

THE DEVIATION OF THE TRUE HEATING RATE WITH RESPECT TO THE PROGRAMMED ONE Consequences for non-isothermal kinetics

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The paper deals with the influence of the deviation of the true heating rate with respect to the programmed one on the values of non-isothermal kinetic parameters for the solid-gas thermal decompositions of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $[\text{Ni}(\text{NH}_3)_6]\text{Br}_2$. An original method, based on integration over small ranges of the variables and making use of local heating rates, was applied in order to determine the non-isothermal kinetic parameter values. The results show significant differences between values of non-isothermal kinetic parameters obtained by using true local heating rates and those obtained by using the programmed heating rate.

Keywords: $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, kinetics, $[\text{Ni}(\text{NH}_3)_6]\text{Br}_2$, true heating rate

Introduction

Conventional non-isothermal kinetics uses linear heating programmes, the change of temperature, T , with time being given by:

$$T = T_0 + \beta \cdot t \quad (1)$$

where T_0 is the initial temperature and β the constant programmed heating rate. Due to the thermal effects which accompany the followed changes of the investigated sample, its temperature differs from the programmed one; thus for the sample [1],

$$T = T_0 + \beta \cdot t + s(t) \quad (2)$$

the supplementary term $s(t)$ being the difference between the two temperatures.

In the following a comparison between the non-isothermal kinetic equation obtained by using Eqs (1) and (2) will be performed. In order to do it we shall start from the well-known isothermal differential kinetic equation:

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot \exp(-E/RT) \quad (T = \text{const.}) \quad (3)$$

where the differential conversion function, $f(\alpha)$, for the general case is given by [2]:

$$f(\alpha) = (1-\alpha)^n \cdot \alpha^m \cdot [-\ln(1-\alpha)]^p \quad (4)$$

Considering Eq. (3) as primary and applying the classical non-isothermal change (CNC) with the temperature given by relationship (1), we get the following non-isothermal kinetic equation [3-6]

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot \exp[-E/R \cdot (T_0 + \beta t)] \quad (5)$$

where taking into account that $dT = \beta \cdot dt$

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot f(\alpha) \cdot \exp(-E/RT) \quad (6)$$

Integration of Eq. (6) leads to

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp(-E/RT) dT \quad (7)$$

where $g(\alpha)$ is the integral conversion function.

In spite of their wide use in evaluating non-isothermal kinetic parameters, Eqs (6) and (7) are not rigorously valid unless $s(t) = 0$. In order to obtain correct kinetic equations, relationship (2) should be used. By applying the CNC in Eq. (3) one obtains:

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot e^{-E/R [T_0 + \beta t + s(t)]} \quad (8)$$

Taking into account that from (2):

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

and

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

Eq. (8) converts to

$$\frac{d\alpha}{dT} = \frac{A}{\beta + \dot{s}(t)} \cdot f(\alpha) \cdot \exp(-E/RT) \quad (11)$$

Eq. (11) is actually the 'corrected' non-isothermal kinetic equation. The complications due to the supplementary terms $\dot{s}(t)$ could be overcome by making use of integration over small ranges of variables [1]. In such conditions from Eq. (11) by integration we obtain [1]:

$$\int_{\alpha_i}^{\alpha_k} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta_{ik}} \int_{T_i}^{T_k} \exp(-E/RT) dT \quad (12)$$

where

$$\beta_{ik} = \frac{T_k - T_i}{t_k - t_i} \quad (13)$$

is the local heating rate corresponding to the range $\alpha \in [\alpha_i, \alpha_k]$. In Eq. (12) the deviation of the true heating rate with respect to the programmed one has been taken into account in contrast with Eqs (6) and (7) which contain the programmed heating rate.

The method used to evaluate the non-isothermal kinetic parameters

An original method to evaluate the non-isothermal kinetic parameters based on Eq. (12) is presented briefly. The method has been described elsewhere [7], being a simplified variant of another presented in paper [8]. The method is based on the following equation obtained as an approximate solution of Eq. (12) for $f(\alpha) = (1 - \alpha)^n$:

$$\frac{(\alpha_k - \alpha_i) \left(1 + \frac{n^2 + n}{24} \frac{(\alpha_k - \alpha_i)^2}{(1 - \alpha_{ik})^2} \right)}{(1 - \alpha_{ik})^n} = \frac{A}{\beta_{ik}} \cdot (T_k - T_i) \cdot e^{-E/RT_{ik}} \cdot \left[1 + \frac{1}{24} \left(\frac{E(T_k - T_i)}{RT_{ik}^2} \right)^2 \right] \quad (14)$$

