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ON A RELATIONSHIP BETWEEN TEMPERATURE AND CONSTANT HEATING RATE FOR A CONSTANT DEGREE OF CONVERSION IN NON-ISOTHERMAL KINETICS

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ABSTRACT

The following relationship has been derived between the temperature T and constant heating rate for a constant value of the degree of conversion

$$1/T = a + b \ln \beta \qquad (a = \text{const.}, \quad b = \text{const.})$$

The validity of the same relationship for non-classical non-isothermal kinetics is also discussed. Some potential applications of the relationship are suggested.

INTRODUCTION

The basic equation of classical non-isothermal kinetics [1–4]

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

with

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

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

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

where n, m and p are constants, is obtained by performing the classical non-isothermal change (CNC) with

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

on the isothermal kinetic equation

$$\mathrm{d}\alpha/\mathrm{d}t = A f(\alpha)\, \mathrm{e}^{-(E/RT)} \tag{6}$$

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accepted as the postulated primary isothermal differential kinetic equation (P-PIDKE) [2–4].

From eqn. (1), by variable separation and integration, we obtain

$$\int_0^\alpha \mathrm{d}\alpha/f(\alpha) = (A/\beta)\int_0^T \mathrm{e}^{-(E/RT)}\,\mathrm{d}T \tag{7}$$

with β considered as being rigorously constant.

DERIVATION OF THE RELATIONSHIP BETWEEN TEMPERATURE AND HEATING RATE FOR $\alpha = \text{const.}$

In order to perform such a derivation we need to consider some of our earlier ideas concerning constant heating rate as a variable in non-isothermal kinetics [5–7].

Introducing the notation

$$Z = \int_0^\alpha \mathrm{d}\alpha/f(\alpha) \tag{8}$$

into relationship (7) and taking its derivative with respect to β for $\alpha = \text{const.}$, we obtain

$$Z/A = \mathrm{e}^{-[E/RT(\beta)]}[\mathrm{d}T(\beta)/\mathrm{d}\beta] \tag{9}$$

where $T(\beta)$ means that for $\alpha = \text{const.}$, the corresponding temperature depends on the heating rate. The left-hand side of eqn. (8) can be rewritten to take relationship (7) into account. Equation (8) then becomes

$$A/\beta\int_0^{T(\beta)} \mathrm{e}^{-(E/RT)}\,\mathrm{d}T = \mathrm{e}^{-[E/RT(\beta)]}[\mathrm{d}T(\beta)/\mathrm{d}\beta] \tag{10}$$

Introducing into eqn. (9) the approximation [8]

$$\mathrm{e}^{-(E/RT)}\,\mathrm{d}T = (RT^2/E)Q(T,\ E)\,\mathrm{e}^{-(E/RT)} \tag{11}$$

where $Q(T,\ E)$ is a function with smooth variation whose value is close to unity (in a first approximation, $Q(T,\ E)$ can be considered as constant), we obtain

$$(1/\beta)[RT^2(\beta)/E]\ \mathrm{e}^{-[E/RT(\beta)]}Q(T(\beta),\ E) = \mathrm{e}^{-[E/RT(\beta)]}[\mathrm{d}T(\beta)/\mathrm{d}\beta] \tag{12}$$

or

$$[RQ(T(\beta),\ E)/E](\mathrm{d}\beta/\beta) = \mathrm{d}T(\beta)/T^2(\beta) \tag{13}$$

The relationship we are seeking is obtained from eqn. (13) through integration, considering $Q(T(\beta),\ E) \approx \text{const.}$ in the form

$$1/T(\beta) = a - [RQ(T_1,\ E)/E]\ln\beta \tag{14}$$

where T_1 is an average temperature and the integration constant a is given by

$$a = 1/T(\beta = 1) \tag{15}$$

It is interesting to compare relationship (14) with a number of other simple relationships, derived by Ozawa [9] and Flynn and Wall [10].

Ozawa's relationship for $\alpha = \text{const.}$ is

$$-\log \beta - 0.4567[E/RT(\beta)] = \text{const.} \tag{16}$$

After rearrangement, this leads to

$$1/T(\beta) = a_1 - (R/E)0.9509 \ln \beta \qquad (a_1 = \text{const.}) \tag{17}$$

It is easy to see that relationship (17) is a particular case of relationship (14).

The Flynn–Wall relationship

$$\log F(\alpha) = \log(AE/R) - \log \beta - 2.315 - 0.457[E/RT(\beta)] \tag{18}$$

can be rearranged into the form

$$1/T(\beta) = a_2 - (R/E)0.9503 \ln \beta \qquad (a_2 = \text{const.}) \tag{19}$$

which is practically identical to relationship (17).

