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Note

ON THE TEMPERATURE INTEGRAL IN NON-ISOTHERMAL KINETICS WITH LINEAR HEATING RATE

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The equation of non-isothermal kinetics

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

where α, β, A, E, R, T have the usual meanings, leads to the following integral form for linear heating rate

$$\mathrm{F}(\alpha) = \int_0^{\alpha} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{A}{\beta} \int_{T_1}^{T_2} \exp(-E/RT)\, \mathrm{d}T \tag{1a}$$

The right-hand side of eqn. (1a), called "temperature integral", leads to a solution by series and, in order to obtain a better approximation, some finite solutions have been proposed.

(1) Coats and Redfern [1] have suggested the form

$$F_{(\alpha)}^{C-R} = \frac{A}{\beta}\left(1 - \frac{2RT}{E}\right)\frac{RT^2}{E} \exp(-E/RT) \tag{2}$$

for this integral, which is the result of an integration by parts of eqn. (1a).

(2) Doyle [2] and Gorbachev [3] have suggested another equation, namely

$$F_{(\alpha)}^{D-G} = \frac{A}{\beta} \cdot \frac{RT^2}{E + 2RT} \exp(-E/RT) \tag{3}$$

A method of comparing the approximation degree of these two solutions was proposed by Gorbachev [3], and consists of considering the derivatives of eqns. (2) and (3) with temperature

$$\frac{\mathrm{d}F^{C-R}}{\mathrm{d}T} = \frac{A}{\beta}\left(1 - \frac{6R^2T^2}{E^2}\right) \exp(-E/RT) \tag{2a}$$

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$$\frac{\mathrm{d}F^{D-G}}{\mathrm{d}T} = \frac{A}{\beta}\left[1 - \frac{2R^2T^2}{(E+2RT)^2}\right]\exp(-E/RT) \tag{3a}$$

and comparing the results with the right-hand side of eqn. (1). As

$$\frac{6R^2T^2}{E^2} > \frac{2R^2T^2}{(E+2RT)^2}$$

eqn. (3) is a better approximation of the solution.

Based on Gorbachev's suggested method, a general finite approximative solution of the temperature integral is proposed.

Let us suppose

$$I(T) = \int_{T_1}^{T_2} \exp(-E/RT)\,\mathrm{d}T = \mathrm{q}(T)\exp(-E/RT) \tag{4}$$

q(T) being an unknown T function which will be determined by calculus. The derivative of eqn. (4) with temperature leads to the differential equation

$$\frac{\mathrm{d}q}{\mathrm{d}T} + \frac{E}{RT^2}q = 1 \tag{4a}$$

For the next form of q(T)

$$\mathrm{q}(T) = bT^i, \qquad i \in R \tag{5}$$

equation (4a) becomes

$$b\left(iT + \frac{E}{R}\right)T^{i-2} = 1 \tag{4b}$$

or

$$b = \frac{1}{\left(iT + \frac{E}{R}\right)T^{i-2}}$$

Taking into account eqn. (5), eqn. (4) becomes

$$\mathrm{I}(T) = \frac{RT^2}{E + iRT}(-E/RT) \tag{6}$$

Equation (1a) with eqn. (6) becomes

$$F_{(\alpha)}^{(i)} = \frac{A}{\beta}\cdot\frac{RT^2}{E+iRT}\exp(-E/RT) \tag{7}$$

and it is obvious that $F_{(\alpha)}^{(2)} \equiv F_{(\alpha)}^{D-G}$

From eqn. (7) other approximations can be derived for different values of i.

In a previous paper [4], based on a non-linear heating programme assumption, the following equation has been proposed

$$\mathrm{F}(\alpha) = AaT\exp(-E/RT) \tag{8}$$

where

$$a = \frac{R}{E} T_0 \frac{1}{\frac{\Delta T}{\Delta t}}$$

But for $\Delta t \to 0$ which means also $T_0 \to T$

$$a = \lim_{\Delta t \to 0} \frac{R}{E} T_0 \frac{1}{\frac{\Delta T}{\Delta t}} = \frac{R}{E} T \frac{1}{\beta}$$

and eqn. (8) becomes

$$F_{(\alpha)} = \frac{A}{\beta} \cdot \frac{RT^2}{E} \exp(-E/RT) \tag{8a}$$

which can also be obtained from eqn. (7) for $i = 0$. This identity leads to the conclusion that kinetics with linear and non-linear heating programmes show two sides of the same reality, the linear heating programme kinetics being the limit, for short time intervals, of the non-linear heating programme kinetics [5].