where

$$\alpha_{ik} = \frac{\alpha_i + \alpha_k}{2} \quad (15)$$

and

$$T_{ik} = \frac{T_i + T_k}{2} \quad (16)$$

The logarithmic form of Eq. (14) is:

$$\ln A + n \ln(1 - \alpha_{ik}) - \frac{E}{RT_{ik}} = \ln \frac{\alpha_k - \alpha_i}{T_k - T_i} \beta_{ik} + \ln \frac{1 + \frac{n^2 + n}{24} \frac{(\alpha_k - \alpha_i)^2}{(1 - \alpha_{ik})^2}}{1 + \frac{1}{24} \left(\frac{E}{R} \cdot \frac{T_k - T_i}{T_{ik}^2} \right)^2} \quad (17)$$

which is actually the equation applied to evaluate non-isothermal kinetic parameters. The second term in the right-hand member of Eq. (17) will be noted by $q(n, E)$.

In order to calculate values of the non-isothermal kinetic parameters, a number of N pairs (α_i, α_k) together with the corresponding N equations of the form (17) will be considered. By applying the least-squares method we obtain the sum S , given by

$$S = \sum_1^N \left(\ln A + n \ln(1 - \alpha_{ik}) - \frac{E}{RT_{ik}} - \ln \frac{\alpha_k - \alpha_i}{T_k - T_i} \cdot \beta_{ik} - q(n, E) \right)^2 \quad (18)$$

whose minimisation with respect to $\ln A$, n and E leads to the following system of three equations:

$$\frac{\partial S}{\partial \ln A} = 0; \quad \frac{\partial S}{\partial n} = 0; \quad \frac{\partial S}{\partial E} = 0 \quad (19)$$

In order to solve the system (19) with respect to A , n , and E an iterative procedure is used.

Iteration 1

The linear system (19) is solved for $g(n, E) = 0$, and the values A_1 , n_1 and n_2 obtained.

Iteration 2

By introducing $q(n_1, E_1)$ in the sum (18) and solving the system (19), the values A_2 , n_2 and E_2 are obtained.

Iteration (j)

By introducing $q(n_{(j-1)}, E_{(j-1)})$ in (18) and solving the system (19) the values A_j , n_j and E_j are obtained.

The iterations j and $j-i$ decrease under a given value as for instance

$$|n_j - n_{j-1}| < \epsilon_n \quad (20)$$

In our experience the necessary number of iterations is three. As far as the value of N is concerned this should be within the range $3 < N < 20$. In our experience a value between 6 and 9 for N is quite reasonable to obtain significant

results. Special care should be taken that the intervals $[\alpha_i, \alpha_k]$ should cover almost all the values of the degree of conversion. As far as range $[T_i, T_k]$ is concerned this should be chosen in such a way that $10 < T_k - T_i < 15$.

The method was checked on a modelled curve. The results obtained showed a satisfactory agreement between the values of the non-isothermal kinetic parameters.

Applications

The method was applied for evaluation of the non-isothermal kinetic parameters of dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and decomposition of $[\text{Ni}(\text{NH}_3)_6]\text{Br}_2$. The following two variants of the method were considered:

- in relationship (18) the local heating rates, β_{ik} , have been used
- in a relationship similar to (18) the programmed heating rate, has been used; obviously in this case a sum S based on Eq. (6) should be considered.

In all the calculations the value $N = 6$ was used.

Dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$

Calcium oxalate monohydrate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (Merck), was used. The sample weight was 36.60 mg. The TG curves were recorded on DuPont 1090 equipment at a heating rate of $\beta = 5 \text{ deg} \cdot \text{min}^{-1}$.

The investigated reaction was

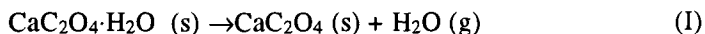
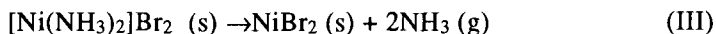
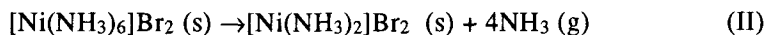


Table 1 lists the combinations (α_i, α_k) with the corresponding temperatures (T_i, T_k) and time values (t_i, t_k) . The local heating rates β_{ik} are also listed in this Table.

