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# ADVANCED ISOCONVERSIONAL METHOD

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## Abstract

A nonlinear algorithm has been suggested to increase the accuracy of evaluating the activation energy by the integral isoconversional method. A minor modification of the algorithm has made it possible to adapt the isoconversional method for an arbitrary variation of the temperature. This advanced isoconversional method allows for trustworthy estimates of the activation energy when the thermal effect of a reaction makes the temperature of a sample deviate from a prescribed heating program.

**Keywords:** activation energy, isoconversional method, non-isothermal kinetics, reaction kinetics in solids

## Introduction

It is well known that force-fitting non-isothermal data to different reaction models results in widely varying Arrhenius parameters. The only chance to obtain trustworthy kinetic parameters is to extract them in a way that is independent of the reaction model. Isoconversional methods are known to allow for model-independent estimates of the activation energy, $E_\alpha$, related to different extents of conversion, $\alpha$. Unfortunately these methods are not used very often which is probably because of the problems accompanying their application. For instance, $E_\alpha$ frequently reveals a dependence on $\alpha$ which poses a problem in interpreting the results of the computations. Another problem is that the original isoconversional methods (e.g., Ozawa [1] and Flynn and Wall [2]) do not suggest a model-independent way to evaluate the preexponential factor. Determination of the reaction model is one more problem. Let us dwell briefly on these problems. The problem of the interpretation of the dependence of $E_\alpha$ on $\alpha$ comes from the theoretical concepts which prescribe the activation energy of an elementary reaction step to be constant. However thermal analysis experiments have never been capable of measuring the reaction rate of elementary steps, but the overall rate of a process which usually involves several steps with different activation energies. Therefore the constancy of the experimentally determined value of $E_\alpha$ should be expected rather as an anomaly indicating that a single reaction step is likely to determine the rate of the whole process. Generally we have to put up with the fact that $E_\alpha$ may vary with $\alpha$. The analysis of the dependence of

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$E_\alpha$ on $\alpha$ is very instructive because it helps not only to disclose the complexity of a process but also to gain an insight into its mechanism [3, 4]. It is also noteworthy that the sole dependence of the activation energy on conversion is sufficient to predict reliably the kinetics of a process over a wide region of the temperatures [3–5]. A possibility to obtain information about the mechanism of a process and to predict its kinetics without the knowledge of both the reaction model and the preexponential factor gives rise to an alternative concept [3, 6] of the kinetic analysis. Note, that the preexponential factor can, however, be evaluated independently of the reaction model using parameters of a false isokinetic relationship [7]. Once the values of the activation energy and the preexponential factor have been determined, the reaction model can be reconstructed [3].

All these compelling advantages of the isoconversional method have stimulated our efforts to further extend the capabilities of the method. This paper describes a non-linear algorithm which markedly increases the accuracy of evaluating the activation energy by the isoconversional method. A minor modification of the algorithm allowed us to develop the advanced isoconversional method which is applicable to an arbitrary variation in the temperature.

## Non-linear isoconversional method

Integral isoconversional methods are based on the kinetic Eq. (1)

$$g(\alpha) = (A/\beta)\int_0^T \exp(-E/RT)\mathrm{d}T = (A/\beta)I(E,T) \tag{1}$$

where $g(\alpha)$ is the integral form of the reaction model, $A$ is the preexponential factor, $E$ is the activation energy, $R$ is the gas constant, $T$ is the temperature, $\beta$ is the heating rate. The temperature integral in Eq. (1) is replaced by an approximation to derive a linear equation to evaluate the activation energy. Equation (1) is usually represented in the form (2) [8, 9]

$$g(\alpha) = (AE/\beta R)p(x) \tag{2}$$

where $x = E/RT$ and $p(x)$ is an approximation of the temperature integral. The generalized Eq. (3) [10]

$$p(x) = \exp(-x)/x^2[(1 - 2/x)(1 - m/x^2)] \tag{3}$$

combines several previously suggested approximations ($m$ is a parameter specifying a given approximation). Combining Eqs (2 and 3) one can obtain Eq. (4)

$$\ln(\beta_i/T^2_{\alpha,i}) = \ln\{[A_\alpha R/E_\alpha g(a)][(1 - 2/x)/(1 - m/x^2)]\} - E_\alpha/RT_{\alpha,i} \tag{4}$$

