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Note

ON THE TEMPERATURE INTEGRAL IN NON-ISOTHERMAL KINETICS WITH NON-LINEAR TEMPERATURE PROGRAMME

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In a previous paper [1], dealing with linear heating rate, a general function was proposed

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

which gives two exact solutions, $F_{(\alpha)}^{(i_{1,2})}$, of temperature integral and generates approximate solutions of this integral for different i-values.

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

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

which was previously proposed by Doyle [2] and Gorbachev [3].

In the present paper we aim to establish some similar results for the temperature integral assuming a non-linear heating rate.

The equation of non-isothermal kinetics, with a non-linear heating rate, leads to the following form of the temperature integral

$$\mathrm{I}(T) = \int_0^T \mathrm{L}(T)\exp(-E/RT)\mathrm{d}T \tag{1}$$

where E, R and T have the usual meanings, and $\mathrm{L}(T) = 1/\beta$. Supposing, as previously [1]

$$\mathrm{I}(T) = \mathrm{q}(T)\exp(-E/RT) \tag{2}$$

$\mathrm{q}(T)$ being an unknown function which has to be computed. Taking the derivative of eqn. (1) with temperature and taking into account eqn. (2) leads

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to

$$\frac{\mathrm{d}q}{\mathrm{d}T} + \frac{E}{RT^2} q = \mathrm{L}(T) \tag{3}$$

and for

$$\mathrm{q}(T) = bT^i \qquad i \in R \tag{4}$$

we get

$$b = \frac{\mathrm{L}(T)}{(iT + E/R)T^{i-2}} \tag{5}$$

Equation (5) leads to the following solution of eqn. (1)

$$\mathrm{I}(T) = \frac{\mathrm{L}(T)RT^2}{E + iRT} \exp(-E/RT) \tag{1'}$$

With eqns. (4) and (5), eqn. (3) becomes

$$\mathrm{L}(T)\left\{1 - \frac{RT}{E} \frac{i^2 \frac{RT}{E} - i\left(\frac{RT}{E} + \frac{RT}{E} T \frac{L'}{L} - 1\right) - T\frac{L'}{L} - 2}{[1 + i(RT/E)]^2}\right\} = \mathrm{L}(T)$$

The condition of an exact solution for the temperature integral will then be given by

$$\mathrm{g}(i) = \frac{i^2 \frac{RT}{E} - i\left(\frac{RT}{E} + \frac{RT}{E} T \frac{L'}{L} - 1\right) - T\frac{L'}{L} - 2}{(1 + iRT/E)^2} = 0 \tag{6}$$

which has two roots

$$i_{1,2} = \frac{\frac{RT}{E}\left(1 + T\frac{L'}{L}\right) - 1 \pm \left\{\left[\frac{RT}{E}\left(1 + T\frac{L'}{L}\right) + 1\right]^2 + 4\frac{RT}{E}\right\}^{1/2}}{2RT/E}$$

As the roots have different signs, $i_1 > 0$ and $i_2 < 0$.

It is evident that $1 + T(L'/L) < i_1 < 2 + T(L'/L)$.

As $\mathrm{g}(i)$ is a continuous growing function and TL'/L cannot be estimated for an unknown non-linear heating rate, the absolute values of $\mathrm{g}(i)$ are compared for $i = 1$, 2 and 3, hence

$$|\mathrm{g}(1)| = \frac{L(RT/E)}{\left(1 + \frac{RT}{E}\right)^2}\left[1 + T\frac{L'}{L}\left(\frac{RT}{E} + 1\right)\right]$$

$$|\mathrm{g}(2)| = \frac{L(RT/E)}{\left(1 + 2\frac{RT}{E}\right)^2}\left[2\frac{RT}{E} - \frac{L'}{L}T\left(2\frac{RT}{E} + 1\right)\right]$$

$$|\mathrm{g}(3)| = \frac{L(RT/E)}{\left(1 + 3\frac{RT}{E}\right)^2}\left[6\frac{RT}{E} + 1 - T\frac{L'}{L}\left(1 + 3\frac{RT}{E}\right)\right]$$

Since

$$\begin{cases} |g(2)| < |g(1)| \\ |g(2)| < |g(3)| \end{cases}$$

we find that $1 < i_1 < 2$ and g(2) is the best approximation of eqn. (1) with i an integer value.

Hence

$$F_{(\alpha)}^{(2)} = \frac{RT^2}{E + 2RT} \frac{1}{\beta(T)} \exp(-E/RT) \tag{7}$$

is the proposed solution to approximate the temperature integral in the non-linear heating rate assumption.

From the mathematical viewpoint eqn. (7) is identical to $F_{(\alpha)}^{(2)}$ (b) for $\beta(T)$ tending to a constant value, which is true for short time intervals. This conclusion supports our idea that linear heating rate kinetics is a rough approximation to that described more precisely by non-linear heating rate [1,4].

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