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An iterative integral method to evaluate the classical non-isothermal kinetic parameters from a single curve obtained at quasi-constant heating rate using integration over small intervals of variables and the least-squares method.
Part 2

E. Urbanovici[a] and E. Segal[b,*]

[a] *Thermosis Ltd., P.O. Box 187, Sfîntu Gheorghe, 4000 (Romania)*
[b] *Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bulevardul Carol 1, Nr. 13, Bucharest (Romania)*

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Abstract

A new, improved variant of a method for evaluating the non-isothermal kinetic parameters (Urbanovici and Segal, Thermochim. Acta, 141 (1989) 9) using integration over small ranges of variables is presented. By applying the method to a theoretical curve, values of the non-isothermal kinetic parameters in good agreement with those used for modelling were obtained.

INTRODUCTION

In non-isothermal kinetics, the programmed temperature T is usually given by

$$T = T_0 + \beta t \tag{1}$$

where T_0 is the initial temperature and β the constant heating rate. Because of thermal changes occurring in the investigated samples, the true sample temperature differs from the programmed value, being expressed in a modified form of eqn. (1) [2]

$$T = T_0 + \beta t + s(t) \tag{2}$$

where the supplementary term $s(t)$ accounts for this deviation.

In order to derive the non-isothermal kinetic equations based on

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* Corresponding author.

relationships (1) and (2), we shall begin with the general rate equation

$$\frac{d\alpha}{dt} = Af(\alpha)e^{-E/RT} \qquad (T = \text{const}) \tag{3}$$

with $f(\alpha)$ being given as [3]

$$f(\alpha) = (1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p \tag{4}$$

Applying eqn. (3) to the classical non-isothermal change, one obtains [4–7]

$$\frac{d\alpha}{dt} = Af(\alpha)e^{-E/R(T_0+\beta t)} \tag{5}$$

From eqn. (1), $dT = \beta\, dt$; and by changing the variable t with the variable T, eqn. (5) can be rewritten in the form

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha)e^{-E/RT} \tag{6}$$

The integral form of eqn. (6) is

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T e^{-E/RT}\, dT \tag{7}$$

To a certain extent, eqns. (6) and (7) are used erroneously as non-isothermal expressions; they are strictly correct for only $s(t) = 0$ in relationship (2). In order to obtain the correct non-isothermal kinetic equation, relationship (2) should be used.

Thus, the classical non-isothermal change applied to eqn. (3), taking into account relationship (2), leads to

$$\frac{d\alpha}{dt} = Af(\alpha)e^{-E/R(T_0+\beta t+s(t))} \tag{8}$$

In order to substitute t for T, by differentiation of eqn. (2), one obtains

$$dT = \beta\, dt + \dot{s}(t)\, dt \tag{9}$$

and

$$dt = \frac{dT}{\beta + \dot{s}(t)} \tag{10}$$

Incorporating this into eqn. (8)

$$\frac{d\alpha}{dt} = \frac{A}{\beta + \dot{s}(t)} f(\alpha)e^{-E/RT} \tag{11}$$

which is a corrected non-isothermal kinetic equation, the true heating rate being $\beta + \dot{s}(t)$.

The complication introduced by the supplementary term $s(t)$ in eqn. (11) can be avoided by using its integration over small ranges of the variables [1,2]. In such a way, and after performing the detailed calculations from eqn. (11), by integrating one obtains

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta_{ik}} \int_{T_i}^{T_k} \mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{12}$$

where β_{ik}, the local heating rate in the range $\alpha \in [\alpha_i, \alpha_k]$ is given by

$$\beta_{ik} = \frac{T_k - T_i}{t_k - t_i} \tag{13}$$

Using eqn. (12) corrects for the deviation of the true heating rate with respect to the programmed value. In eqns. (6) and (7), such a deviation is not taken into account.

A new method for evaluating the non-isothermal kinetic parameters starting from eqn. (12) will now be described: the result will be a simplified variant of the method described in ref. 1.

