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ITERATIVE INTEGRAL METHOD TO EVALUATE THE CLASSICAL NON-ISOTHERMAL KINETIC PARAMETERS FROM A SINGLE CURVE OBTAINED AT CONSTANT HEATING RATE USING INTEGRATION OVER SMALL INTERVALS OF VARIABLES AND THE LEAST-SQUARES METHOD

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ABSTRACT

Following our research concerning the procedures used in non-isothermal kinetics [1,2], we present here a new method for evaluating the non-isothermal kinetic parameters. The method takes into account the difference between the sample temperature and the programmed one using local heating rates. By applying the method to a theoretically modelled curve, values of the non-isothermal kinetic parameters which are in fairly good agreement with those used in modelling have been obtained.

INTRODUCTION

The fundamental isothermal rate equation used to derive the non-isothermal kinetic equations is

$$\frac{d\alpha}{dt} = A f(\alpha) \exp - \frac{E}{RT} \tag{1}$$

with the classical conditions

$$A = \text{const.} \tag{2}$$

$$E = \text{const.} \tag{3}$$

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

where n, m and p are constants [3]. By applying the classical non-isothermal change (CNC) [4–6] to equation (1), considered as postulated primary

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isothermal differential kinetic equation (P-PIDKE) [5,6], using a linear heating programme where

$$T = T_0 + \beta t \tag{5}$$

it turns out that

$$\frac{d\alpha}{dt} = Af(\alpha) \exp - \frac{E}{R(T_0 + \beta t)} \tag{6}$$

Equation (6), taking into account that

$$\frac{dT}{dt} = \beta \tag{7}$$

becomes

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) \exp - \frac{E}{RT} \tag{8}$$

The differential non-isothermal kinetic eqns. (6) and (8) are fundamental in non-isothermal kinetics [4–10].

THE PRINCIPLE OF THE METHOD

The integration of the eqn. (8) leads to [1,2]

$$\int_{\alpha_i}^{\alpha_k} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta_{ik}} \int_{T_i}^{T_k} \exp - \frac{E}{RT} dT \tag{9}$$

where β_{ik} is the local heating rate corresponding to the closed interval $\alpha \in [\alpha_i, \alpha_k]$ [2,11].

$$\beta_{ik} = \frac{T_k - T_i}{t_k - t_i} \tag{10}$$

By applying the mean value theorem from mathematical analysis to the integrals from (9), we obtain [1,2,12]

$$\frac{\alpha_k - \alpha_i}{f(\alpha_{ik})} = \frac{A}{\beta_{ik}} (T_k - T_i) \exp - \frac{E}{RT_{ik}} \tag{11}$$

where

$$\alpha_{ik} \in (\alpha_i, \alpha_k) \tag{12}$$

$$T_{ik} \in (T_i, T_k) \tag{13}$$

To simplify the notations, we shall use λ to denote the variables (i, k), i.e. $\alpha_{ik} \equiv \alpha_\lambda$; $T_{ik} \equiv T_\lambda$; $\alpha_k - \alpha_i \equiv \Delta\alpha_\lambda$; $T_k - T_i \equiv \Delta T_\lambda$; $t_k - k_i \equiv \Delta t_\lambda$. In such conditions, taking into account relationship (10), eqn. (11) becomes

$$\frac{\Delta\alpha_\lambda}{f(\alpha_\lambda)} = A\ \Delta t_\lambda \exp - \frac{E}{RT_\lambda} \tag{14}$$

From eqn (14), by taking the logarithms, one obtains

$$\ln A + \ln f(\alpha_\lambda) - \frac{E}{RT_\lambda} = \ln \frac{\Delta\alpha_\lambda}{\Delta t_\lambda} \tag{15}$$

This is the equation upon which our proposed method is based.

