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Note

THE HEATING RATE AS A VARIABLE IN NON-ISOTHERMAL KINETICS. A NEW METHOD TO EVALUATE THE NON-ISOTHERMAL KINETIC PARAMETERS

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Starting from the fundamental rate equation of non-isothermal kinetics [1,2]

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

for constant values of A and E, through variable separation and integration, one obtains

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)}=\frac{A}{\beta}\int_0^T \mathrm{e}^{-E/RT} \tag{2}$$

Considering several constant values of the conversion degree, α_i ($i=1, 2,\ldots, m$), and introducing the notation

$$Z_{\alpha_i}=\int_0^{\alpha_i}\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} \tag{3}$$

where Z_{α_i} depends on the particular form of $\mathrm{f}(\alpha)$, from eqn. (2) for $\alpha_i = ct$, one obtains

$$Z_{\alpha_i}\beta = A\int_0^{T_{\alpha_i}(\beta)}\mathrm{e}^{-E/RT}\mathrm{d}T \tag{4}$$

where $T_{\alpha_i}(\beta)$ means that the temperature corresponding to $\alpha_i = ct$ depends on the heating rate, β. From eqn. (4), taking the derivative with respect to β, it turns out that

$$Z_{\alpha_i}=A\ \mathrm{e}^{-E/RT_{\alpha i}(\beta)}\frac{\mathrm{d}T_{\alpha_i}(\beta)}{\mathrm{d}\beta} \tag{5}$$

or

$$\log\frac{\mathrm{d}T_{\alpha_i}(\beta)}{\mathrm{d}\beta}=\log\frac{Z_{\alpha_i}}{A}+\frac{E}{2.303R}\frac{1}{T_{\alpha_i}(\beta)} \tag{6}$$

Thus, from a plot of $\log[\mathrm{d}T_{\alpha_i}(\beta)/\mathrm{d}\beta]$ values against $1/T_{\alpha_i}(\beta)$ values one can evaluate E_i and (Z_{α_i}/A) both corresponding to α_i.

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In order to determine the form of $f(\alpha)$, one has to calculate an average value of the activation energy, $\bar{E}$.

$$\bar{E} = \frac{E_1 + E_2 + \ldots + E_m}{m} \tag{7}$$

This is associated with the value, $\bar{A}$, of the pre-exponential factor. Using the $\bar{E}$ value one can calculate

$$\frac{Z_{\alpha_i}}{\bar{A}} = R_{\alpha_i} = \frac{e^{-\bar{E}/RT_{\alpha_i}(\beta_1)}\left(\frac{dT_{\alpha_i}(\beta)}{d\beta}\right)_{\beta_1} + \ldots + e^{-\bar{E}/RT_{\alpha_i}(\beta_k)}\left(\frac{dT_{\alpha_i}(\beta)}{d\beta}\right)_{\beta_k}}{k} \tag{8}$$

$(i = 1, 2, 3, \ldots, m)$

where k is the number of points for which $T_{\alpha_i}(\beta)$ and $dT_{\alpha_i}(\beta)/d\beta$ are known. The function $f(\alpha)$ can be found from the relationship

$$\frac{Z_{\alpha_1} + Z_{\alpha_2} + \ldots Z_{\alpha_j}}{Z_{\alpha_{j+1}} + Z_{\alpha_{j+2}} + \ldots Z_{\alpha_m}} = \frac{R_{\alpha_1} + R_{\alpha_2} + \ldots + R_{\alpha_j}}{R_{\alpha_{j+1}} + R_{\alpha_{j+2}} + \ldots R_{\alpha_m}} \tag{9}$$

Once $f(\alpha)$ is known, the pre-exponential factor can be evaluated from the relationship

$$A_i(\beta_k) = Z_{\alpha_i} e^{E_i/RT_{\alpha_i}(\beta_k)} \frac{1}{\left(\frac{dT_{\alpha_i}(\beta)}{d\beta}\right)_{\beta_k}} \quad (k = 1, 2) \tag{10}$$

$$\log A_i = \frac{\log A_{\alpha_i}(\beta_1) + \ldots + \log A_{\alpha_i}(\beta_k)}{k} \tag{11}$$

From relationship (5) for two heating rates, β_1 and β_2 ($\beta_2 > \beta_1$), one obtains

$$E = R\frac{T_{\alpha_i}(\beta_1)T_{\alpha_i}(\beta_2)}{T_{\alpha_i}(\beta_2) - T_{\alpha_i}(\beta_1)} \ln \frac{\left(dT_{\alpha_i}(\beta)/d\beta\right)_{\beta_1}}{\left(\frac{dT_{\alpha_i}(\beta)}{d\beta}\right)_{\beta_2}} \tag{12}$$

In order to obtain $dT_{\alpha_i}(\beta)/d\beta$ one can use numerical derivation or, if one knows several pairs of values $[T_{\alpha_i}(\beta), \beta]$, an interpolation polynomial can be written

$$T_{\alpha_i}(\beta) = a_0 + a_1\beta + a_2\beta^2 + \ldots \tag{13}$$

The method was applied for the dehydration of $CaC_2O_4 \cdot H_2O$. The experimental data and the results are given in Tables 1 and 2.

