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SOME PROBLEMS CONCERNING THE MATHEMATICAL THEORY OF NON-ISOTHERMAL KINETICS. IV. ON THE CLASSICAL NON-ISOTHERMAL CHANGE IN THE ISOTHERMAL DIFFERENTIAL QUASI-KINETIC EQUATION $d^2\alpha/dt^2 = \mathcal{G}(\alpha) f(T)$

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ABSTRACT

Following our work concerning the mathematical theory of non-isothermal kinetics, an attempt to apply the classical non-isothermal change (CNC) to the second-order differential equation derived from the rate equation $d\alpha/dt = f(\alpha)k(T)$ is discussed. The authors show that such a CNC is not valid for the "reaction order" conversion function, $f(\alpha) = (1-\alpha)^n$ and seems not to be valid for other forms of $f(\alpha)$.

In some previous papers [1–4] concerning the mathematical aspects of non-isothermal kinetics, the possibility of deriving non-isothermal kinetic differential and integral kinetic equations through the classical non-isothermal change (CNC) has been considered. It has been shown that the correct way to derive non-isothermal differential kinetic equations is to perform the CNC on the first-order isothermal kinetic equation (rate equation) considered as the postulated primary isothermal differential kinetic equation (P-PIDKE).

This paper deals with the possibility of applying the CNC to the second-order isothermal quasi-kinetic equation which is the first derivative with respect to time of the isothermal rate equation, $d\alpha/dt$. Considering the general isothermal rate equation

$$d\alpha/dt = f(\alpha)k(T) \qquad (T = \text{const.}) \tag{1}$$

with the classical conditions

$$f(\alpha) = (1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p \tag{2}$$

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with $m = \text{const.}$, $n = \text{const.}$ and $p = \text{const.}$

$$k(T) = A\,\mathrm{e}^{-E/RT} \qquad (A = \text{const.},\ E = \text{const.}) \tag{3}$$

and introducing, treated as P-PIDKE, the general heating program

$$T = \theta(t) \tag{4}$$

one obtains

$$\mathrm{d}\alpha/\mathrm{d}t = f(\alpha)k(\theta(t)) \tag{5}$$

The first derivative with respect to t of $\mathrm{d}\alpha/\mathrm{d}t$ from eqn. (5) in isothermal conditions is

$$\mathrm{d}^2\alpha/\mathrm{d}t^2 = f'(\alpha)(\mathrm{d}\alpha/\mathrm{d}t)k(T) \qquad (T = \text{const.}) \tag{6}$$

or taking into account eqn. (1), eqn. (6) becomes

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2} = f'(\alpha)f(\alpha)k^2(T) \qquad (T = \text{const.}) \tag{7}$$

The problem is whether a CNC could be applied to eqn. (7) with the heating program (4), namely into the equation

$$\mathrm{d}^2\alpha/\mathrm{d}t^2 = f'(\alpha)f(\alpha)k^2(\theta(t)) \tag{8}$$

If the CNC is valid for eqn. (8), it is valid for any form of $f(\alpha)$. The degree of conversion for any chemical change fulfils the condition

$$\alpha \in [0, 1] \qquad \text{for } t \in [0, +\infty] \tag{9}$$

If

$$f'(\alpha)f(\alpha) < 0 \qquad \forall t \in [0, +\infty] \tag{10}$$

then relationship (8) is not valid. In order to demonstrate this statement, let us consider the function $v(t)$ given by

$$f'(\alpha)f(\alpha) = v(t) \tag{11}$$

where

$$v(t) < 0 \qquad \forall t \in [0, +\infty] \tag{12}$$

Under these conditions, eqn. (8) becomes

$$\mathrm{d}^2\alpha/\mathrm{d}t^2 = v(t)k^2(\theta(t)) \tag{13}$$

which, with two successive integrations, gives

$$\mathrm{d}\alpha/\mathrm{d}t = \int_0^t v(t_1)k^2(\theta(t_1))\,\mathrm{d}t_1 \tag{14}$$

and

$$\alpha = \int_0^t \left\{ \int_0^t v(t_1)k^2[\theta(t_1)]\,\mathrm{d}t_1 \right\} \mathrm{d}t_2 \tag{15}$$

