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Note

ON A NEW "CLASSICAL" METHOD TO EVALUATE NON-ISOTHERMAL KINETIC PARAMETERS

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In a previous paper [1] we described a classical method to evaluate non-isothermal kinetic parameters, using integration over small ranges of the variables [2] and only one heating rate. Following our research, i.e. keeping the classical framework which means $A = \text{const}$, $E = \text{const}$, and $f(\alpha)$ does not change its form for all the α values, a new method to evaluate the non-isothermal kinetic parameters was derived. The new features of the method with respect to the old one [1] are:

(1) owing to the dependence of the heating rate on α, the method uses local heating rates;

(2) to determine the values of the non-isothermal kinetic parameters as accurately as possible an iterative procedure is used.

Although the conversion function $f(\alpha) = (1-\alpha)^n$ was used, the method is easy to extend to other conversion functions.

ITERATIVE METHOD TO EVALUATE THE NON-ISOTHERMAL KINETIC PARAMETERS

Starting from the fundamental equation of non-isothermal kinetics [3]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) e^{-E/RT} \tag{1}$$

by integration over the closed range $\alpha \in [\alpha_i, \alpha_k]$ it turns out that

$$\int_{\alpha_i}^{\alpha_k} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta_{ik}} \int_{T_i}^{T_k} e^{-E/RT}\, dT \tag{2}$$

where β_{ik} is the heating rate corresponding to the α range $\alpha \in [\alpha_i, \alpha_k]$, i.e.

$$\beta_{ik} = \frac{T_k - T_i}{t_k - t_i} \tag{3}$$

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For $f(\alpha) = (1-\alpha)^n$, using the average theorem [4] to operate the integrations in (2) one gets:

$$\frac{\alpha_k - \alpha_i}{(1-\alpha_{ik})^n} = \frac{A}{\beta_{ik}}(T_k - T_i)\mathrm{e}^{-E/RT_{ik}} \tag{4}$$

with $\alpha_{ik} \in [\alpha_i, \alpha_k]$ and $T_{ik} \in [T_i, T_k]$.

By taking logarithms of eqn. (4) with β_{ik} given by (3) it turns out that:

$$\log A + n\log(1-\alpha_{ik}) - \frac{E}{2.303RT_{ik}} = \log\frac{\alpha_k - \alpha_i}{t_k - t_i} \tag{5}$$

The problem is how to evaluate α_{ik} and T_{ik}, the values of A, n and E being unknown.

Let us consider four values of the conversion degree, α_1, α_2, α_3 and α_4, with the following pairings:

$\alpha_1\alpha_2\alpha_3\alpha_4\ (\alpha_1 < \alpha_2 < \alpha_3 < \alpha_4)$

These values and pairing enable us to write a system of three equations like (5) whose solutions are A, n and E.

It is recommended that the values α_1, α_2, α_3 and α_4 should cover almost all the α range as, for instance:

$\alpha_1 = 0.1 \quad \alpha_2 = 0.3 \quad \alpha_3 = 0.6 \quad \alpha_4 = 0.9$

$\Delta\alpha_{ik} = \alpha_k - \alpha_i \leq 0.3\text{–}0.4$

and

$\Delta T_{ik} = T_k - T_i \in (4\text{–}5\ \mathrm{K},\ 15\text{–}20\ \mathrm{K})$

As a first approximation (zero order approximation) α_{ik} and T_{ik} will be taken at the middle of their ranges, i.e.

$$\alpha_{ik}^{(0)} = \frac{\alpha_i + \alpha_k}{2} \tag{6}$$

$$T_{ik}^{(0)} = \frac{T_i + T_k}{2} \tag{7}$$

By introducing the values $\alpha_{12}^{(0)}$, $\alpha_{23}^{(0)}$, $\alpha_{34}^{(0)}$, $T_{12}^{(0)}$, $T_{23}^{(0)}$ and $T_{34}^{(0)}$ into the above mentioned system and solving it one gets the values of $A^{(0)}$, $n^{(0)}$ and $E^{(0)}$. These values can be used to calculate the integrals $\int_{\alpha_i}^{\alpha_k} \mathrm{d}\alpha/(1-\alpha)^{n^{(0)}}$ and $\int_{T_i}^{T_k} \mathrm{e}^{-E^{(0)}/RT}\,\mathrm{d}T$ (this one by a numerical procedure) and thus to evaluate $\alpha_{ik}^{(1)}$ and $T_{ik}^{(1)}$ from the equations:

