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NON-ISOTHERMAL KINETICS WITH NON-LINEAR TEMPERATURE PROGRAMME. V. NON-LINEAR HEATING PROGRAMMES WITH EXACT SOLUTIONS FOR THE TEMPERATURE INTEGRAL

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ABSTRACT

This paper deals with some general non-linear heating programmes which allow the temperature integral to be solved exactly. Some possible uses of these programmes are discussed.

One of the most important problems connected with non-isothermal kinetics involves obtaining exact solutions for the temperature integral. Indeed, for the heating of a sample at a constant rate a ($a = \mathrm{d}T/\mathrm{d}t$), the integral kinetic equation has the form

$$\mathrm{F}(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{A}{a}\int_{T_0}^{T} \mathrm{e}^{-E/RT}\,\mathrm{d}T \qquad (1)$$

or, neglecting as usual the lower limit, T_0

$$\mathrm{F}(\alpha) = \frac{A}{a}\int_0^{T} \mathrm{e}^{-E/RT}\,\mathrm{d}T \qquad (2)$$

The right-hand side of eqns. (1) and (2) is called the temperature integral. For the given linear programme of heating this integral cannot be solved exactly [1].

In order to obtain exact solutions for the temperature integral, hyperbolic and parabolic programmes of heating were used. These programmes are given by

$$\mathrm{d}T/\mathrm{d}t = a_2 T^2 \qquad (3)$$

$$1/T = b - a_2 t \qquad (4)$$

for the hyperbolic programme [2], and

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{1}{b_1}\,\frac{E}{2RT + E} \qquad (5)$$

$$b_1 \frac{RT^2}{E} + b_1 T + c = t \qquad (6)$$

for the parabolic programme [3] (a_2, b and c are constants for a given programme). These equations may be used as starting points for working some more general non-linear heating programmes. Thus, if instead of the value 2 for the temperature exponent, one takes positive integers p, so as $p \geqslant 2$, eqn. (3) becomes

$$\frac{dT}{dt} = a_p T^p \tag{7}$$

which defines a family of non-linear heating programmes for different values of p.

Equation (2), with the heating rate given by eqn. (7), takes the form

$$F(\alpha) = \frac{A}{a_p} \int_0^T \frac{e^{-E/RT}}{T^p} \, dT \tag{8}$$

where the temperature integral can now be solved exactly. In order to obtain the solution, one has to operate the usual change of variable

$$x = -E/RT \tag{9}$$

In terms of the variable x, eqn. (8) can be written as

$$F(\alpha) = (-1)^p \frac{A}{a_p} \left(\frac{R}{E}\right)^{p-1} \int_{-\infty}^{x} x^{p-2} e^x \, dx \tag{10}$$

The integral

$$I = \int x^{p-2} e^x \, dx$$

can be calculated exactly through repeated integration by parts, with the result [4]

$$I = e^x \left[x^{(p-2)} - (p-2)x^{p-3} + (p-2)(p-3)x^{p-4} \ldots + (-1)^{(p-3)}(p-2)!x + (-1)^{(p-2)}(p-2)! \right] \tag{11}$$

Returning to the old variable by means of eqn. (9), eqn. (10) becomes

$$F(\alpha) = (-1)^p \frac{A}{a_p} \left(\frac{R}{E}\right)^{(p-1)} e^{-E/RT} \left[\left(\frac{E}{RT}\right)^{(p-2)} - (p-2)\left(\frac{E}{RT}\right)^{(p-3)} + (p-2)(p-3)\left(\frac{E}{RT}\right)^{(p-4)} \ldots + (-1)^{(p-3)}(p-2)! \frac{E}{RT} + (-1)^{(p-2)}(p-2)! \right] \tag{12}$$

Obviously, for $p = 2$, one gets

$$F(\alpha) = \frac{A}{a_2} \frac{R}{E} e^{-E/RT} \tag{13}$$

which is the particular form of eqn. (12) for the hyperbolic heating programme [2]. Equation (12) could be used in working integral methods for non-isothermal kinetics, like the method given by Coats and Redfern [5].

Another family of non-linear heating programmes which allows the temperature integral to be solved exactly may be obtained from the general form of eqn. (2)

$$F(\alpha) = A \int_0^T f(T) \, e^{-E/RT} \, dT \tag{14}$$

where

$$f(T)=\frac{1}{dT/dt} \tag{15}$$

The problem involves the proper choice of a function $f_1(T)$ which has to fulfil the condition [3]

$$\int f(T)\,e^{-E/RT}\,dT=f_1(T)\,e^{-E/RT} \tag{16}$$

where the right-hand side is implied by the form of the left-hand integrand. Operating the derivative of both members in eqn. (16), one gets:

$$f(T)=f_1'(T)+\frac{E}{RT^2}\,f_1(T) \tag{17}$$

a condition which $f_1(T)$ has equally to fulfil. If f_1 is chosen as

$$f_1=\frac{R}{a_2 E} \tag{18}$$

from relationship (17), one gets eqn. (3) for the hyperbolic programme of heating. For $f_1(T)$ given by

$$f_1(T)=\frac{RT}{bE} \tag{19}$$

eqn. (17) leads to

$$f(T)=\frac{R}{bE}+\frac{1}{bT} \tag{20}$$

or, taking into account eqn. (15) and integrating eqn. (20), it turns out that

$$t=b_1\frac{RT}{E}+b_1\ln T+c \tag{21}$$

where $b_1=1/b$.

