formula, Eq. (8), along with Eq. (7) as a solution of the Arrhenius integral for various  $x$  ( $15 \leq 1/x \leq 60$ , a physically realistic domain of  $1/x$ ) over different small intervals ( $kx$ ,  $k = 0.002\text{--}0.01$ ) are plotted in Fig. 1. As shown in Fig. 1, for  $k \rightarrow 0$  and small values of  $1/x$ , Eqs. (7) and (8) lead to values practically equal to those obtained by the numerical integral method. For higher values of  $k$  and  $1/x$ , the accuracy of Eq. (8) is very poor. Therefore, the range of its applicability is localized to small values of  $k$  and  $1/x$ . On the contrary, as for Eq. (7), increasing the value of  $k$  under constant  $1/x$ , the percent deviation from Simpson's procedure increases slightly. This fact indicates that the accuracy of Eq. (7) is high with large value of  $k$ , which means that the influence of  $\Delta\alpha$  value on the kinetic parameters is small. Eq. (7) is significantly more accurate than Eq. (8) in all the range of  $1/x$ . Fig. 1 shows that Eq. (7) is much superior to Eq. (8).

### 3. Simulations and comparison

Along with the LL-INT method, the Friedman (Eq. (12)) method and some regular integral isoconversional methods (Tang [24], FWO, and KAS) for evaluating the activation energy are applied for process I (simulated data for a single reaction) and process II (simulated data for two parallel reactions). The relationships that form the bases of these methods are

- for Friedman method

$$\ln(d\alpha/dt) = \ln(A/f(\alpha)) - E/RT \quad (12)$$

- for Tang method

$$\begin{aligned} \ln[\beta/T^{1.89466100}] \\ = \ln[AE/g(\alpha)R] + 3.63504095 - 1.89466100 \ln E \\ - 1.00145033E/RT \end{aligned} \quad (13)$$

- for FWO method

$$\ln \beta = \ln[AE/Rg(\alpha)] - 5.331 - 1.052E/RT \quad (14)$$

- for KAS method

$$\ln[\beta/T^2] = \ln[AR/Eg(\alpha)] - E/RT \quad (15)$$

Activation energy of process I, as shown in Eq. (16), is independent of the extent of conversion, which is simulated by means of numerical integration. Process II, which is simulated by means of the Runge–Kutta algorithm, describes two parallel reactions of different reaction orders [16], as shown in Eq. (17), each of which has significantly different kinetic parameters. A strong variation in the apparent activation energy may be observed for process II:

$$d\alpha/dt = A_1 \exp(-E_1/RT)(1 - \alpha)^{n_1} \quad (16)$$

$$\begin{aligned} d\alpha/dt = A_1 \exp(-E_1/RT)(1 - \alpha)^{n_1} \\ + A_2 \exp(-E_2/RT)(1 - \alpha)^{n_2} \end{aligned} \quad (17)$$

The parameters of Eqs. (16) and (17) are:  $n_1 = 1$ ,  $E_1 = 200 \text{ kJ mol}^{-1}$ ,  $A_1 = 10^{16} \text{ min}^{-1}$ ,  $n_2 = 2$ ,  $E_2 = 100 \text{ kJ mol}^{-1}$ ,  $A_2 = 10^8 \text{ min}^{-1}$ . Both of the processes have been simulated for linear heating rates of 2, 4, 6, 8, and  $10 \text{ K min}^{-1}$ . Nonlinear interpolation has been employed to evaluate the values of  $T_\alpha$ ,  $T_{\alpha - \Delta\alpha}$ ,  $T_{\alpha + \Delta\alpha}$  and  $(d\alpha/dt)_\alpha$  used to evaluate the activation energies from simulated data with Eqs. (16) and (17). The dependence of activation energy on the conversion degree for processes of I and II are displayed in Figs. 2 and 3, respectively.

For process I, the activation energy does not vary significantly with the extent of conversion (Fig. 2). In this case, Friedman, LL-INT method, and regular integral methods lead to almost identical  $E$  dependence. The LL-INT technique gives rise to a slightly larger scatter in the  $E$  values because LL-INT technique involves more numerical calculations.

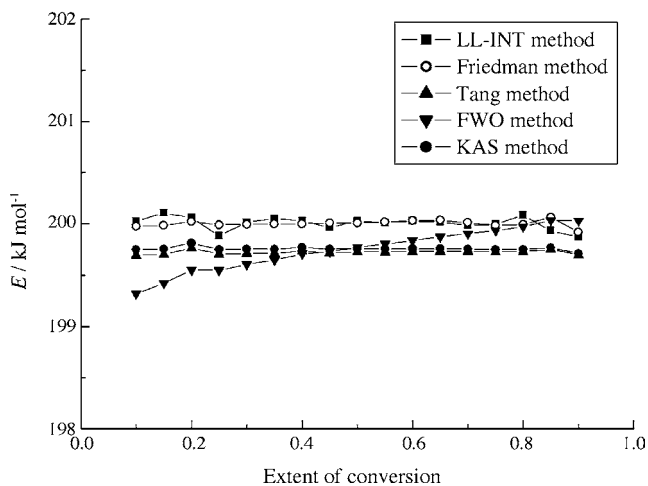


Fig. 2.  $E$  dependencies evaluated for the simulated process I by various methods.

