Note

Non-isothermal kinetics with non-linear temperature programme

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(Received 10 October 1975)

Among the most important methods used to determine the kinetic parameters of solid phase reactions, we can point out the non-isothermal methods[1-3]. One of the approximations these methods are based on, consist in the identification of the sample temperature with the programmed one. In fact, the reactions that occur in the sample, take place with an absorption or with a heat release. This fact leads to the deviations of the sample temperature from the programmed one. In this paper we aim to find a temperature programme for which the average difference between the sample temperature and the programmed one should be minimum. The necessity of solving this problem to increase the accuracy of the kinetic parameter values, was pointed out by Šesták and Berggren[+].

THEORY

For simplicity sake, we shall neglect the thermal inertia of the crucible and of the sample. We shall also neglect the variation of sample heat capacity. Under these conditions the equation of heat balance is:

$$d(n\alpha\Delta H) + mc\,dT_c(t) = mc\,dT(t) \tag{1}$$

or

$$\frac{n\Delta H}{mc}\frac{d\alpha}{dt} = \frac{d(T - T_c)}{dt} \tag{1'}$$

where: m, c = mean specific heat and mass of the reaction system:

ΔH = the thermal effect of the reaction;
n = the amount of reactant (in moles):
α = the conversion degree of the reaction:
$T_c(t)$ = the programmed temperature;
$T(t)$ = the sample temperature.

Considering that the model of the reaction order is valid, it follows that:

$$\frac{d\alpha}{dt} = f(\alpha) Z e^{-E/RT} \tag{2}$$

where $f(\alpha) = (1 - \alpha)^n$.

Writing the function $T_c(t)$ in the form $T_c(t) = T_0 \xi(\beta t)$ ($\langle \beta \rangle = \text{time}^{-1}$ and $\xi(0) = 1$) and introducing the dimensionless magnitudes:

$$a = \frac{n \Delta H}{T_0 mc}; \ b = \frac{Z}{\beta}; \ c = \frac{E}{RT_0}; \ \theta = \frac{T}{T_0} \ \text{and} \ \eta = \beta t \ \text{the eqns (1') and (2) become:}$$

$$a \frac{d\alpha}{d\eta} = \frac{d\theta}{d\eta} - \xi'(\eta) \tag{3}$$

and

$$\frac{d\alpha}{d\eta} = b f(\alpha) e^{-c/\theta} \tag{4}$$

integration of eqn (3) gives:

$$a\alpha(\eta) + \xi(\eta) = \theta(\eta) \tag{5}$$

From the relationships (4) and (5) it follows that:

$$\frac{d\theta}{d\eta} = \xi'(\eta) + abf\left(\frac{\theta - \xi}{a}\right) \exp\left[-\frac{c}{\theta}\right] \tag{6}$$

The variation in time of the sample temperature follows from the integration of eqn (6). To integrate eqn (6) we take the iteration method using the recurrence formula:

$$\theta_k(\eta) = \xi(\eta) + ab \int_0^{\eta} f\left(\frac{\theta_{k-1} - \xi(\eta)}{a}\right) \exp\left[-\frac{c}{\theta_{k-1}}\right] d\eta \tag{7}$$

For $\theta_0(\eta)$, we consider the value $\xi(\eta)$. If a is small, then θ and ξ are close enough and therefore we can stop at the first iteration:

$$\theta(\eta) \cong \theta_1(\eta) = \xi(\eta) + ab \int_0^{\eta} \exp\left[-\frac{c}{\xi(\eta)}\right] d\eta \tag{8}$$

Even if a is small, the validity of eqn (8) is limited. Unlike $\theta(\eta)$ which approaches $\xi(\eta)$ asymptotically for $\eta \to \infty$, θ_1 is continually removing from $\xi(\eta)$ as η is increasing. As we can see in Fig. 1, we can consider that for a given time smaller than $t_M = \lambda\beta$ corresponding to the maximum of the difference $|\theta(\eta) - \xi(\eta)|$, $\theta_1(\eta) \cong \theta(\eta)$.

As we have already mentioned, our aim is to find the temperature programme which minimizes the mean value of the difference $|T_c(t) - T(t)|$ or, in other words, to find the programme that minimizes the area limited by the curves $T = T(t)$ and
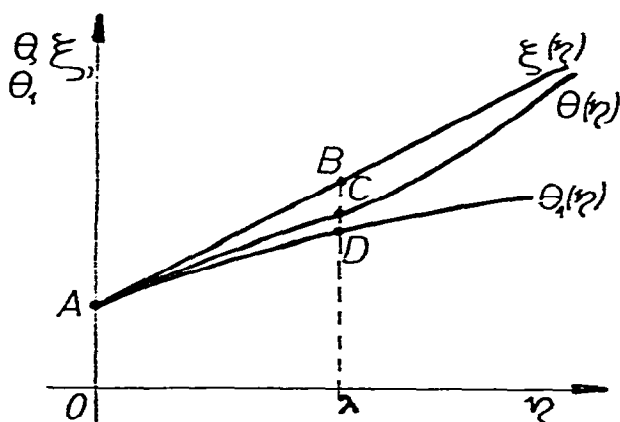
Fig. 1. θ, ξ and θ, versus dimensionless time η.

