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Note

NON-ISOTHERMAL KINETICS WITH NON-LINEAR TEMPERATURE PROGRAMME. PART III

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Being required by a mathematical treatment closer to reality, non-linear temperature programmes are more and more used [1—3]. They have been established not only to minimize the deviation of the sample temperature from the programmed temperature [3], but also to solve exactly the temperature integral. This paper aims to establish a general equation from which a particular non-linear temperature programme, able to solve exactly the temperature integral, can be derived.

If the required experimental conditions are met, the rate equation of heterogeneous reaction is supposed to be [4]

$$\frac{d\alpha}{dt} = f(\alpha)\, g(T) \tag{1}$$

where α is the degree of conversion, t is time and T is the temperature (K). $f(\alpha)$ in the simplest form can be taken as

$$f(\alpha) = (1\text{-}\alpha)^n \tag{2}$$

n being the reaction order.

The function $g(T)$ is considered to follow the Arrhenius relationship

$$g(T) = A \exp(-E/RT) \tag{3}$$

where A is the pre-exponential factor ($dA/dT = 0$, as is general admitted), E is the activation energy, and $R = 1.987$ cal mole^{-1} K^{-1}.

Using, also, the reciprocal heating rate

$$L(T) = \frac{1}{\beta} = \frac{dt}{dT} \tag{4}$$

and introducing eqns. (2)—(4) into eqn. (1) gives

$$\frac{d}{(1-\alpha)^n} = A L(T) \exp(-E/RT) \tag{1a}$$

which on integration leads to

$$A \int_{T_0}^{T} L(T) \exp(-E/RT)\, dT = \begin{cases} \dfrac{1-(1-\alpha)^{1-n}}{1-n} & \text{for } n \neq 1 \\ -\ln(1-\alpha) & \text{for } n = 1 \end{cases} \tag{1b}$$

Problems arise with the left-hand side of this equation, i.e. the temperature integral

$$F(T) = A \int_{T_0}^{T} L(T) \exp(-E/RT)\, dT \tag{5}$$

due to the unknown form of $L(T)$.

The simplest case is to presume $L(T) = a_0$, which means a linear heating programme, but then $F(T)$ will be expressed by an asymptotic series [5] and the result will always be approximate [5,6]. This is one of the reasons for the search for non-linear programmes.

The second reason is that, during an experiment, some endothermic and/or exothermic effects of the studied reaction cause deviation from linearity of the $T(t)$ graph, and the mathematical model has to represent them. We discuss here two of the ways to obtain $F(T)$.

(a) Assuming temperature programmes of the general form [7]

$$L(T) = \frac{1}{T^2} \sum_i b_i T^i \tag{6}$$

The problem, in this form, was studied by Smutek for thermal desorption. From eqn. (6) he gets, by integration

$$\Delta t = b_1 \ln \frac{T}{T_0} + \sum_{i \neq 1}^{z} \frac{b_i}{i-1} \Delta T^{i-1} \tag{7}$$

where $\Delta t = t - t_0$ and $\Delta T^k = T^k - T_0^k$ and also obtains $F(T)$ for the general heating regime

$$F(T) = \frac{A}{T} \sum_i^z b_i T^i \left[E_{i(x)} - \left(\frac{T_0}{T}\right)^{i-1} E_{i(x_0)} \right] \tag{8}$$

where

$$E_{i(x)} = \int_1^{\infty} t^{-i}\, e^{-xt}\, dt \qquad \text{and} \qquad x = E/RT\,.$$

For positive integer values of i and large values of x, $E_{i(x)}$ becomes

$$E_{o(x)} = \frac{e^{-x}}{x}$$

which allows us to write the exact solution of $F(T)$ in the form

$$F(T) = A \frac{R}{E} \sum_i^z b_i T^{i-1} \exp(-E/RT) \tag{9}$$

(b) By generalization of a method earlier described by Marcu and Segal [2]

$$F(T) = A \sum_i^z a_i T^i \exp(-E/RT) \tag{10}$$

This method selects from the beginning the solutions which fulfil the condition of solving exactly eqn. (5).

Noting

$$l(T) = \sum_{i}^{z} a_i T^i \tag{11}$$

$$F(T) = \int_{T_0}^{T} L(T) \exp(-E/RT)\, dT = Al(T) \exp(-E/RT)$$

which, by derivation and substituting eqn. (4) for L(T) leads to

$$dt = \left(l' + \frac{E}{RT^2}\, l\right) dT \tag{12}$$

The integration of eqn. (12) using eqn. (11) give us the heating programmes as follows.

$$\Delta t = a_1 \left(\Delta T + \frac{E}{R} \ln \frac{T}{T_0}\right) + \sum_{i \neq 1}^{z} a_i\, \Delta T^{i-1} \left(\frac{E}{R} \cdot \frac{1}{i-1} + \Delta T\right) \tag{13}$$

Comparing eqn. (7) with eqn. (13), it is obvious that for small ΔT and $a_i(E/R) = b_i$ the two equations give the same solution.

With these results eqn. (1b) becomes

$$A \sum_{i}^{z} a_i T^i \exp(-E/RT) = \begin{cases} \dfrac{1-(1-\alpha)^{1-n}}{1-n} & \text{for } n \neq 1 \\ -\ln(1-\alpha) & \text{for } n = 1 \end{cases} \tag{1c}$$

which allows kinetic parameters to be determined.

Using equation (1c) for $z = 1$, the kinetic parameters of $Ca(COO)_2 \cdot H_2O$ dehydration were determined. The results ($n = 0.95$; $E = 24.5$ kcal mole^{-1}; $A = 10^6$ sec^{-1}) are in good agreement with those found in the literature [1].

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