Introducing the notation

$$b = -RQ(T_1, E)/E \tag{20}$$

into relationship (14), we obtain

$$1/T(\beta) = a + b \ln \beta \qquad (a = \text{const.}, b = \text{const.}) \tag{21}$$

For non-classical non-isothermal kinetics (with kinetic parameters depending on the degree of conversion), eqn. (1) takes the form [11]

$$\mathrm{d}\alpha/\mathrm{d}T = [A(\alpha)/\beta] f^\star(\alpha)\, \mathrm{e}^{-[E(\alpha)/RT]} \tag{22}$$

with $n(\alpha)$, $m(\alpha)$ and $p(\alpha)$ as in $f^\star(\alpha)$. For $\alpha = \text{const.}$, $\mathrm{d}\alpha/\mathrm{d}T$ and T depend on the heating rate, and can therefore be written as $(\mathrm{d}\alpha/\mathrm{d}T)(\beta)$ and $T(\beta)$. From eqn. (22), taking the logarithms, we obtain

$$\ln \beta + \ln[(\mathrm{d}\alpha/\mathrm{d}T)(\beta)] = \ln A(\alpha) f^\star(\alpha) - [E(\alpha)/RT(\beta)] \tag{23}$$

Experience has shown that $(\mathrm{d}\alpha/\mathrm{d}T)(\beta)$ changes smoothly with β and $1/T(\beta)$. We can therefore consider

$$\ln[(\mathrm{d}\alpha/\mathrm{d}T)(\beta)] \simeq c + d \ln \beta \tag{24}$$

where c and d are constants.

Taking into account relationship (24) and the fact that for a given α, $A(\alpha)$, $f^\star(\alpha)$ and $E(\alpha)$ are constants, we obtain

$$1/T(\beta) = \ln A(\alpha) f^\star(\alpha) - c - [R/E(\alpha)](1 + d) \ln \beta \tag{25}$$

Thus in non-classical non-isothermal kinetics, a relationship of the form

$$1/T(\beta) = a^x + b^x \ln \beta \qquad (a = \text{const.}, b = \text{const.}) \tag{26}$$

is also valid.

Taking into account the fact that in relationships (21) and (26) $a \geqslant b$, the temperature $T(\beta)$, given by

$$T(\beta) = 1/a[1 + (b/a) \ln \beta] \tag{27}$$

can be developed in series. Keeping only two terms from such a development, we obtain

$$T(\beta) = (1/a) - (b/a^2) \ln \beta = a_1 + b_1 \ln \beta \qquad (a_1 = \text{const.}, b_1 = \text{const.}) \tag{28}$$

The same relationship has been derived in a different way in a previous work [7].

CHECKING RELATIONSHIPS (21) AND (26)

Let us suppose that for the general case of a non-isothermal process at $\alpha = \text{const.}$, the temperatures $T_1, T_2, \ldots, T_n$ for the heating rates $\beta_1, \beta_2, \ldots, \beta_n$ are known (experimental or modelled data). Let us also suppose that the process under investigation does not change its mechanism within the range of variables considered. To determine the constants a and b we suggest the least-squares method. In such a case, the sum S given by

$$S = \sum_{i=1}^{n} [a + b \ln \beta_i - (1/T_i)]^2 \tag{29}$$

should be minimized, i.e.

$$\partial S/\partial a = 0 \tag{30}$$

and

$$\partial S/\partial b = 0 \tag{31}$$

After performing the detailed calculations, we obtain

$$an + b \sum_{i=1}^{n} \ln \beta_i = \sum_{i=1}^{n} 1/T_i \tag{32}$$

$$a \sum_{i=1}^{n} \ln \beta_i + b \sum_{i=1}^{n} \ln^2 \beta_i = \sum_{i=1}^{n} (1/T_i) \ln \beta_i \tag{33}$$

the constants a and b being the solutions of the system comprised by eqns. (32) and (33). Using these values, and eqn. (21), the temperatures $T_{\text{calc}}(\beta_1), T_{\text{calc}}(\beta_2), \ldots, T_{\text{calc}}(\beta_n)$ may be calculated and subsequently compared with $T_1, T_2, \ldots, T_n$.

In Tables 1–3, the results of such a comparison are given for the dehydration of calcium oxalate monohydrate [12] at three values of the degree of conversion.

TABLE 1

Comparison between T_i and $T_{\text{calc}}(\beta_i)$ for calcium oxalate dehydration at $\alpha = 0.10$ [a]

No.	β_i (K min^{-1})	T_i (K)	$T_{\text{calc}}(\beta_i)$ (K)	$T_i - T_{\text{calc}}(\beta_i)$ (K)
1	0.987	412.2	412.86	−0.66
2	2.353	420.9	419.63	1.27
3	4.988	425.3	425.66	−0.36
4	9.573	430.8	431.04	−0.24

[a] $a = 2.42155\ 10^{-3}\ \text{K}^{-1}$; $b = -4.49790\ 10^{-5}\ \text{K}^{-1}$.