(the subscript $\alpha$ designates values related to a given value of the extent of conversion) which is practically linear with respect to $T^{-1}_{\alpha,i}$ at $x > 10$ and thus allows $E_\alpha$ to be found from the slope of the plot of $\ln(\beta_i/T^2_{\alpha,i})$ *vs.* $T^{-1}_{\alpha,i}$. Generally, the use of this plot means that the part $(1-2/x)/(1-m/x^2)$ of the approximation (4) is neglected, giving rise to an oversimplified approximation (5)

$$p(x) = \exp(-x)/x^2 \tag{5}$$

As an alternative to approximate linear equations an exact non-linear equation can be derived. Using a general assumption [1, 2] that the reaction model is independent of the heating rate, we can write for a given α and a set of experiments performed under different heating rates, $\beta_i$ ($i = 1,\ldots,n$) Eq. (6)

$$(A_\alpha/\beta_1)I(E_\alpha,T_{\alpha,1}) = (A_\alpha/\beta_2)I(E_\alpha,T_{\alpha,2}) = \ldots = (A_\alpha/\beta_n)I(E_\alpha,T_{\alpha,n}) \tag{6}$$

It can be shown [11] that Eq. (6) is equivalent to the condition of minimum (7)

$$\sum_{i}^{n}\sum_{j\neq i}^{n}\left[I(E_\alpha,T_{\alpha,i})\beta_j\right] / \left[I(E_\alpha,T_{\alpha,j})\beta_i\right] = \min \tag{7}$$

The non-linear Eq. (7) can be used to obtain $E_\alpha$. Substituting experimental values of $T_\alpha$ and β into Eq. (7) and varying $E_\alpha$ to reach the minimum gives the value of the activation energy at a given conversion. The values of $I(E,T)$ may be found by numerical integration as well as with the help of an accurate approximation. In our calculations we have used the Senum-Yang approximation [12]

$$p(x) = \exp(-x)/x\ (x^2 + 10x + 18)/(x^3 + 12x^2 + 36x + 24) \tag{8}$$

which at $x=5$ gives only 0.02% deviation from the exact value of the temperature integral [12].

Equations (4) and (7) have been compared by model data simulated for a wide variation of $x$ [11]. Figure 1 shows relative deviations of the computed activation

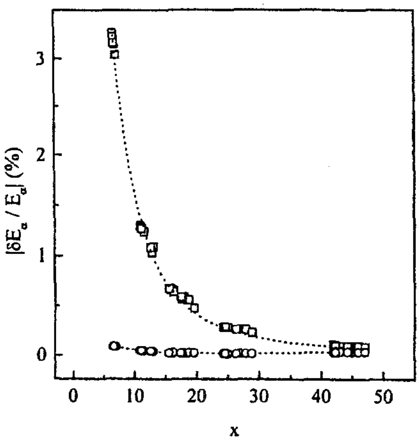

**Fig. 1** Relative error in the activation energy computed by the linear Eq. (4) (squares) and non-linear Eq. (7) (circles)

energy from the exact value as a function of the $x$ value. The linear Eq. (4) demonstrates increasing deviation with decreasing $x$. The non-linear Eq. (7) reveals extremely low errors ($<0.1\%$) in the activation energy, and virtually shows no dependence of $|\delta E_\alpha/E_\alpha|$ on $x$. Therefore, non-linear Eq. (7) can be employed to increase markedly the accuracy of evaluating the activation energy by the isoconversional method.