THE EVALUATIONS OF THE PRE-EXPONENTIAL FACTOR A AND OF THE ACTIVATION ENERGY FOR A KNOWN $f(\alpha)$

Considering the pairs (i, k) or λ and applying the least-squares method [13,14] to the N equations of the form (15), the sum S_1, which should be minimized, is obtained

$$S_1 = \sum_{\lambda=1}^{N} \left(\ln A - \frac{E}{RT_\lambda} + \ln \frac{f(\alpha_\lambda)\ \Delta t_\lambda}{\Delta\alpha_\lambda} \right)^2 \tag{16}$$

From the minimum conditions of S_1

$$\frac{\partial S_1}{\partial \ln A} = 0 \tag{17}$$

$$\frac{\partial S_1}{\partial E} = 0 \tag{18}$$

the unknowns $\ln A$ and E can be evaluated as solutions of the system of equations (17) and (18), or (19) and (20) written in explicit forms

$$N \ln A - E \sum_{\lambda=1}^{N} \frac{1}{RT_\lambda} = \sum_{\lambda=1}^{N} \ln \frac{\Delta\alpha_\lambda}{f(\alpha_\lambda)\ \Delta t_\lambda} \tag{19}$$

$$(\ln A) \sum_{\lambda=1}^{N} -\left(\frac{1}{RT_\lambda}\right) + E \sum_{\lambda=1}^{N} \left(\frac{1}{RT_\lambda}\right)^2 = \sum_{\lambda=1}^{N} \frac{1}{RT_\lambda} \ln \frac{f(\alpha_\lambda)\ \Delta t_\lambda}{\Delta\alpha_\lambda} \tag{20}$$

THE EVALUATION OF A, E AND THE ESTABLISHING OF THE FORM OF $f(\alpha)$

For the general form (4) of $f(\alpha)$, using eqn. (15), the sum S_2, which should be minimized with respect to $\ln A$, E, n, m and p, is obtained

$$S_2 = \sum_{\lambda=1}^{N} \left(\ln A + n \ln(1-\alpha_\lambda) + m \ln \alpha_\lambda + p \ln[-\ln(1-\alpha_\lambda)] - \frac{E}{RT_\lambda} - \ln \frac{\Delta\alpha_\lambda}{\Delta t_\lambda} \right)^2 \tag{21}$$

The minimum conditions of S_2 are

$$\frac{\partial S_2}{\partial \ln A} = 0; \quad \frac{\partial S_2}{\partial n} = 0; \quad \frac{\partial S_2}{\partial m} = 0; \quad \frac{\partial S_2}{\partial p} = 0; \quad \frac{\partial S_2}{\partial E} = 0 \tag{22}$$

which, explicitly written, leads to the following system of equations whose solutions are the kinetic parameters

$$N \ln A + n \sum_{\lambda=1}^{N} \ln(1-\alpha_\lambda) + m \sum_{\lambda=1}^{N} \ln \alpha_\lambda + p \sum_{\lambda=1}^{N} \ln[-\ln(1-\alpha_\lambda)] - E \sum_{\lambda=1}^{N} \frac{1}{RT_\lambda} = \sum_{\lambda=1}^{N} \ln \frac{\Delta\alpha_\lambda}{\Delta t_\lambda} \tag{23}$$

$$(\ln A) \sum_{\lambda=1}^{N} \ln(1-\alpha_\lambda) + n \sum_{\lambda=1}^{N} \ln^2(1-\alpha_\lambda) + m \sum_{\lambda=1}^{N} \ln \alpha_\lambda \ln(1-\alpha_\lambda) + p \sum_{\lambda=1}^{N} \ln[-\ln(1-\alpha_\lambda)] \ln(1-\alpha_\lambda) - E \sum_{\lambda=1}^{N} \frac{1}{RT_\lambda} \ln(1-\alpha_\lambda) = \sum_{\lambda=1}^{N} \ln \frac{\Delta\alpha_\lambda}{\Delta t_\lambda} \ln(1-\alpha_\lambda) \tag{24}$$