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{(1-\alpha)^{n^{(0)}}} = \frac{\alpha_k - \alpha_i}{\left(1-\alpha_{ik}^{(1)}\right)^{n^{(0)}}} \tag{8}$$

$$\int_{T_i}^{T_k} \mathrm{e}^{-E^{(0)}/RT}\,\mathrm{d}T = (T_k - T_i)\ \mathrm{e}^{-E^{(0)}/RT_{ik}^{(1)}} \tag{9}$$

TABLE 1

Values of the non-isothermal kinetic parameters for the dehydration of $CaC_2O_4 \cdot H_2O$

β(K min^{-1})	$n^{(0)}$	$E^{(0)}$ (kcal mol^{-1})	$A^{(0)}$ (s^{-1})	$n^{(1)}$	$E^{(0)}$ (kcal mol^{-1})	$A^{(1)}$ (s^{-1})	$n^{(2)}$	$E^{(2)}$ (kcal mol^{-1})	$A^{(2)}$ (s^{-1})
$\beta_1 = 0.987$	0.514	27.39	7.62×10^{10}	0.445	27.02	4.71×10^{10}	0.448	27.05	4.87×10^{10}
$\beta_2 = 2.353$	0.462	23.14	4.87×10^{8}	0.403	22.84	3.32×10^{8}	0.405	22.86	3.40×10^{8}
$\beta_3 = 4.988$	0.576	21.65	1.04×10^{8}	0.501	21.37	7.12×10^{7}	0.506	21.40	7.38×10^{7}
$\beta_4 = 9.573$	0.644	20.01	1.93×10^{7}	0.554	19.63	1.20×10^{7}	0.560	19.67	1.25×10^{7}

With the values $\alpha_{ik}^{(1)}$ and $T_{ik}^{(1)}$ a new system can be written, whose solutions are $A^{(1)}$, $n^{(1)}$ and $E^{(1)}$.

By repeating the procedure after j iterations one gets:

$$\int_{\alpha_i}^{\alpha_k} \frac{d\alpha}{(1-\alpha)^{n^{(j)}}} = \frac{\alpha_k - \alpha_i}{\left(1-\alpha_{ik}^{(j+1)}\right)^{n^{(j)}}} \tag{10}$$

$$\int_{T_i}^{T_k} e^{-E^{(j)}/RT} \, dT = (T_k - T_i) \, e^{-E^{(j)}/RT_{ik}^{(j+1)}} \tag{11}$$

From these equations the values $\alpha_{ik}^{(j+1)}$ and $T_{ik}^{(j+1)}$ can be obtained and used to write a new system of equations whose solutions are $A^{(j+1)}$, $n^{(j+1)}$ and $E^{(j+1)}$.

The iterative procedure continues until

$$| n^{(j+1)} - n^{(j)} | \leq n \tag{12}$$

$$| E^{(j+1)} - E^{(j)} | \leq \Delta E \tag{13}$$

$$|\log A^{(j+1)} - \log A^{(j)} | \leq \log A \tag{14}$$

Concerning the integrals from eqns. (8)–(11) one has to notice that:

$$\int_{\alpha_i}^{\alpha_k} \frac{d\alpha}{(1-\alpha)^n} = \frac{(1-\alpha_i)^{1-n}(1-\alpha_k)^{1-n}}{1-n} \tag{15}$$

while for the integral $\int_{T_i}^{T_k} e^{-E/RT} \, dT$ a good approximation can be obtained using Simpson's method [5,6]:

$$\int_{T_i}^{T_k} e^{-E/RT} \, dT = \frac{T_k - T_i}{6}\left(e^{-E/RT_i} + 4e^{-E/RT_{ik}^{(0)}} + e^{-E/RT_k}\right) \tag{16}$$

APPLICATIONS

The method was applied for the dehydration of $CaC_2O_4 \cdot H_2O$ with $\beta_1 = 0.987$ K min^{-1}, $\beta_2 = 2.353$ K min^{-1}, $\beta_3 = 4.988$ K min^{-1}, $\beta_4 = 9.573$ K min^{-1}, $\alpha_1 = 0.10$, $\alpha_2 = 0.30$, $\alpha_3 = 0.60$, $\alpha_4 = 0.90$. The experimental data are given in table 1 of a previous paper [7]. The results obtained for two iterations are listed in Table 1. According to these results two iterations are sufficient to get accurate values of the non-isothermal kinetic parameters. The values of the non-isothermal kinetic parameters obtained for β_2, β_3 and β_4 are in fairly good agreement with those reported in the literature [8–10].

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