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Note

THE TEMPERATURE INTEGRAL *

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This note deals with a comparison between temperature integrals for non-linear and linear heating rates in non-isothermal kinetics. The integral equation of non-isothermal kinetics may be written as:

$$\mathrm{F}(1-\alpha) = A\mathrm{I}(T) \tag{1}$$

where $\mathrm{F}(1-\alpha)$, the conversion integral and $\mathrm{I}(T)$, the temperature integral, are given by the equations [1]:

$$\mathrm{F}(1-\alpha) = \int_0^{\alpha} \frac{\mathrm{d}x}{\mathrm{f}(1-x)} \tag{2}$$

$$\mathrm{I}(T) = \int_{T_1}^{T} \frac{1}{b(y)} \exp(-E/Ry)\mathrm{d}y \tag{3}$$

where the notations have their usual meanings. Let us assume

$$\mathrm{I}(T) = q(T)\exp(-E/RT) \tag{4}$$

The derivative of eqn. (4) with temperature, taking into account eqn. (3), leads to the following relationship between the heating programme and the unknown function $q(T)$:

$$b(T) = \frac{1}{\mathrm{d}q/\mathrm{d}T + \left(E/RT^2\right)^q} \tag{5}$$

* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

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Since $b(T) = \mathrm{d}T/\mathrm{d}t$, eqn. (5) can be integrated in order to obtain the temperature profile. One obtains:

$$t = q + \frac{E}{R}\int q/T^2 \mathrm{d}T \tag{6}$$

(a) For

$$q(T) = aT^i \tag{7}$$

one obtains through integration:

$$t = \begin{cases} aT^i + a\dfrac{E}{R}T^{i-1} & i \neq 1 \\ aT + a\dfrac{E}{R}\ln T & i = 1 \end{cases} \tag{8}$$

It is easy to observe that:

$i = 0$ leads to $t = a - aE/RT$ which is the hyperbolic programme

$i = 2$ leads to $t = aT^2 + aE/RT$ which is the parabolic programme

The assumed form of $q(T)$ together with eqns. (1) and (4) allow us to write:

$$\ln \mathrm{F}(1-\alpha) - i \ln T = -\frac{E}{RT} + \ln A + \ln a \tag{9}$$

(b) Let us assume another form for $q(T)$:

$$q(T) = a \exp(j/T) \tag{10}$$

From eqn. (6) one obtains the following relationship:

$$t = a\left(1 - \frac{E}{R}\frac{1}{j}\right)\exp(j/T) \tag{11}$$

which is the exponential programme. Substituting eqn. (10) into eqn. (4) we obtain:

$$\ln \mathrm{F}(1-\alpha) = -\frac{E/R - j}{T} + \ln A + \ln a \tag{9a}$$

For $j \ll E/R$, which is the common situation, eqn. (9a) becomes eqn. (9) for $i = 0$ (i.e. hyperbolic programme).

Summing up, the integral equation of non-isothermal kinetics with a non-linear heating rate may be written in a general form as

$$\ln \mathrm{F}(1-\alpha) - i \ln T = -\frac{E}{RT} + \ln A + \ln a$$

The particular values of i give the temperature programme which is used, and i can be considered as a new variable.

In a previous paper [2] the following equation was derived for the temperature integral with a linear heating programme:

$$\ln \mathrm{F}(1-\alpha) - i \ln T = -\frac{E}{RT} + \ln A + \ln b + L \quad i \in \{0, 1, 2\} \tag{12}$$

where b is the heating rate, L is an adjusting parameter and i has no physical meaning. It appears that both non-linear and linear heating programmes lead to the same form of the temperature integral but i has a physical meaning only for the non-linear heating programme when it becomes a variable. The three values of i in eqn. (12) may be interpreted as giving, together with the value of L, an approximation of the temperature integral with an exact solution given by a non-linear heating programme. Thus, even if the formal aspect of the integral equation is similar for linear and non-linear heating programmes, the meaning of i changes from eqn. (9) to eqn. (12). Another aspect indicated by eqn. (9) is the dependence of the conversion function on the temperature programme when a non-linear heating programme is used. It is obtained since i is independent of the right-hand side of eqn. (9). The necessity for i to be independent of the left-hand side also leads to the following form of the conversion integral under a non-linear heating programme:

$$\mathrm{F}(1-\alpha) = \exp(i \ln T) \cdot \mathrm{H}(1-\alpha) \tag{13}$$

where $\mathrm{H}(1-\alpha)$ may be interpreted as the integral under a linear heating programme.

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