$$(\ln A) \sum_{\lambda=1}^{N} \ln \alpha_\lambda + n \sum_{\lambda=1}^{N} (1-\alpha_\lambda) \ln_\lambda + m \sum_{\lambda=1}^{N} \ln^2 \alpha_\lambda + p \sum_{\lambda=1}^{N} \ln[-\ln(1-\alpha_\lambda)] \ln \alpha_\lambda - E \sum_{\lambda=1}^{N} \frac{1}{RT_\lambda} \ln \alpha_\lambda = \sum_{\lambda=1}^{N} \ln \frac{\Delta\alpha_\lambda}{\Delta t_\lambda} \ln \alpha_\lambda \tag{25}$$

$$(\ln A) \sum_{\lambda=1}^{N} \ln[-\ln(1-\alpha_\lambda)] + n \sum_{\lambda=1}^{N} \ln(1-\alpha_\lambda) \ln[-\ln(1-\alpha_\lambda)] + m \sum_{\lambda=1}^{N} \ln \alpha_\lambda \ln[-\ln(1-\alpha_\lambda)] + p \sum_{\lambda=1}^{N} \ln^2[-\ln(1-\alpha_\lambda)] - E \sum_{\lambda=1}^{N} \frac{1}{RT_\lambda} \ln[-\ln(1-\alpha_\lambda)] = \sum_{\lambda=1}^{N} \ln \frac{\Delta\alpha_\lambda}{\Delta t_\lambda} \ln[-\ln(1-\alpha_\lambda)] \tag{26}$$

$$(\ln A) \sum_{\lambda=1}^{N} \left(-\frac{1}{RT_\lambda}\right) + n \sum_{\lambda=1}^{N} \left(-\frac{1}{RT_\lambda}\right) \ln(1-\alpha_\lambda) + m \sum_{\lambda=1}^{N} \left(-\frac{1}{RT_\lambda}\right) \ln \alpha_\lambda + p \sum_{\lambda=1}^{N} \left(-\frac{1}{RT_\lambda}\right) \ln[-\ln(1-\alpha_\lambda)] + E \sum_{\lambda=1}^{N} \left(\frac{1}{RT_\lambda}\right)^2 = \sum_{\lambda=1}^{N} \left(-\frac{1}{RT_\lambda}\right) \ln \frac{\Delta\alpha_\lambda}{\Delta t_\lambda} \tag{27}$$

In principle, this system allows the evaluation of $\ln A$, E, n, m and p. Nevertheless, taking into account ideas from ref. 15 concerning the instability of the systems of equations derived from eqn. (8), one can state that the

evaluation of more than three kinetic parameters is impossible; thus A, E, n, m and p cannot be determined simultaneously.

If, for the same N, several forms of $f(\alpha)$ have to be considered, the form for which S_2 has the minimum value will be chosen.

THE WIDTH OF THE INTERVALS $\Delta\alpha_\lambda$ AND ΔT_λ

To choose the best width of the intervals $\Delta\alpha_\lambda$ and ΔT_λ it must be remembered that too small a width leads to high experimental errors in $\Delta\alpha_\lambda$ and ΔT_λ and thus to a poorly conditioned problem; nor is too large a width recommended because of errors in the values of T_λ^0 and α_λ^0 (see arguments following) which can cause a weak convergence (eventually a divergence) of the iterative method. Taking into account our experience [1,2,11,12], we recommend the following intervals

$$0.05 \leq \Delta\alpha_\lambda \leq 0.40 \tag{28}$$

$$5\ \text{K} \leq \Delta T_\lambda \leq 20\ \text{K} \tag{29}$$

THE EVALUATION OF T_λ AND α_λ

Zero-order approximation

This approximation, taking into account [1,2,11,12], is

$$T_\lambda^0 = \frac{T_k + T_i}{2} \tag{30}$$

$$\alpha_\lambda^0 = \frac{\alpha_k + \alpha_i}{2} \tag{31}$$

Using these values, the system of eqns. (19) and (20) or the system of eqns. (23)–(27) are solved, leading to ln A^0, E^0, n^0, m^0 and p^0.

