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AN INTEGRAL METHOD TO EVALUATE THE NON-ISOTHERMAL KINETIC PARAMETERS

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ABSTRACT

This paper describes a new classical (with constant values of the kinetic parameters) integral method to evaluate the non-isothermal kinetic parameters at the same heating rate using integration over small ranges of variables. The method was checked on a model $\alpha(T)$ curve with known values of the kinetic parameters.

INTRODUCTION

The classical isothermal differential kinetic equation describing the change of the degree of conversion with time is [1–4]

$$\frac{d\alpha}{dt} = Af(\alpha)\,e^{-E/RT} \quad (T = \text{const}) \tag{1}$$

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. Considering eqn. (1) as the postulated primary isothermal differential kinetic equation (P-PIDKE) [2–4] and applying the classical non-isothermal change (CNC) [1–4] with a linear heating program of the form

$$T = T_0 + \beta t \quad (\beta = \text{const}) \tag{5}$$

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one obtains

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

Taking into account that

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

eqn. (6) becomes

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha)\, e^{-E/RT} \tag{8}$$

The differential eqns. (6) and (8) are considered fundamental for classical non-isothermal kinetics [1–9].

METHOD

From eqn. (8), through integration for $\alpha \in [\alpha_1, \alpha_2]$, one obtains

$$\int_{\alpha_1}^{\alpha_2} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta_{12}} \int_{T_1}^{T_2} e^{-E/RT}\, dT \tag{9}$$

where β_{12} is the local heating rate corresponding to the closed interval $\alpha \in [\alpha_1, \alpha_2]$ [10,11]

$$\beta_{12} = \frac{T_2 - T_1}{t_2 - t_1} \tag{10}$$

For $T_2 - T_1 \leqslant 20$ K, using the theorem of average from mathematical analysis [12,13], the integral from the right side of eqn. (9) takes the form

$$\int_{T_1}^{T_2} e^{-E/RT}\, dT \simeq (T_2 - T_1)\, e^{-E/RT_{12}} \tag{11}$$

where

$$T_{12} = \frac{T_1 + T_2}{2} \tag{12}$$

Introducing into eqn. (9) three values for the degree of conversion with the condition that $\alpha_i < \alpha_j < \alpha_k$, one obtains

$$\int_{\alpha_i}^{\alpha_j} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta_{ij}} \int_{T_i}^{T_j} e^{-E/RT}\, dT \tag{13}$$

$$\int_{\alpha_j}^{\alpha_k} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta_{jk}} \int_{T_j}^{T_k} e^{-E/RT}\, dT \tag{14}$$

Taking into account relationship (11), from eqns. (13) and (14) one obtains

$$F(ij) = \frac{A}{\beta_{ij}}(T_j - T_i)\ \mathrm{e}^{-E/RT_{ij}} \tag{15}$$

$$F(jk) = \frac{A}{\beta_{jk}}(T_k - T_j)\ \mathrm{e}^{-E/RT_{jk}} \tag{16}$$

where $F(ij)$ and $F(jk)$ are the corresponding integrals from the left sides of the equations. From the ratio of relationships (15) and (16) one obtains, after performing the detailed calculations, the following formula to calculate the activation energy

$$E = R\frac{(T_{ij} - T_{jk})}{(T_{jk} - T_{ij})}\ln\left[\frac{F(jk)(t_j - t_i)}{F(ij)(t_k - t_j)}\right] \tag{17}$$

or if β is kept at a strictly constant value

$$E = R\frac{(T_{ij} - T_{jk})}{(T_{jk} - T_{ij})}\ln\left[\frac{F(jk)(T_j - T_i)}{F(ij)(T_k - T_j)}\right] \tag{18}$$

We recommend that the values of α_i, α_j and α_k be chosen such that

$$T_k - T_j \simeq T_j - T_i \tag{19}$$

One has to use as many combinations of α_i, α_j and α_k as possible in order to cover the whole range of change of the degree of conversion.

Among various forms of $f(\alpha)$, that correspond to the minimum value at the standard deviation, s, of the individual values E_λ, from the average value, $\bar{E}$, has to be chosen

$$s = \sqrt{\frac{1}{N-1}\sum_{\lambda=1}^{N}(E_\lambda - \bar{E})^2} \tag{20}$$

$$\bar{E} = \frac{E_1 + E_2 + \ldots + E_\lambda + \ldots + E_N}{N} \tag{21}$$

where N is the number of combinations $(\alpha_i, \alpha_j, \alpha_k)$ and λ is the general symbol for these combinations.