DESCRIPTION OF THE METHOD

The method is based on eqn. (12) and differs from that previously described [1] in the integration procedure. In the earlier variant, integrating eqn. (12) gave

$$\frac{\alpha_k - \alpha_i}{f(\alpha_{ik})} = \frac{A}{\beta_{ik}} (T_k - T_i)\mathrm{e}^{-E/RT_{ik}} \tag{14}$$

To first approximations

$$\alpha_{ik} \in [\alpha_i, \alpha_k] \tag{15}$$

$$\alpha_{ik} = \frac{\alpha_i + \alpha_k}{2} \tag{16}$$

$$T_{ik} \in [T_i, T_k] \tag{17}$$

$$T_{ik} = \frac{T_i + T_k}{2} \tag{18}$$

Because the values of α_{ik} and T_{ik} should be recalculated for each interval $[\alpha_i, \alpha_k]$, each iteration of the procedure requires a considerable calculation effort. The new variant uses better approximations for the integrals from eqn. (12) which substantially reduce the calculation time.

In order to approximate the integral of the right-hand side of eqn. (12), one must consider the previously determined [8] relationship

$$\int_{T_i}^{T_k} \mathrm{e}^{-E/RT}\,\mathrm{d}T = (T_k - T_i)\left(1 + \frac{1}{24}\left(\frac{E(T_k - T_i)}{RT_{ik}^2}\right)^2\right)\mathrm{e}^{-E/RT_{ik}} \tag{19}$$

with T_{ik} given by eqn. (18). The term $\frac{1}{24}[E(T_k - T_i)/RT_{ik}^2)]^2$ is a correction term with respect to the approximation (14).

The integral of the left-hand side of eqn. (12) can be approximated as follows (see the Appendix)

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{(\alpha_k - \alpha_i)}{f(\alpha_{ik})}\left[1 + \frac{(\alpha_k - \alpha_i)^2}{24}\left(\frac{2f'^2(\alpha_{ik}) - f(\alpha_i, \alpha_k)f''(\alpha_{ik})}{f^2(\alpha_{ik})}\right)\right] \tag{20}$$

with α_{ik} given by eqn. (16). Equation (20) can be compared with eqn. (14). A supplementary term with respect to eqn. (14) should be noted.

By introducing the notations

$$q_1(E, T_i, T_k) = 1 + \frac{1}{24}\left[\frac{E(T_k - T_i)}{RT_{ik}^2}\right]^2 \tag{21}$$

and

$$q_2(n, m, p, \alpha_i, \alpha_k) = 1 + \frac{(\alpha_k - \alpha_i)^2}{24}\left[\frac{2f'^2(\alpha_{ik}) - f(\alpha_{ik})f''(\alpha_{ik})}{f^2(\alpha_{ik})}\right] \tag{22}$$

and taking into account relationships (16) and (18), relationship (12) can be rewritten

$$\frac{\alpha_k - \alpha_i}{f(\alpha_{ik})} q_2(n, m, p, \alpha_i, \alpha_k) = \frac{A}{\alpha_{ik}}(T_k - T_i)\mathrm{e}^{-E/RT_{ik}} q_1(E, T_i, T_k) \tag{23}$$

or by taking logarithms and rearranging

$$\ln A + \ln f(\alpha_{ik}) - \frac{E}{RT_{ik}} = \ln\left(\frac{\alpha_k - \alpha_i}{T_k - T_i}\right)\beta_{ik} + \ln\left[\frac{q_2(n, m, p, \alpha_i, \alpha_k)}{q_1(E, T_i, T_k)}\right] \tag{24}$$

Equation (24) is the fundamental relationship for the proposed procedure.

In order to determine the values of the non-isothermal kinetic parameters, N pairs (α_i, α_k) and N equations of the form of eqn. (24) should be considered. Applying the least-squares method, one obtains

$$S = \sum_{i=1}^{N} \left(\ln A + \ln f(\alpha_{ik}) - \frac{E}{RT_{ik}} - \ln\left(\frac{\alpha_k - \alpha_i}{T_k - T_i}\right)\beta_{ik} - \ln\left[\frac{q_2(n, m, p, \alpha_i, \alpha_k)}{q_1(E, T_i, T_k)}\right]\right)^2 \tag{25}$$

Minimization of the sum S allows the values of the non-isothermal kinetic parameters to be obtained.