First-order approximation

The zero-order kinetic parameters being known, the values T_λ^1 and α_λ^1 can be obtained from the relationship [2]

$$\int_{\alpha_i}^{\alpha_k} \frac{d\alpha}{f^0(\alpha)} = \frac{\alpha_k - \alpha_i}{f^0(\alpha_\lambda^1)} = \frac{\Delta\alpha_\lambda}{f^0(\alpha_\lambda^1)} \tag{32}$$

$$\int_{T_i}^{T_k} \exp - \frac{E^0}{RT_\lambda^0} dT = \Delta T_\lambda \exp - \frac{E^0}{RT_\lambda^1} \tag{33}$$

where $f^0(\alpha)$ means that in relationship (4), n^0, m^0 and p^0 are used. The

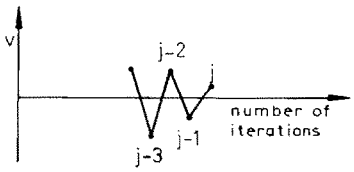

Fig. 1. Trend of v values towards the exact value through successive iterations.

values of T_λ^1 and α_λ^1 determined from eqns. (32) and (33) are introduced in the above-mentioned systems which are solved with respect to ln A^1, E^1, n^1, m^1 and p^1. By repeating this procedure we arrive at

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{\mathrm{f}^{(j-1)}(\alpha)} = \frac{\Delta\alpha_\lambda}{\mathrm{f}^{(j-1)}(\alpha_\lambda^j)} \tag{34}$$

$$\int_{T_i}^{T_k} \exp - \frac{E^{(j-1)}}{RT}\mathrm{d}T = \Delta T_\lambda \exp - \frac{E^{(j-1)}}{RT_\lambda^j} \tag{35}$$

Using T_λ^j and α_λ^j, the values of ln A^j, E^j, n^j, m^j and p^j can be obtained in the usual way.

The iteration is stopped when

$$| v^{(j)} - v^{(j-1)} | < \epsilon \tag{36}$$

where v is one of the parameters ln A, E, n, m or p. The values v^0, $v^1, \cdots, v^j$ tend to the exact value as shown in fig. 1.

The result is given as:

$$v = \frac{v^j + v^{(j-1)}}{2} \tag{37}$$

where

$$v = \ln A,\ E,\ n,\ m\ or\ p \tag{38}$$

THE APPROXIMATE EVALUATION OF THE TEMPERATURE INTEGRAL

This work uses the approximation of Senum and Yang [16]

$$\int_0^T \exp - \frac{E}{RT}\mathrm{d}T = T \exp - x\left(\frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120}\right) \tag{39}$$

where

$$x = \frac{E}{RT} \tag{40}$$

which gives an error of less than 10^{-3}%.

The integrals of the form $\int_{T_i}^{T_k} \exp -(E/RT)\, dT$ will be calculated according to the relationship

$$\int_{T_i}^{T_k} \exp -\frac{E}{RT} dT = \int_0^{T_k} \exp -\frac{E}{RT} dT - \int_0^{T_i} \exp -\frac{E}{RT} dT \tag{41}$$

The advantages of the method can be summarized as follows: it uses the least-squares method, which allows the solution of a large number of relationships of the form of eqn. (15) ($N \sim 10$–20) covering a range of α values ($0.05 \leq \alpha < 0.95$); it uses iteration enabling the calculation to be stopped at the desired approximation; it uses local heating rates, thus removing the error arising from using a programmed heating rate; the non-isothermal kinetic parameters are directly obtained using solutions of a linear system of equations; and the method can be applied, in principle, to any form of $f(\alpha)$.

The disadvantages of the method, which in principle can be avoided, are the following: large volumes of calculations which can be managed by using programmable computers; if the selected intervals $\Delta\alpha_\lambda$ and ΔT_λ are too low, there is a negative effect on the experimental errors; if $\Delta\alpha_\lambda$ and ΔT_λ are too high, problems of convergence could appear; and, when more than three kinetic parameters are being evaluated, stability problems could appear.