## Advanced isoconversional method

Whatever the prescribed heating program is, the actual variation of the temperature inside the reaction system tends to deviate from that prescribed, primarily due to the thermal effects of the reactions. Experimental measurements performed on $CaC_2O_4{\cdot}H_2O$ and on a mixture of $CaCO_3$ with $Ca(OH)_2$ have shown [13] that the endothermic effects of the thermal decomposition of these substances make the actual sample temperature deviate from the prescribed linear program by as much as 10 K. Such deviations obviously affect the reaction kinetics as well as invalidate the use of equations based on the assumption that a prescribed heating program holds. Therefore, if integrating Eq. (2) does not account for the actual variation of the temperature, the difference between the prescribed and actual temperature will inevitably result in erroneous values of computed Arrhenius parameters.

Although Eq. (7) underlying the non-linear isoconversional method only holds for a linear heating program, it can be adapted to an arbitrary variation of the temperature. Let us introduce a function

$$J[E,T(t)] = \int_0^t \exp[-E/RT(t)]\mathrm{d}t \tag{9}$$

Assuming that the reaction model, $g(\alpha)$, is independent of the variation of the temperature, we can write Eq. (10) by analogy with Eq. (7)

$$\sum_{i}^{n}\sum_{j\neq i}^{n} J\left[E_\alpha,T_i(t_\alpha)\right] / J\left[E_\alpha,T_j(t_\alpha)\right] = \min \tag{10}$$

where $T_i(t)$ ($i=1,\ldots,n$) are actual variations of the temperature. Substituting the time, $t_\alpha$, for which a given conversion has been reached and the actual temperature at that moment, into (10) and varying $E_\alpha$ until the minimum is attained gives an estimate of the activation energy. Details of numerical algorithm to solve Eq. (10) can be found elsewhere [14].

Equation (10) has been tested by model data on a first order reaction ($E=125.4$ kJ mol$^{-1}$ and $A=10^{10}$ min$^{-1}$) proceeding at a linear variation of the temperature complicated by non-linear deviations

$$T_i(t) = T_0 + \beta_i t + \delta T\Theta(T_0 + \beta_i t) \tag{11}$$

where $\delta T$ is the maximum deviation from the prescribed temperature. The non-linear deviation has been assumed to follow the Gaussian function

$$\Theta(T) = (a/w)(\pi/2)^{-1/2}\exp\{-2[(T - T_m)/w^2]^{1/2}\} \tag{12}$$

In Eq. (12), $T_m$ is the temperature corresponding to a maximum deviation of the actual temperature from a prescribed program. The values of $T_m$ were taken equal to the temperatures at which $d\alpha/dT$ is maximum under linear heating. Parameters $w$ and $a$ were respectively set as 10 and 12.6 so that the amplitude, $\Theta(T_m)$ was about 1 and width, $T_f-T_i$ was about 30 K (the initial $T_i$ and final $T_f$ temperatures are defined as $\Theta(T_i)$ and $\Theta(T_f)$ ˜ 0.1 K). The temperature has been varied, by Eq. (11), at five $\delta T$ values of 0, ±5, and ±10 K. For each $\delta T$, the data have been simulated at ($\beta_i$ = 8, 12, and 16 K min$^{-1}$. Equation (13)

$$\alpha = 1 - \exp\{-J[E,T_i(t)]\} \tag{13}$$

has been used to find the values of $t$, $T$, and $\alpha$. The integrals in Eqs (10) and (13) have been computed by Simpson's rule.

The model data have been processed by Eqs (7) and (10). The results of computations by Eq. (7) which does not account for the actual variation of the temperature are presented in Fig. 2. Since the data have been simulated for a single-step reaction, the computed values of the activation energy must be constant throughout the entire interval of conversions. The results, however, clearly demonstrate a systematic dependence of $E_\alpha$ on $\alpha$. The occurrence of such a dependence could be interpreted in terms of complex reaction mechanisms [3]. The present example shows that an adequate mechanistic interpretation of the dependence of $E_\alpha$ on $\alpha$ is allowable only if a prescribed program has been obeyed. Otherwise the interpretation is problematic because both factors, temperature deviations and complex kinetics,