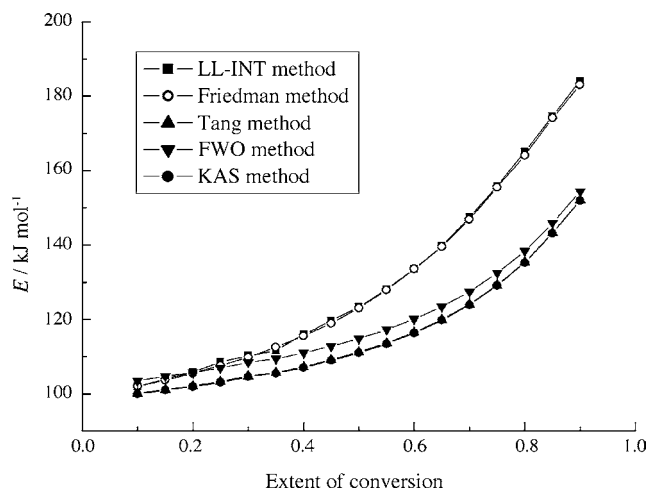


Fig. 3.  $E$  dependencies evaluated for the simulated process II by various methods.

For process II, in Fig. 3, the  $E$  dependence on  $\alpha$  obtained from regular integral methods deviates noticeably from the Friedman method. However, the  $E$  dependence on  $\alpha$  yielded by the LL-INT method is practically identical to that estimated by Friedman method. For a given value of  $\alpha$ ,  $E_{FR} \approx E_{LL-INT} > E_{Tang} \approx E_{FWO} \approx E_{KAS}$ . The average relative deviation of LL-INT method is 0.35% and the maximum relative deviation is 0.74%. The average relative deviation of regular integral methods is about 6.0% and the maximum relative deviation is 17.5%, which is in agreement with that claimed [16] about 18%. The regular methods (Tang, FWO and KAS) are based on the integration of the rate equation for constant  $E_\alpha$ . That is the reason that for  $E_\alpha$  dependence on  $\alpha$ , only results of the LL-INT method is in agreement with that of the Friedman method.

#### 4. Experimental example

The thermal decomposition of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  was carried out in a  $20 \text{ ml min}^{-1}$  flow of  $\text{N}_2$  at 5, 10, 15, and  $20 \text{ K min}^{-1}$  from room temperature (20) to  $900^\circ\text{C}$  on a Setaram Setsys TG/DTA/DSC16 thermal analyzer. The samples weight was about 3 mg. The actual values of heating rates for the temperature region of dehydration were obtained from the sample temperature versus time curve. The reaction rate data were estimated with numerical differential method.

The dependence of activation energy on the degree of conversion for dehydration of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  obtained by means of various isoconversional methods is shown in Fig. 4. The activation energy decreases with the degree of conversion irrespective of the method used. Similar results were reported by Budrugaec and Segal [25] and Vyazovkin [16]. For a given value of  $\alpha$ ,  $E_{FR} < E_{LL-INT} < E_{Tang} \approx E_{FWO} \approx E_{KAS}$ .  $E_{FWO}$  and  $E_{KAS}$  are quite close to values obtained by these with the same methods [25].  $E_{LL-INT}$  is close to those presented in literature [25] obtained by Friedman method. A possible reason for

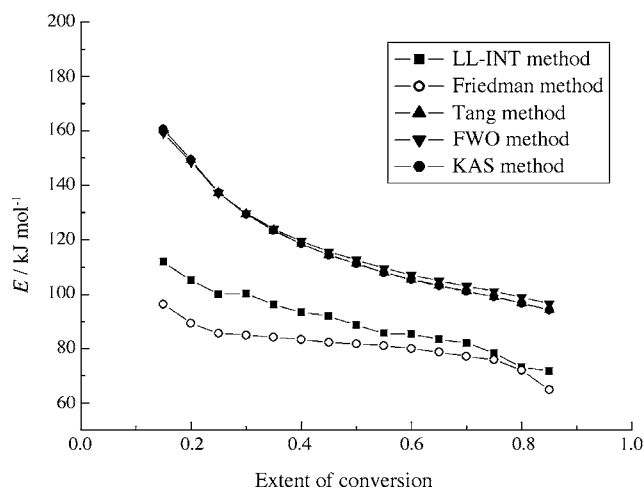


Fig. 4.  $E$  dependencies evaluated for the dehydration process of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  by various methods.

the difference is that the experimental data must be numerically differentiated to estimate activation energy by Friedman method and numerical differentiation considerably lowers the signal-to-noise ratio.

#### 5. Conclusions

If the activation energy does not vary with the conversion degree, LL-INT technique leads to  $E$  values identical with those obtained by Friedman and regular integral techniques. The systematic error of regular integration techniques with the extent of conversion is eliminated with the LL-INT method. The estimation of activation energy dependence for dehydration of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  validated the method.

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