Table 2 lists the non-isothermal kinetic parameters obtained after three iterations using local heating rates, while Table 3 lists the non-isothermal kinetic parameters obtained after three iterations using the programmed heating rate ($\beta = 5 \text{ deg} \cdot \text{min}^{-1}$).

Decomposition of $[\text{Ni}(\text{NH}_3)_6]\text{Br}_2$

Powdered $[\text{Ni}(\text{NH}_3)_6]\text{Br}_2$ synthesized according to a method described elsewhere [9, 10] was used. The heating curves were recorded on a MOM derivatograph (type C) at a heating rate $\beta = 10 \text{ deg} \cdot \text{min}^{-1}$. The sample weight was 56.00 mg. Decomposition occurs in the following two steps



whose kinetic parameters were evaluated. The results are listed in Tables 4–9.

Table 1 Combination of (α_i, α_k) , (T_i, T_k) , (t_i, t_k) values and β_{ik} values for reaction (I)

Number of combination α_i, α_k	α_i	α_k	T_i / K	T_k / K	t_i / min	t_k / min	$\beta_{ik} / \text{deg} \cdot \text{min}^{-1}$
1	0.10	0.30	425.3	440.2	26.40	29.54	4.75
2	0.20	0.40	434.0	445.3	28.27	30.58	4.89
3	0.30	0.60	440.2	453.1	29.54	32.21	4.83
4	0.40	0.70	445.3	456.8	30.58	32.92	4.91
5	0.60	0.90	453.1	465.1	32.21	34.38	5.52
6	0.70	0.95	456.8	468.15	32.92	34.90	5.73

Table 2 Non-isothermal kinetic parameter values for reaction (I) obtained using local heating rates

Kinetic parameter	Iteration 1	Iteration 2	Iteration 3
n	0.660	0.570	0.586
$E / \text{kJ} \cdot \text{mol}^{-1}$	96.26	94.08	94.60
A / sec^{-1}	$5.13 \cdot 10^8$	$2.67 \cdot 10^8$	$3.10 \cdot 10^8$

Table 3 Non-isothermal kinetic parameter values for reaction (I) obtained using the programmed heating rate

Kinetic parameter	Iteration 1	Iteration 2	Iteration 3
n	0.927	0.784	0.814
$E / \text{kJ} \cdot \text{mol}^{-1}$	108.81	105.14	106.06
A / sec^{-1}	$1.83 \cdot 10^{10}$	$6.21 \cdot 10^9$	$8.08 \cdot 10^9$

Table 4 Combination of (α_i, α_k) , (T_i, T_k) , (t_i, t_k) values and β_{ik} values for reaction (II)

Number of combination α_i, α_k	α_i	α_k	T_i / K	T_k / K	t_i / min	t_k / min	$\beta_{ik} / \text{deg} \cdot \text{min}^{-1}$
1	0.0950	0.1777	437.75	450.75	17.4	18.7	10.00
2	0.1777	0.2810	450.75	461.75	18.7	19.9	9.17
3	0.2810	0.4504	461.75	474.25	19.9	21.3	8.93
4	0.4504	0.6694	474.25	487.35	21.3	22.7	9.36
5	0.6694	0.8471	487.35	499.75	22.7	23.9	10.33
6	0.8741	0.9587	499.75	511.15	23.9	24.9	11.40

Discussions

From Tables 1, 4 and 7 a significant change of heating rate can be noticed. Taking into account the endothermic character of all three investigated reactions it is easy to explain why the heating rate decreases at the beginning of the reaction (decrease due to absorption of heat) and increases at its end when heat is no longer absorbed or absorbed to a lesser extent. Thus in final part of the reaction a trend of the heating rate value to the programmed one has to be noticed.

Table 5 Non-isothermal kinetic parameter values for reaction (II) obtained using local heating rates

Kinetic parameter	Iteration 1	Iteration 2	Iteration 3
n	0.783	0.738	0.741
$E / \text{kJ}\cdot\text{mol}^{-1}$	70.57	69.83	69.89
A / sec^{-1}	2.25·10 ⁵	1.81·10 ⁵	1.85·10 ⁵

Table 6 Non-isothermal kinetic parameter values for reaction (II) obtained using the programmed heating rate

Kinetic parameter	Iteration 1	Iteration 2	Iteration 3
n	1.042	0.976	0.981
$E / \text{kJ}\cdot\text{mol}^{-1}$	82.28	81.19	81.29
A / sec^{-1}	5.68·10 ⁶	4.13·10 ⁶	4.25·10 ⁶