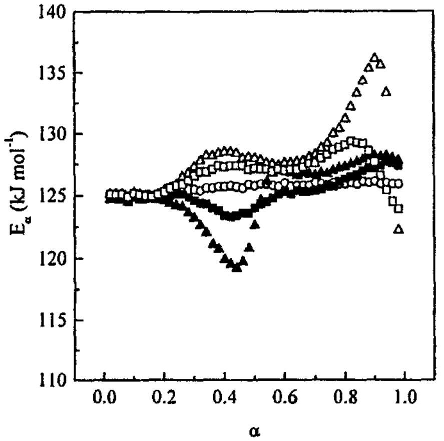

**Fig. 2** The activation energy computed by Eq. (7) for the simulated process at the variations of the temperature (Eq. (11)) with different values $\delta T$ (circles: $\delta T$=0; open squares: $\delta T$=+5; solid squares: $\delta T$=–5; open triangles: $\delta T$=+10; solid triangles: $\delta T$=–10)

manifest themselves as a dependence of $E_\alpha$ on $\alpha$. This means that temperature deviations may disguise the potential complexity of a process.

Figure 3 shows the results of data processing by Eq. (10) which holds for an arbitrary variation of the temperature. It is immediately apparent that the results of computations are entirely independent of the $\delta T$ value. All the values of $E_\alpha$ are clustered around 125.4 kJ mol$^{-1}$ which was used to simulate the data. Extreme deviations do not exceed 2% of this value, amounting on average about 0.7%. Because the value of $\delta T$ does not influence the deviations in the activation energy, they should be attributed to the computational features of the method and most likely to Simpson's rule used for numerical integration.

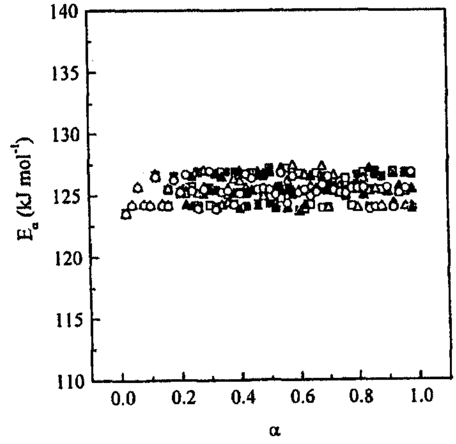

Fig. 3 The activation energy computed by Eq. (10) for the simulated process at the variations of the temperature (Eq. (11)) with different values of $\delta T$ (see notations to Fig. 2)

## Conclusions

The considered non-linear algorithm has been shown to increase the accuracy of evaluating the activation energy computed by isoconversional method. The algorithm has been modified to adapt the isoconversional method to an arbitrary variation of the temperature. The resulting advanced isoconversional method allows for trustworthy estimates of the activation energy in reaction systems whose kinetics are affected by arbitrary variations of the temperature due to the thermal effects.

## References

1 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
2 J. H. Flynn and L. A. Wall, J. Res. Nat. Bur. Standards, 70A (1966) 487.
3 S. Vyazovkin, Int. J. Chem. Kinet., 28 (1996) 95.
4 S. Vyazovkin and N. Sbirrazzuoli, Macromolecules, 29 (1996) 1867.
5 S. Vyazovkin and W. Linert, Anal. Chim. Acta, 295 (1994) 101 .
6 S. Vyazovkin, Thermochim. Acta, 211 (1992) 181.

7 S. Vyazovkin and W. Linert, Chem. Phys., 193 (1995) 109.
8 M. E. Brown, D. Dollimore and A. K. Galwey, Reactions in the Solid State; Comprehensive Chemical Kinetics, Vol.XXII, Elsevier, Amsterdam, 1980.
9 J. Šesták, Thermophysical Properties of Solids. Comprehensive Analytical Chemistry, Elsevier, Amsterdam 1984, Vol. 12D.
10 R. K. Agrawal, Thermochim. Acta, 203 (1992) 93.
11 S. Vyazovkin and D. Dollimore, J. Chem. Inf. Comp. Sci., 36 (1996) 42.
12 G. I. Senum and R. T. Yang, J. Thermal Anal., 11 (1979) 445.
13 D. Chen and D. Dollimore, Thermochim. Acta, 249 (1995) 259.
14 S. Vyazovkin, J. Comp. Chem., in press.