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Note

Non-isothermal kinetics with non-linear temperature-programme (II)

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In the field of non-isothermal kinetics, there is an interesting use of non-linear heating programmes[1–4]. These have been established in order to solve exactly the temperature integral, as well as to minimize the deviation of the sample temperature from the programmed one. This paper aims to establish a simple equation, characteristic for non-isothermal kinetics. From this equation, one could get different non-linear programmes of heating, which solve exactly the temperature integral.

GENERALITIES

Heterogeneous reaction kinetics supposed to follow the rate equation:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

where α = the degree of conversion; t = the time; k = the rate constant; n = the reaction order.

In eqn (1), we shall substitute the Arrhenius equation:

$$k = Ze^{-E/RT} \tag{2}$$

where: Z = the preexponential factor; E = the activation energy; T = the temperature (K); R = 1.987 cal mol^{-1} K^{-1}.

Subsequently, eqn (1) becomes:

$$\frac{d\alpha}{(1-\alpha)^n} = Ze^{-E/RT}dt \tag{1'}$$

Introducing the heating rate:

$$\beta = \frac{dT}{dt} \tag{3}$$

into eqn (1') one obtains:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{Z}{\beta}e^{-E/RT}dT \tag{1''}$$

The integration of eqn (1'') leads to:

$$F(\alpha) = \int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = Z \int_0^T f(T)\, e^{-E/RT}\, dT \tag{1'''}$$

where: $f(T) = 1/\beta$

If $f(T)$ = const, the programme of heating is a linear one and it is impossible to solve exactly the temperature integral.

Assuming a non-linear programme of heating, we shall try for the integral:

$$\int_0^T f(T)\, e^{-E/RT}\, dT \tag{4}$$

exponential solutions, suggested by the shape of the function that has to be integrated:

$$\int_0^T f(T)\, e^{-E/RT}\, dT = f_1(T)\, e^{-E/RT} \tag{5}$$

By derivation of eqn (5) with respect to T, one obtains:

$$f(T) = f'_1(T) + \frac{E}{RT^2} f_1(T) \tag{6}$$

Eqn (6) could be used in two directions:

(A) For a given programme of heating (this means f(T) is known), we search f_1.

(A1) For $f(T)$ = const. (or even $f(T) = 1$), eqn (6) becomes:

$$f'_1 + \frac{E}{RT^2} f_1 = 1 \tag{6'}$$

By introducing a new function f_2:

$$f_1 = T^2 f_2 \tag{7}$$

substituting it in eqn (6), and then trying solutions:

$$f_2 = \sum_{k=0}^{\infty} a_k T^k \tag{8}$$

the identification with respect to the powers of T, leads to:

$$\int_0^T e^{-E/RT}\, dT \simeq \frac{E}{R} \frac{e^{-x}}{x^2} \left[1 - \frac{2!}{x} + \frac{3!}{x^2} + \dots + (-1)^n \frac{(n+1)!}{x^n}\right]$$

where $x = E/RT$; which is the asymptotic expansion[5].

(B) By chosing a certain function $f_1(T)$, we find the corresponding programme of heating. Integration of this heating programme leads to eqn (5). E.g.:

(B1) For $f_1 = R/bE$, where b = a parameter, eqn (6) becomes:
$f(T) = 1/bT^2 = 1/\beta$
and with eqn (3):

$$dT/T^2 = b\,dt$$

$$1/T = a - bt$$

Thus we recover the hyperbolic heating programme[1].

(B2) For

$$f_1 = \frac{RT^2}{bE},$$

eqn (6) becomes:

$$\beta^{-1} = f(T) = \frac{2RT}{bE} + \frac{1}{b} \tag{9}$$

Introducing also eqn. (3), by integration, one gets:

$$t = a + b_1 T + b_1 \frac{RT^2}{E}$$

where $b_1 = 1/b$.

This heating programme is a parabolic one and it solves exactly the temperature integral. Eqn (1') becomes:

$$F(\alpha) = \left\{ \begin{matrix} \left[\dfrac{1-(1-\alpha)^{1-n}}{1-n}\right]_{n\neq 1} \\ [-\ln(1-\alpha)]_{n=1} \end{matrix} \right\} = \frac{ZR}{bE}\, T^2\, e^{-E/RT} \tag{10}$$

Eqn (10) allows to determine kinetic parameters, according to an integral method, similar to the Coats-Redfern[6] one.

The only difficulty that arises is due to the appearance of the activation energy in eqn (9). For its determination, an experimental procedure is used. It starts from a value E_0, supposed to be approximately equal to E. From eqn (10), a new value is determined, E_1, closer to E. The procedure is repeated until the difference between the calculated value and that introduced in eqn (9) is of the same magnitude as the limit of the experimental errors.

(B3) For $f_1(T) = Te^{E_0/RT}$, eqn (6) becomes:

$$1/\beta = f(T) = e^{E_0/RT} - T\frac{E_0}{RT^2}\, e^{E_0/RT} + T\frac{E}{RT^2}\, e^{E_0/RT}$$

As $E \simeq E_0$, and T is large enough:
$f(T) = e^{E_0/RT}$

It turns out that $\beta = e^{-E_0/RT}$, namely an exponential heating programme.

(B4) The suggested method above is general, the choice of the function $f_1(T)$ being just a matter of the experimental possibilities to realise the programme of heating, defined by the function f.

EXPERIMENTAL

The reaction of dehydration of the calcium monohydrate oxalate has been studied. Since a parabolic time-temperature programmer was not available we used the endothermal effect of the reaction, which gives deviation from linearity. By successive trials, we succeeded in getting the desired programme. The obtained data were treated on a computer, by means of a programme presented in another work[7]. The results obtained ($n = 0.95$, $E = 24$ kcal mol^{-1}, $Z = 1.6 \times 10^5$ sec^{-1}) show a good agreement with those found in literature[1-6].

CONCLUSIONS

A non-linear heating programme (parabolic) has been suggested, which allows to solve exactly the temperature integral. On its basis, a new method to determine kinetic parameters under non-linear conditions has been suggested.

The kinetic parameters obtained by this method for the dehydration of Ca $(COO)_2 \cdot H_2O$, are in good agreement with those obtained by means of other methods.

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