From eqn. (7), taking into account the derivative with temperature

$$\frac{\mathrm{d}F_{(\alpha)}^{(i)}}{\mathrm{d}T} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)\left\{1 - \frac{\frac{RT}{E}\left[\frac{RT}{E} i^2 - i\left(\frac{RT}{E} - 1\right) - 2\right]}{\left(1 + i\frac{RT}{E}\right)^2}\right\} \tag{7a}$$

The condition for obtaining an exact solution of eqn. (7a) is

$$g(i) = \left[\frac{RT}{E} i^2 - \left(\frac{RT}{E} - 1\right) i - 2\right] \times \frac{1}{\left(1 + i\frac{RT}{E}\right)^2} = 0 \tag{9}$$

with two roots

$$i_{1,2} = \frac{\frac{RT}{E} - 1 \pm \sqrt{\left(\frac{RT}{E} + 1\right)^2 + 4\frac{RT}{E}}}{2\frac{RT}{E}} \tag{10}$$

The functions $F_{(\alpha)}^{(i_1)}$ and $F_{(\alpha)}^{(i_2)}$ are the exact solutions of the temperature integral. The two roots have different signs, namely $i_1 > 0$, $i_2 < 0$. It is obvious that $1 < i_1 < 2$. The diagram of $g(i)$, presented in Fig. 1, shows that for $i \in (E/RT, +\infty)$, $g(i)$ is a continuous growing function, so that the comparison of $|g(1)|$ with $|g(2)|$ will indicate a better approximation for an integer value of i. As

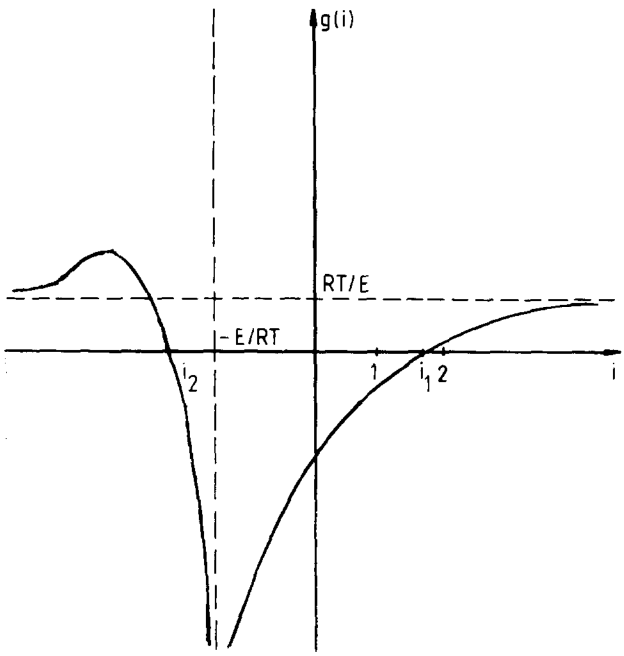

Fig. 1. Plot of g(i) vs. i.

$$\left|\frac{g(1)}{g(2)}\right| = \frac{1}{2\frac{RT}{E}} \cdot \frac{(1+2RT/E)^2}{(1+RT/E)^2} > 1$$

for any T and E values, it appears that $|g(2)|$ is the smallest value, and

$F_{(\alpha)}^{(2)} \equiv F_{(\alpha)}^{\Delta-G}$

is the best i-integer value approximation of the solution $F_{(\alpha)}^{(i_1)}$.

CONCLUSIONS

The general form

$$F_{(\alpha)}^{(i)} = \frac{A}{\beta} \frac{RT^2}{(E+iRT)} \exp(-E/RT), \qquad i \in R$$

proposed in this paper solves the temperature integral by approximations.

Two particular functions, $F_{(\alpha)}^{(i_1)}$, $F_{(\alpha)}^{(i_2)}$, derived from this general function, were obtained. The two functions solve exactly the temperature integral. The values i_1 and i_2 can be computed from

$$i_{1,2} = \frac{\frac{RT}{E} - 1 \pm \sqrt{\left(\frac{RT}{E}+1\right)^2 + 4\frac{RT}{E}}}{2\frac{RT}{E}}$$

The best approximation for an integer value of i was found to be

$$F_{(\alpha)}^{(2)} \equiv F_{(\alpha)}^{D-G} = \frac{A}{\beta} \cdot \frac{RT^2}{E + 2RT} \exp(-E/RT)$$

The kinetics with linear heating programme is the limit for short time intervals of the kinetics with non-linear heating programmes.

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