Using the following theorem from mathematical analysis [5], if for the integral $\int_a^b f(x)\,\mathrm{d}x$ the function $f(x)$ does not change its sign in the range

$[a, b]$, then the value of the integral will be of the same sign as $f(x)$. Applying this theorem to the integral (15), it is easy to see that α should be negative for any $t \in [0, +\infty]$ as $v(t) < 0$. Thus if condition (10) is valid, then

$$\alpha < 0 \qquad \forall t \in [0, +\infty] \tag{16}$$

This result does not correspond to any change, thus eqn. (8) is incorrect.

A common form of the conversion function, $f(\alpha)$ is

$$f(\alpha) = (1-\alpha)^n \qquad \text{for } n > 0 \tag{17}$$

Thus the product $f'(\alpha)f(\alpha)$ is given by

$$f'(\alpha)f(\alpha) = -n(1-\alpha)^{2n-1} < 0 \qquad \forall \alpha \in [0, 1] \tag{18}$$

In this case, the particular form of eqn. (8) is

$$\mathrm{d}^2\alpha/\mathrm{d}t^2 = -A^2 n(1-\alpha)^{(2n-1)}\, \mathrm{e}^{-2E/R\theta(t)} \tag{19}$$

which leads to $\alpha < 0$, and thus, to an incorrect result.

For the general form of $f(\alpha)$ given by (α)

$$f'(\alpha)f(\alpha) = f^2(\alpha)\left\{-\frac{n}{1-\alpha} + \frac{m}{\alpha} + \frac{p}{(1-\alpha)[-\ln(1-\alpha)]}\right\} \tag{20}$$

which gives the following particular form of eqn. (8)

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2} = A^2(1-\alpha)^{2n}\alpha^{2m}[-\ln(1-\alpha)]^{2p} \times\left\{-\frac{n}{1-\alpha} + \frac{m}{\alpha} + \frac{p}{(1-\alpha)[-\ln(1-\alpha)]}\mathrm{e}^{-2E/R\theta(t)}\right\} \tag{21}$$

Obviously, one could imagine combinations of n, m and p for which numerical solutions of eqn. (21) correspond to $\alpha \in [0, 1]$ but this does not necessarily mean that the values are correct. Computer modelling of the particular form of eqn. (21) would be an interesting experiment.

Another general condition fulfilled by non-isothermal kinetics is the existence of a maximum rate, thus

$$(\mathrm{d}^2\alpha/\mathrm{d}t^2)_{\max} = 0 \tag{22}$$

Equation (8) with condition (22) leads to

$$f'(\alpha_{\max}) = 0 \tag{23}$$

The solution of eqn. (23) should be $\alpha_{\max} \in (0, 1)$. For the conversion function (17), the condition (23) takes the form

$$-n(1-\alpha_{\max})^{n-1} = 0 \tag{24}$$

Thus

$$\alpha_{\max} = 1 \tag{25}$$

which is an incorrect result.

The conditions (10) and (23) allow the selection of other conversion functions $f(\alpha)$, for which eqn. (8) is not valid.

CONCLUSIONS

The derivation of non-isothermal kinetic equations of the form of eqn. (8) from the isothermal differential kinetic equation, eqn. (7), through the CNC leads to incorrect results even for a "reaction order" conversion function $f(\alpha) = (1 - \alpha)^n$.

Thus, at present, the only correct procedure for deriving non-isothermal kinetic equaıions consists in the postulation of eqn. (1) as P-PIDKE and submitting it to a CNC. Such a procedure leads to eqn. (5) which is correct [6–8].

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