Equations (20) and (21) define a new heating programme which allows an exact solution of the temperature integral. Taking into account eqns. (19) and (16), eqn. (14) takes the form

$$F(\alpha)=\frac{AR}{bE}T\,e^{-E/RT} \tag{22}$$

whose logarithmic form could be used to determine the activation energy and the pre-exponential factor. These two kinetic parameters are easy to evaluate from the slope and the intercept of the straight line ($\log F(\alpha)/T$, $1/T$).

Equation (17) with

$$f_1(T)=\frac{RT^2}{bE} \tag{23}$$

leads to [3]

$$f(T)=\frac{2RT}{bE}+\frac{1}{b} \tag{24}$$

and

$$\frac{RT^2}{E}b_1+b_1T+c=t \tag{25}$$

where $b_1 = 1/b$, i.e. to a parabolic heating programme. For this programme, the integral kinetic equation (14) takes the particular form

$$\mathrm{F}(\alpha) = \frac{AR}{bE} T^2 \, \mathrm{e}^{-E/RT} \tag{26}$$

This allows evaluation of E and A from the slope and the intercept of the straight line (log $\mathrm{F}(\alpha)/T^2$, $1/T$).

Equation (17) with the general function $\mathrm{f}_1(T)$ given by

$$\mathrm{f}_1(T) = \frac{RT^m}{bE} \tag{27}$$

where m is a positive integer ($m \geqslant 2$) becomes

$$\mathrm{f}(T) = \frac{m\,RT^{m-1}}{bE} + \frac{T^{m-2}}{b} \tag{28}$$

By integration of eqn. (28), one gets

$$t = b_1 \frac{RT^m}{E} + b_1 \frac{T^{m-1}}{m-1} + c \tag{29}$$

where $b_1 = 1/b$. Equations (28) and (29) define another family of non-linear programmes which lead to exact solutions of the temperature integral. In this case, from eqns. (14), (16) and (17), it turns out that

$$\mathrm{F}(\alpha) = A \frac{RT^m}{bE} \, \mathrm{e}^{-E/RT} \tag{30}$$

the logarithmic form of which could be used to evaluate E and A in the usual way.

One more family of non-linear programmes which allow an exact solution of the temperature integral can be obtained for a function $\mathrm{f}_1(T)$ given by:

$$\mathrm{f}_1(T) = T^q \, \mathrm{e}^{kT} \tag{31}$$

where q is a positive integer and k is a constant. Taking into account eqn. (31), eqn. (17) becomes

$$\mathrm{f}(T) = qT^{q-1} \, \mathrm{e}^{kT} + kT^q \, \mathrm{e}^{kT} + \frac{E}{R} T^{q-2} \, \mathrm{e}^{kT} \tag{32}$$

By integration with respect to temperature, the first two terms give $T^q \mathrm{e}^{kT}$. As for the integral of the last term, this is $(E/R)\, I$, where I is given by eqn. (11). Thus, the integration of eqn. (32) leads to

$$t = \mathrm{e}^{kT}\left[T^q + \frac{E}{R}\left(\frac{T^{q-2}}{k} - \frac{(q-2)T^{q-3}}{k^2} + \frac{(q-2)(q-3)}{k^3} T^{q-4} \ldots \right.\right.$$
$$\left.\left. + (-1)^{q-3} \frac{(q-2)!}{k^{n-2}} + \frac{(-1)^{q-2}(q-2)!}{k^{n-1}}\right)\right] \tag{33}$$

with $q \geqslant 2$.

For $\mathrm{f}_1(T)$ given by eqn. (31), eqn. (14) takes the form

$$\mathrm{F}(\alpha) = AT^q \, \mathrm{e}^{kT} \, \mathrm{e}^{-E/RT} \tag{34}$$

Although the three families of non-linear heating programmes mentioned above are mainly suitable for the integral methods in non-isothermal kinetics, they can also be used to work out differential methods. Thus, for the heating rate (7), through generalization of the formulae given for $p = 2^{1,2}$, one gets

$$\frac{d^2\alpha}{d\alpha dT} = -\frac{p}{T} + \frac{E}{RT_{max}^2} + \frac{f'(\alpha)}{f(\alpha)}\frac{d\alpha}{dT} \tag{35}$$

$$\left(\frac{d}{dT}\right)_{max} = \frac{pRT_{max} - E}{RT_{max}^2}\frac{f(\alpha_{max})}{f'(\alpha_{max})} \tag{36}$$

$$\frac{d \ln a_p T_{max}^{p-2}}{d\left(\frac{1}{T_{max}}\right)} = -\frac{E}{R} \tag{37}$$

All these equations lead to variants of the classical differential methods for evaluating the kinetic parameters under non-isothermal conditions [1,6].

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