As seen from Table 1, three values of the heating rate were used. Under such conditions

$$T_{\alpha_i}(\beta) = a_0 + a_1\beta + a_2\beta^2 \tag{14}$$

TABLE 1

Experimental data for the dehydration of $CaC_2O_4 \cdot H_2O(s)$

No.	α_i	$T_{\alpha_i}(\beta_1)$ (K) ($\beta_1 = 1$ K min^{-1})	$T_{\alpha_i}(\beta_2)$ (K) ($\beta_2 = 5$ K min^{-1})	$T_{\alpha_i}(\beta_3)$ (K) ($\beta_3 = 10$ K min^{-1})
1	0.1667	416.8	431.5	437.9
2	0.3333	424.2	442.0	449.6
3	0.5000	429.2	449.2	458.0
4	0.6667	433.2	456.0	465.0
5	0.8333	437.3	462.2	472.0

The coefficients a_0, a_1 and a_2 can be determined from the system

$$T_{\alpha_i}(\beta_k) = a_0 + a_1\beta_k + a_2\beta_k^2 \ (k = 1, 2, 3) \tag{15}$$

Once a_0, a_1 and a_2 are known, one can easily obtain $T_{\alpha_i}(\beta)$ and $dT_{\alpha_i}(\beta)/d\beta$ for every value of β in the interval $\beta \in [\beta_1, \beta_3]$. The following values were considered

$$\beta_a = \frac{\beta_1 + \beta_2}{2} = 3 \text{ K min}^{-1} \tag{16}$$

$$\beta_b = \frac{\beta_2 + \beta_3}{2} = 7.5 \text{ K min}^{-1} \tag{17}$$

The values of E were determined by using formula (12). To get the function $f(\alpha) = (1 - \alpha)^m$ by help of relationship (9), the $\bar{E}$ value was calculated according to the formula

$$\bar{E} = \frac{E_2 + E_3 + E_4 + E_5}{4} \tag{18}$$

the value E_1 ($\alpha_1 = 0.1667$) being excluded as it does not belong to the linear portion of the TG decomposition curve. The obtained value is

$\bar{E} = 28.2$ kcal mol^{-1}

The value of the reaction order was obtained from the solution of the equation

$$\frac{2 - 0.6667^{(1-\bar{n})} - 0.5000^{(1-\bar{n})}}{2 - 0.3333^{(1-\bar{n})} - 0.1667^{(1-\bar{n})}} = 0.3402 \tag{19}$$

which led to a value of $\bar{n} = 1.22$. Using this value one can calculate A_{α_i} through relationships (10) and (11).

The results are given in Table 2. For comparison, E was also calculated using Ozawa's method [3].

From Table 2 one obtains: $\bar{A} = 2.55 \times 10^{11}$ s^{-1} (for $i = 2, 3, 4, 5$); and $E_{\text{Ozawa}} = 29.4$ kcal mol^{-1} (for $i = 2, 3, 4, 5$). The two methods give values in rather good agreement with each other.

TABLE 2

Results concerning the evaluation of non-isothermal kinetic parameters of the dehydration of $CaC_2O_4 \cdot H_2O$ (s)

No.	α_i	a_0(K)	a_1(min)	a_2(min^2 K^{-1})	$T_{\alpha_i}(\beta_a)$ ^{a}(K)	$t_{\alpha_i}(\beta_b)$ ^{a}(K)	$\left[\frac{dT_{\alpha_i}(\beta)}{d\beta}\right]_{\beta_a}$ (min)	$\left[\frac{dT_{\alpha_i}(\beta)}{d\beta}\right]_{\beta_b}$ (kcal mol^{-1})	E_i(kcal mol^{-1})	A_i (s^{-1})	E_{Ozawa} (kcal mol^{-1})
1	0.1667	411.798	5.270	−0.266	425.214	436.361	3.674	1.280	34.876	7.13×10^{14}	37.836
2	0.3333	418.121	6.404	−0.326	434.403	447.835	4.450	1.520	30.918	5.72×10^{12}	32.983
3	0.5000	422.400	7.160	−0.360	440.640	455.880	5.000	1.760	27.400	9.73×10^{10}	29.877
4	0.6667	425.333	8.300	−0.433	446.333	463.210	5.700	1.800	28.058	2.00×10^{11}	28.255
5	0.8333	428.705	9.069	−0.474	451.646	470.062	6.225	1.960	26.471	3.80×10^{10}	26.574

[a] Calculated according to relationship (14).

CONCLUSIONS

(1) A method to evaluate non-isothermal kinetic parameters using several heating rates was developed.

(2) The values of the activation energy for the dehydration of calcium oxalate are in quite good agreement which those obtained using Ozawa's method.

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