Table 7 Combination of (α_i, α_k) , (T_i, T_k) , (t_i, t_k) values and β_{ik} values for reaction (III)

Number of combination α_i, α_k	α_i	α_k	T_i / K	T_k / K	t_i / min	t_k / min	$\beta_{ik} / \text{deg}\cdot\text{min}^{-1}$
1	0.1102	0.3136	574.35	586.75	30.9	32.3	8.86
2	0.1864	0.4153	579.65	592.15	31.5	32.9	9.00
3	0.3136	0.5763	586.75	599.65	32.3	33.7	9.21
4	0.4153	0.7034	592.15	605.45	32.9	34.3	9.50
5	0.5763	0.8136	599.65	611.55	33.7	34.9	9.92
6	0.7034	0.9153	605.45	618.15	34.3	35.5	10.58

Concerning the method of non-isothermal kinetic analysis, as shown by our data, three iterations are sufficient to obtain reliable values for non-isothermal kinetic parameters. Differences between values of non-isothermal kinetic parameters corresponding to iterations 2 and 3 are not significant. As the non-isothermal kinetic parameter values calculated with local heating rates have been obtained taking into account the deviation of the true temperature with respect to

the programmed ones, we consider these values, given in Table 2, 5, and 8, the reliable ones. In order to confirm this statement, values of α_{\max} (corresponding to the maximum reaction rate) were calculated [11–14] and compared with the experimental ones. The results are given in Table 10.

Table 8 Non-isothermal kinetic parameter values for reaction (III) obtained using local heating rates

Kinetic parameter	Iteration 1	Iteration 2	Iteration 3
n	0.848	0.772	0.780
$E / \text{kJ}\cdot\text{mol}^{-1}$	132.60	129.06	129.40
A / sec^{-1}	2.52·10 ⁹	1.18·10 ⁹	1.27·10 ⁹

Table 9 Non-isothermal kinetic parameter values for reaction (III) obtained using the programmed heating rate

Kinetic parameter	Iteration 1	Iteration 2	Iteration 3
n	0.987	0.894	0.906
$E / \text{kJ}\cdot\text{mol}^{-1}$	134.79	130.59	131.05
A / sec^{-1}	4.63·10 ⁹	1.88·10 ⁹	2.07·10 ⁹

Table 10 Comparison between calculated and experimental α_{\max} values

Reaction	$\alpha_{\max}(\text{exp})$	$\alpha_{\max}(\beta_{ik})$	$\alpha_{\max}(\beta)$
(I)	0.708	0.702	0.648
(II)	0.638	0.650	0.603
(III)	0.647	0.653	0.626

As seen from this Table the values $\alpha_{\max}(\beta_{ik})$ are closer to $\alpha_{\max}(\text{exp})$ values. This is another reason for considering the values of the non-isothermal kinetic parameters obtained by using local heating rates as more reliable.

Conclusions

1. An investigation concerning the influence of the deviation of the true heating rate with respect to the programmed one on the values of non-isothermal kinetic parameters has been performed.

2. The dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and the decomposition of $[\text{Ni}(\text{NH}_3)_6]\text{Br}_2$ were used as test reactions.

3. The data presented show significant deviation of the true heating rates compared to the programmed one.

4. Differences between values of non-isothermal kinetic parameters are significant also.

5. The use of the α_{\max} criterion confirms the reliability of the non-isothermal kinetic parameters values obtained by using the local heating rates.

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Zusammenfassung — Es wird der Einfluß der Abweichung der tatsächlichen Aufheizgeschwindigkeit (bezogen auf die programmierte Aufheizgeschwindigkeit) auf die Werte von nichtisothermen kinetischen Parametern der thermischen Feststoff-Gas-Zersetzungsreaktionen von $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ und $[\text{Ni}(\text{NH}_3)_6]\text{Br}_2$ untersucht. Zur Bestimmung der nichtisothermen kinetischen Parameter wird eine Methode verwendet, die auf der Integration kleiner Variablen-Intervalle und der Ausnutzung lokaler Aufheizgeschwindigkeiten beruht. Die Resultate zeigen signifikante Unterschiede zwischen den nichtisothermen kinetischen Parametern, die für die tatsächlichen bzw. die programmierten Aufheizgeschwindigkeiten erhalten wurden.