In order to simplify the notations, we introduce

$$q(i, k, E, n, m, p) = \ln\left[\frac{q_2(n, m, p, \alpha_i, \alpha_k)}{q_1(E, T_i, T_k)}\right] \tag{26}$$

Relationship (25) can then be applied in the following cases.

Determination of the values of A *and* E *for a known conversion function* f(α)

The minimization conditions of the sum S

$$\frac{\partial S}{\partial \ln A} = 0 \tag{27}$$

$$\frac{\partial S}{\partial E} = 0 \tag{28}$$

are actually equivalent to the linear system in $\ln A$ and E

$$N \ln A - E \sum_1^N \frac{1}{RT_{ik}} = \sum_1^N \ln \frac{(\alpha_k - \alpha_i)\beta_{ik}}{(T_k - T_i) f(\alpha_{ik})} + q(i, k, E, n, n, p) \tag{29a}$$

$$(\ln A) \sum_1^N \left(-\frac{1}{RT_{ik}}\right) + E \sum_1^N \left(\frac{1}{RT_{ik}}\right)^2$$
$$= \sum_1^N \left(-\frac{1}{RT_{ik}}\right) \ln\left[\frac{(\alpha_k - \alpha_i)\beta_{ik}}{(T_k - T_i) f(\alpha_{ik})}\right] + \sum_1^N \left(-\frac{1}{RT_{ik}}\right) q(i, k, E, n, m, p) \tag{29b}$$

In order to solve this system, we propose the following iterative procedure.

Iteration (1)
For $q(i, k, E, n, m, p) = 0$, we solve the system and obtain the values $\ln A^{(1)}$ and $E^{(1)}$.

Iteration (2)
The value $q(i, k, E^{(1)}, n, m, p)$ is calculated. By solving the system we obtain the values $\ln A^{(2)}$ and $E^{(2)}$.

Iteration (j)
The value $q(i, k, E^{(j-2)}, n, m, p)$ is calculated. By solving the system we obtain the values $\ln A^{(j)}$ and $E^{(j)}$.

The iterations are stopped for

$$|\ln A^{(j)} - \ln A^{(j-1)}| < \varepsilon_1 \tag{30}$$

$$|E^{(j)} - E^{(j-1)}| < \varepsilon_2 \tag{31}$$

This procedure can be applied in order to select the best conversion function. For each tried conversion function, the calculated $\ln A$ and E values are used to evaluate S. The most probable conversion function corresponds to the lowest value of S.

Simultaneous determination of A *and* E, *and of the conversion function*

In this case, one has to solve iteratively the following linear system of five equations with five unknowns

$$\frac{\partial S}{\partial \ln A} = 0; \quad \frac{\partial S}{\partial n} = 0; \quad \frac{\partial S}{\partial m} = 0; \quad \frac{\partial S}{\partial p} = 0; \quad \frac{\partial S}{\partial E} = 0 \tag{32}$$

For example, consider the most usual case, $m = p = 0$; and thus $f(\alpha) = (1 - \alpha)^n$. In this case, the system of eqns. (32) reduces to a system of three equations:

$$N \ln A + n \sum_1^N \ln(1 - \alpha_{ik}) - E \sum_1^N \frac{1}{RT_{ik}} = \sum_1^N \ln \frac{(\alpha_k - \alpha_i)\beta_{ik}}{T_k - T_i} + \sum_1^N q(i, k, E, n) \tag{33a}$$

$$\ln A \sum_1^N \ln(1 - \alpha_{ik}) + n \sum_1^N \ln(1 - \alpha_{ik}) - E \sum_1^N \frac{1}{RT_{ik}} \ln(1 - \alpha_{ik}) = \sum_1^N \ln(1 - \alpha_{ik}) \ln\left[\frac{(\alpha_k - \alpha_i)\beta_{ik}}{T_k - T_i}\right] + \sum_1^N q(i, k, E, n) \ln(1 - \alpha_{ik}) \tag{33b}$$

$$-\ln A \sum_1^N \frac{1}{RT_{ik}} - n \sum_1^N \frac{1}{RT_{ik}} \ln(1 - \alpha_{ik}) + E \sum_1^N \left(\frac{1}{RT_{ik}}\right)^2 = \sum_1^N \left(-\frac{1}{RT_{ik}}\right) \ln\left[\frac{(\alpha_k - \alpha_i)\beta_{ik}}{T_k - T_i}\right] + \sum_1^N \left(-\frac{1}{RT_{ik}}\right) q(i, k, E, n) \tag{33c}$$

In order to solve this system of equations, the following iterative procedure is applied:

Iteration (1)

The system (33) is solved for $q(i, k, E, m) = 0$. The values $\ln A^{(1)}$, $n^{(1)}$ and $E^{(1)}$ are obtained.