Considering, for instance $f(\alpha) = (1 - \alpha)^n$, the values s_1, s_2, ... corresponding to n_1, n_2, ... are calculated. Using the dependence $s(n)$, n_{minimum} is determined from the condition

$$\frac{\mathrm{d}s(n)}{\mathrm{d}n} = 0 \tag{22}$$

Using the determined form of $f(\alpha)$, the values of the activation energy for the N combinations $(\alpha_i, \alpha_j, \alpha_k)$ are calculated using formula (18). Then these values are averaged according to relationship (21). The pre-exponential factor is evaluated using relationships (15) or (16). Thus, from (15) one obtains

$$A_{ij} = \mathrm{e}^{\bar{E}/RT_{ij}} \times \frac{F(ij)\beta_{ij}}{T_j - T_i} \tag{23}$$

Using the values A_{ij}, calculated according to eqn. (23) for all the combinations (ij) used in formula (18), the geometric average value A, is given by

$$A = (A_1 A_2 \ldots A_M)^{1/M} \tag{24}$$

where M is the total number of combinations (ij).

Taking into account our previous experience [10–15], we recommend the following values for the differences $\alpha_2 - \alpha_1$ and $T_2 - T_1$

$0.05 \leqslant \alpha_2 - \alpha_1 \leqslant 0.40$

$5\ K \leqslant T_2 - T_1 \leqslant 20\ K$

APPLICATION OF THE METHOD

The method was applied to an $\alpha(T)$ curve theoretically modelled with the following values of the kinetic parameters [15]: $E = 25\,000$ cal mol^{-1}, $A = 6 \times 10^{11}$ min^{-1}, $f(\alpha) = (1 - \alpha)$ $(n = 1)$, $\beta = 10$ K min^{-1}, and $R = 1.987$ cal mol^{-1} K^{-1}. The thermal effect of the reaction was not taken into account, thus the local heating rate is considered to be equal to the global one.

TABLE 1

Modelled data

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	434.021
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

Combinations of α_i, α_j and α_k

λ	α_i	α_j	α_k
1	0.05	0.10	0.20
2	0.10	0.20	0.35
3	0.15	0.30	0.50
4	0.20	0.35	0.55
5	0.25	0.45	0.70
6	0.30	0.50	0.75
7	0.35	0.55	0.80
8	0.40	0.65	0.85
9	0.45	0.70	0.90
10	0.50	0.75	0.95

TABLE 3

Values of the activation energy for various values of n corresponding to the ten values of α_i, α_j and α_k from Table 2

λ	E (kcal mol^{-1})			
	λ	$n = 0.9000$	$n = 1.0000$	$n = 1.1000 n = 0.9978$
1	24.745	25.057	25.367	25.068
2	24.212	24.829	25.447	24.824
3	23.800	24.778	25.757	24.756
4	23.722	24.926	26.134	24.893
5	23.236	24.943	26.658	24.906
6	23.034	25.055	27.088	25.010
7	22.773	25.153	27.550	25.098
8	21.950	24.776	27.616	24.714
9	21.536	24.909	28.310	24.831
10	20.958	25.133	29.372	25.041

TABLE 4

Results obtained from the data in Table 3

	$n = 0.9000$	$n = 1.0000$	$n = 1.1000$	$n_{\text{minimum}} = 0.9978$
$\bar{E}$ (kcal mol^{-1})	22.997	24.956	26.930	24.914
s^2 (kcal mol^{-1})	1.4666	1.9292×10^{-2}	1.7193	1.8153×10^{-2}
s (kcal mol^{-1})	1.2110	0.1389	1.3112	0.1347

Tables 1–4 list all the necessary elements required to evaluate the non-isothermal kinetic parameters according to the presented method, as well as the results concerning the values of the reaction order, n, and the activation energy $\bar{E}$ (average value).

Considering the following form of the function $s(n)$

$$s(n) = a + bn + cn^2 \tag{25}$$

and from the known values of $s(n)$ for $n = 0.9$, $n = 1.0$ and $n = 1.1$, the values of a, b and c can be obtained by solving a system of three equations with three unknowns. The following values have been obtained: $a = 111.858$, $b = -223.929$, and $c = 112.22$. The values of n_{minimum} are obtained from condition (22) applied to $s(n)$ given by relationship (25)

$$b + 2Cn_{\text{minimum}} = 0$$

$$n_{\text{minimum}} = -\frac{b}{2C} = 0.9978$$

The average value $\bar{E}$ corresponding to n_{minimum} is given in Table 4. The value of the pre-exponential factor was obtained as previously indicated using relationships of the form of eqn. (23) and averaging the results for all the combinations (ij) using formula (24).

Thus the values of the non-isothermal kinetic parameters obtained according to our method are: $n_{\text{minimum}} = 0.9978$, $E = 24.914$ kcal mol^{-1} and $A = 5.54 \times 10^{11}$ min^{-1} which are in very good agreement with the values used for modelling.

CONCLUSIONS

An integral method to evaluate the non-isothermal kinetic parameters has been determined. The advantages of the method are: its validity for any form of $f(\alpha)$, and thus it generality; that it uses local heating rates; and that it uses practically all the range of values of the degree of conversion.

A disadvantage of the method is the large number of calculations involved. This disadvantage could be removed by the use of computers for automatic data processing.

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