EXAMPLE OF APPLICATION OF THE METHOD

To apply the method, we shall model a non-isothermal curve describing a solid–gas decomposition of the form

$$A_s \rightarrow B_s + C_g \tag{42}$$

using the following data: $E = 25.000$ kcal mol^{-1}; $A = 6 \times 10^{11}$ min $^{-1}$; $f(\alpha) = 1 - \alpha$; $\beta = 10$ K min^{-1}; and $R = 1.987$ cal mol^{-1} K^{-1}.

When modelling the curve, the local heating rate is considered to be equal to the overall heating rate.

Instead of eqn. (15), the following equivalent equation can be used

$$\ln A + \ln f(\alpha_\lambda) - \frac{E}{RT_\lambda} = \ln \frac{\Delta\alpha_\lambda}{\Delta T_\lambda} \beta \tag{43}$$

Modelling was performed using the relationship

$$\int_0^\alpha \frac{d\alpha}{1-\alpha} = \frac{A}{\beta} \int_0^T \exp -\frac{E}{RT} dT \tag{44}$$

or

$$-\ln(1-\alpha) = \frac{A}{\beta} T \exp -x \left(\frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \right) \tag{45}$$

TABLE 1

Pairs of values α and T for $0.05 \leq \alpha \leq 0.95$

No.	α	T (K)
1	0.05	414.665
2	0.10	424.115
3	0.15	430.009
4	0.20	434.421
5	0.25	438.021
6	0.30	441.113
7	0.35	443.863
8	0.40	446.374
9	0.45	448.717
10	0.50	450.942
11	0.55	453.090
12	0.60	455.198
13	0.65	457.301
14	0.70	459.438
15	0.75	461.657
16	0.80	464.029
17	0.85	466.670
18	0.90	469.819
19	0.95	474.163

TABLE 2

Various combinations of α_i and α_k for $N = 16$

λ	α_i	α_k
1	0.05	0.10
2	0.10	0.20
3	0.15	0.30
4	0.20	0.35
5	0.25	0.45
6	0.30	0.50
7	0.35	0.55
8	0.40	0.65
9	0.45	0.70
10	0.50	0.75
11	0.55	0.80
12	0.60	0.85
13	0.65	0.85
14	0.70	0.90
15	0.75	0.90
16	0.80	0.95

TABLE 3

Values of the non-isothermal kinetic parameters corresponding to three iterations

j	E^j (kcal mol^{-1})	M^j	A^j (min^{-1})
0	25.462	1.093	10.68×10^{11}
1	24.986	0.996	5.90×10^{11}
2	25.022	1.001	6.16×10^{11}

where

$$x = \frac{E}{RT}$$

By solving eqn. (44) for various values of α, the values of T given in Table 1 have been calculated.

To determine A, E and n (for $f(\alpha) = (1-\alpha)^n$), the system of eqns. (23), (24) and (27) are solved ($m = p = 0$). Instead of $\ln(\Delta\alpha_\lambda/\Delta t_\lambda)$ we shall use $\ln(\Delta\alpha_\lambda/\Delta T_\lambda)\beta$ (see relationship (43).

For $N = 16$ the considered combinations of α_i and α_k are given in Table 2. The results obtained for three iterations are given in Table 3.

The values of the non-isothermal kinetic parameters calculated using relationship (37) are: $E = 25.004$ kcal mol^{-1}; $n = 0.9985$; and $A = 6.03 \times 10^{11}$ min^{-1}. There is excellent agreement with the values used for modelling.

CONCLUSIONS

A new method of evaluating non-isothermal kinetic parameters has been worked out. The use of local heating rates removes the errors generated by the deviation from linearity of the programmed temperature. The values of the non-isothermal kinetic parameters obtained by applying the method are in excellent agreement with those used in modelling the non-isothermal curve.

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