Iteration (2)

The value $q(i, k, E^{(1)}, n^{(1)})$ is calculated and then the system (33) is solved. The values $\ln A^{(2)}$, $n^{(2)}$ and $E^{(2)}$ are obtained.

With the values $n^{(j-1)}$ and $E^{(j-1)}$, we can calculate $q(i, k, E^{j-1}), n^{j-1}$, and then solve the system (33). The values $\ln A^{(j)}$, $n^{(j)}$ and $E^{(j)}$ are thus obtained. The iterations are stopped when conditions of the form (30) and (31) and a new condition

$$|n^{(j)} - n^{(j-1)}| < \varepsilon_3 \tag{34}$$

are fulfilled.

TABLE 1

Combinations of (α_i, α_k) and the corresponding (T_i, T_k) for $N = 6$

N	i	k	T_i/K	T_k/K
1	0.10	0.25	424.115	438.021
2	0.20	0.40	434.421	446.374
3	0.30	0.55	441.113	453.090
4	0.45	0.70	448.717	459.438
5	0.10	0.85	455.198	466.670
6	0.75	0.95	461.657	474.163

The minimal value of N is 3 and the maximal value could be 15–20 (in such conditions one needs a large number of calculations). According to our experience, values of N located in the range 6–9 are reasonable in order to yield significant results if the ranges cover almost all the range of variations.

The difference $T_i - T_k$ should fulfill the condition

$$10\,\mathrm{K} < T_k - T_i < 15\,\mathrm{K} \tag{35}$$

APPLICATIONS

The method was applied to a theoretical curve obtained with the following values for the kinetic and operational parameters [1]: $E = 25.00\,\mathrm{kcal\,mol^{-1}}$, $A = 6.10\,\mathrm{min^{-1}}$, $n = 1$, $\beta = 10\,\mathrm{K\,min^{-1}}$ and with $R = 1.986\,\mathrm{cal\,mol^{-1}\,K^{-1}}$.

The unique value considered for the local heating rate, $\beta = 10\,\mathrm{K\,min^{-1}}$, does not influence the result of this verification. The (α, T) data for the modelled curve were taken from ref. 1. Table 1 lists the data used to check the method for $N = 6$. Using these data to solve the system (33), the results listed in Table 2 were obtained after three iterations, showing that three iterations are enough to fulfill the conditions (30), (31) and (34), and that the values of the non-isothermal kinetic parameters agree satisfactorily with those used to obtain the theoretical curve.

TABLE 2

Values of the non-isothermal kinetic parameters after 3 iterations

j (iteration)	$E^{(j)}$/(kcal mol^{-1})	$n^{(j)}$	$A^{(j)}$/(min^{-1})
1	26.14	1.165	2.40×10^{12}
2	25.43	1.026	9.82×10^{11}
3	25.49	1.032	1.04×10^{12}

In ref. 9, we report the application of the described method to construct an experimental curve. Significant differences were found between the values of the non-isothermal kinetic parameter estimated using local heating rates and those estimated using the programmed heating rate.

DISCUSSION

Comparing the method described here with the variant described in ref. 1, it is apparent that both variants are based on eqn. (12) obtained from eqn. (11) by integration over small ranges of variables and using local heating rates, and that both variants use an iterative procedure. However, in the first variant [1] the values of α_{ik} and T_{ik} are recalculated at each iteration, while in the new variant the term $q(i, k, E, n, m, p)$ is recalculated.

Because the first variant requires the recalculation of α_{ik} and T_{ik}, it follows that the second variant has a lower calculation effort. However, a disadvantage of the new variant lies in its relatively lower precision as a result of approximations (18) and (20).

CONCLUSIONS

A variant of an iterative integral method for evaluating the non-isothemal kinetic parameters has been described. Despite its lower precision with respect to the variant described in a previous work [1], the method is suitable for use due to the lower calculation effort required in its application.