TABLE 2

Comparison between T_i and $T_{\text{calc}}(\beta_i)$ for calcium oxalate dehydration at $\alpha = 0.50$ [a]

No.	β_i (K min^{-1})	T_i (K)	$T_{\text{calc}}(\beta_i)$ (K)	$T_i - T_{\text{calc}}(\beta_i)$ (K)
1	0.987	429.2	429.64	−0.44
2	2.353	441.0	440.10	0.90
3	4.988	449.2	449.56	−0.36
4	9.573	458.0	458.11	−0.11

[a] $a = 2.32672\ 10^{-3}\ \text{K}^{-1}$; $b = -6.36679\ 10^{-5}\ \text{K}^{-1}$.

TABLE 3

Comparison between T_i and $T_{\text{calc}}(\beta_i)$ for calcium oxalate dehydration at $\alpha = 0.90$ [a]

No.	β_i (K min^{-1})	T_i (K)	$T_{\text{calc}}(\beta_i)$ (K)	$T_i - T_{\text{calc}}(\beta_i)$ (K)
1	0.987	439.0	439.25	−0.25
2	2.353	452.9	452.60	0.30
3	4.988	465.1	464.81	0.29
4	9.573	475.6	475.95	−0.35

[a] $a = 2.27559\ 10^{-3}\ \text{K}^{-1}$; $b = -7.72559\ 10^{-5}\ \text{K}^{-1}$.

Let us now consider three non-isothermal curves modelled by computer for the following variable kinetic parameters [11]

$$E(\alpha) = 40000 - 20000\alpha \qquad (\text{cal mol}^{-1}) \tag{34}$$

$$f(\alpha) = (1 - \alpha)^{1.5 - \alpha} \tag{35}$$

$$A(\alpha) = 10^{(15 - 10\alpha)} \qquad (\text{s}^{-1}) \tag{36}$$

The results of a similar comparison are given in Tables 4–6. Examination of the results given in Tables 1–6 indicates a very good agreement between the calculated and experimental temperature values.

TABLE 4

Comparison between T_i and T_{calc} (β_i) for $\alpha = 0.10$ [a]

No.	β_i (K min^{-1})	T_i (K)	$T_{\text{calc}}(\beta_i)$ (K)	$T_i - T_{\text{calc}}(\beta_i)$ (K)
1	2	474.125	474.128	−0.003
2	6	486.475	486.468	0.007
3	12	494.586	494.590	−0.004

[a] $a = 2.14289\ 10^{-3}\ \text{K}^{-1}$; $b = -4.87015\ 10^{-5}\ \text{K}^{-1}$.

TABLE 5

Comparison between T_i and $T_{\text{calc}}(\beta_i)$ for $\alpha = 0.50$ [a]

No.	β_i (K min^{-1})	T_i (K)	$T_{\text{calc}}(\beta_i)$ (K)	$T_i - T_{\text{calc}}(\beta_i)$ (K)
1	2	504.440	504.436	0.004
2	6	520.648	520.658	−0.010
3	12	531.448	531.441	0.007

[a] $a = 2.02138\ 10^{-3}\ \text{K}^{-1}$; $b = -5.62219\ 10^{-5}\ \text{K}^{-1}$.

TABLE 6

Comparison between T_i and $T_{\text{calc}}(\beta_i)$ for $\alpha = 0.90$ [a]

No.	β_i (K min^{-1})	T_i (K)	$T_{\text{calc}}(\beta_i)$ (K)	$T_i - T_{\text{calc}}(\beta_i)$ (K)
1	2	537.414	537.394	0.020
2	6	561.097	561.154	−0.057
3	12	577.293	577.256	0.037

[a] $a = 1.91054\ 10^{-3}\ \text{K}^{-1}$; $b = -7.17171\ 10^{-5}\ \text{K}^{-1}$.

POSSIBLE APPLICATIONS OF RELATIONSHIPS (21) AND (26)

Evaluation of a T_λ corresponding to an uninvestigated β_λ

According to relationship (21) or (26), we have

$$T_\lambda = 1/a + b \ln \beta_\lambda \tag{37}$$

or

$$T_\lambda = 1/a^\star + b^\star \ln \beta_\lambda \tag{38}$$

Assessment of changes of mechanism

If, for one or several heating rates at the boundary of the range under consideration, (e.g. β_1 and β_n) the calculated temperatures for $\alpha = \text{const.}$ differ appreciably from the experimental values, it may be concluded that for the heating rates used, the mechanism of the process under investigation undergoes a change.

CONCLUSIONS

Relationships have been derived between temperature and constant heating rate at $\alpha = \text{const.}$ for both classical and non-classical non-isothermal kinetic systems.

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