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APPENDIX

In order to calculate the integral $\int_{\alpha_i}^{\alpha_k} \mathrm{d}\alpha/f(\alpha)$ we shall try an approximation of the form

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{\alpha_k - \alpha_i + a}{f(\alpha_{ik})} \tag{A1}$$

where a is a correction term which depends on ε and α_{ik} where

$$\varepsilon = \frac{\alpha_k - \alpha_i}{2} \tag{A2}$$

Because

$$\alpha_{ik} = \frac{\alpha_i + \alpha_k}{2} \tag{A3}$$

one can write

$$\alpha_i = \alpha_{ik} - \varepsilon \tag{A4}$$

$$\alpha_k = \alpha_{ik} + \varepsilon \tag{A5}$$

With these notations, eqn. (A1) takes the form

$$\int_{\alpha_{ik}+\varepsilon}^{\alpha_{ik}+\varepsilon} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{2\varepsilon + a}{f(\alpha_{ik})} \tag{A6}$$

Taking the derivative with respect to ε

$$\frac{1}{f(\alpha_{ik}+\varepsilon)} + \frac{1}{f(\alpha_{ik}-\varepsilon)} = \frac{2 + a/\mathrm{d}\varepsilon}{f(\alpha_{ik})} \tag{A7}$$

After developments in Taylor series [10] of the functions

$$\frac{1}{f(\alpha_{ik}+\varepsilon)} \quad \text{and} \quad \frac{1}{f(\alpha_{ik}-\varepsilon)}$$

around the point α_{ik}, and keeping the first four terms, one obtains

$$\frac{1}{f(\alpha_{ik}+\varepsilon)} = \frac{1}{f(\alpha_{ik})} + \left(\frac{1}{f(\alpha_{ik})}\right)'\varepsilon + \frac{\varepsilon^2}{2!}\left(\frac{1}{f(\alpha_{ik})}\right)'' + \frac{\varepsilon^3}{3!}\left(\frac{1}{f(\alpha_{ik})}\right)''' \tag{A8}$$

and

$$\frac{1}{f(\alpha_{ik}-\varepsilon)} = \frac{1}{f(\alpha_{ik})} - \left(\frac{1}{f(\alpha_{ik})}\right)'\varepsilon + \frac{\varepsilon^2}{2!}\left(\frac{1}{f(\alpha_{ik})}\right)'' - \frac{\varepsilon^3}{3!}\left(\frac{1}{f(\alpha_{ik})}\right)''' \tag{A9}$$

Taking into account eqns. (A8) and (A9), eqn. (A7) takes the form

$$\frac{\mathrm{d}a}{\mathrm{d}\varepsilon} = \frac{(1/f(\alpha_{ik}))''}{1/f(\alpha_{ik})} = \varepsilon^2\left(\frac{2f'(\alpha_{ik}) - f(\alpha_{ik})f''(\alpha_{ik})}{f^2(\alpha_{ik})}\right) \tag{A10}$$

Integrating eqn. (A10) gives

$$a = \frac{\varepsilon^3}{3!}\,\frac{2f'(\alpha_{ik}) - f(\alpha_{ik})f''(\alpha_{ik})}{f^2(\alpha_{ik})} + C \tag{A11}$$

where $C = 0$ for $\varepsilon \to 0$ and $a \to 0$.

From (A11) and using the initial notations, relationship (A1) becomes

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{\alpha_k - \alpha_i}{f(\alpha_{ik})}\left[1 + \frac{(\alpha_k - \alpha_i)^2}{24}\left(\frac{2f'(\alpha_{ik}) - f(\alpha_{ik})f''(\alpha_{ik})}{f^2(\alpha_{ik})}\right)\right] \tag{A12}$$

For $f(\alpha) = (1 - \alpha)^n$, the particular form of eqn. (A12) is

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{(1 - \alpha)^n} = \frac{\alpha_k - \alpha_i}{(1 - \alpha_{ik})^n}\left[1 + \frac{n(n+1)}{24}\frac{(\alpha_k - \alpha_i)^2}{(1 - \alpha_{ik})^2}\right] \tag{A13}$$