$T_c = T_c(t)$. The problem can be reduced to the calculus of the functional (9) extremium:

$$I' = \int_0^\varkappa (T_c(t) - T(t))\,dt \tag{9}$$

or

$$I = -I' \frac{\beta}{T_0 ab} = \int_0^\varkappa (\theta - \xi)\,d\eta \tag{9'}$$

As for θ we have a formula approximately valid up to the moment $t_M = \beta\lambda$, we have to substitute the upper bound of the integral (9') by λ. The problem, formulated in this way, leads to a banal result ($\xi(\eta) = \text{const.}$). To find a significant result from the sum of functions $\xi(\eta)$ we have to choose a set which may offer the same property and among the elements of this set we have to look for the function $\xi(\eta)$ which achieves the extremum of the functional (9'). If, for instance we choose all the programmes that lead to the same average temperature $T_m = \xi_m T_0$, the isoperimetric condition that has to be taken into account is the following:

$$h = \xi_m \lambda = \int_0^\lambda \xi(\eta)\,d\eta \tag{10}$$

By introducing the function $y(\eta) = \int_0^\eta e^{-c/\xi}\,d\eta$ and taking into account eqns (8), (9') and (10), it follows that the problem leads to the finding of the functional extremum: $I' = \int_0^\lambda y\,d\eta$ with the isoperimetric condition $h = -c\int_0^\lambda d\eta/\ln y'$ and the boundary conditions $y(0) = 0$ and $y(\lambda) = \text{const.}$

Using the theorems of the variational calculus we get:

$$\phi(y', y, \eta, \omega) = \int_0^\lambda \left(\frac{\omega}{\ln y'} + y\right)d\eta \tag{11}$$

$$\frac{\mathrm{d}}{\mathrm{d}\eta}\left[\frac{\partial}{\partial y'}\left(\frac{\omega}{\ln y'}+y\right)\right]=\frac{\partial}{\partial y}\left(\frac{\omega}{\ln y'}+y\right); \quad -\frac{\mathrm{d}}{\mathrm{d}\eta}\left(\frac{\omega}{y'(\ln y')^2}\right)=1 \tag{12}$$

As $1/y'(\ln y')^2 = \xi/c^2 e^{c/\xi}$ from (12), by integration, we have: $\xi^2 e^{c/\xi} = \mu\eta + b$. Taking into account that $\xi(0) = 1$ we have $b = e^c$ and $\xi^2 e^{c/\xi} = \mu\eta + e^c$ (13) or:

$$\frac{T^2}{T_0^2}e^{E/RT} = \mu' t + e^{E/RT_0}$$

where μ' is determined from the condition:

$$T_m t_M = \int_0^{t_M} T(t)\,\mathrm{d}t$$

To put into practice the eqn (13') of the extremal programme we shall use the following approximations:

(1) As the pre-exponential term T^2 varies by less than the exponential itself, we shall substitute within this term the temperature T by its mean value $\overline{T} = (T_0 + T_{max})/2$.

(2) As the value of the activation energy E, which appears in eqn (13') is unknown (but it is going to be determined) we substitute its value for a magnitude E_0 which will be considered as an adjustment parameter.

Under such conditions, eqn (13') becomes:

$$\text{f}e^{E_0/RT} = e^{E_0/RT_0}(1+\lambda t)$$

$$\left(\lambda = \mu' e^{-E_0/RT_0}; \quad \text{f} = \left(\frac{T_0 + T_M}{2T_0}\right)^2\right) \tag{14}$$

From eqns (2) and (14) we get:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Z(1-\alpha)^n \frac{1}{\left(e^{E_0/RT_0}\dfrac{1+\lambda t}{\text{f}}\right)^{E/E_0}} \tag{15}$$

Because of its complexity eqn (15) can be used in the determination of the kinetic parameters using only the differential methods. From eqn (15), through logarithmation, it turns out that:

$$\log\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \log Z + n\log(1-\alpha) - \frac{E}{E_0}\log\left(\frac{e^{E_0/RT_0}}{\text{f}}(1+\lambda t)\right) \tag{15'}$$

From eqn (15') we can determine the values $\log Z$, n and E/E_0 making use of the bilinear regression equations.

We can also use some variants of the Freeman–Carroll method[5]. From eqn (15'), it follows that:

$$\frac{\Delta\log\dfrac{\mathrm{d}\alpha}{\mathrm{d}t}}{\Delta\log(1-\alpha)} = n - \frac{E}{E_0\Delta\log(1-\alpha)}\Delta\log\left(\frac{e^{E_0/RT_0}}{\text{f}}(1+\lambda t)\right) \tag{16}$$

$$\frac{\Delta \log \dfrac{d\alpha}{dt}}{\Delta \log \left(\dfrac{e^{E_0/RT_0}}{f}(1+\lambda t)\right)} = n \frac{\Delta \log (1-\alpha)}{\Delta \log \left(\dfrac{e^{E_0/RT_0}}{f}(1+\lambda t)\right)} - \frac{E}{E_0} \qquad (16')$$

$$\frac{\Delta \log \left(\dfrac{e^{E_0/RT_0}}{f}(1+\lambda t)\right)}{\Delta \log \dfrac{d\alpha}{dt}} = n \frac{Z\Delta \log (1-\alpha)}{E\Delta \log \dfrac{d\alpha}{dt}} - \frac{E}{E_0} \qquad (16'')$$

All these relationships can be used to determine the kinetic parameters.

EXPERIMENTAL

The thermograms were recorded with the help of a Paulik, Paulik and Erdey[6] derivatograph. The dehydration of calcium oxalate was carried out in air. We used a temperature programme which in the interval $423\ \mathrm{K} \leqslant T \leqslant 508\ \mathrm{K}$ is described by the equation:

$$(\mathrm{K})\,T = \frac{2461}{5.7 \div \ln\left(1 - \dfrac{t}{15.2}\right)} \quad (\langle t \rangle = \text{minutes})$$

The kinetic parameters were determined from eqns (15') and (16) using the least squares method. The obtained results together with the values obtained by means of a hyperbolic programme[7] and with the values obtained with the DTA method[7,8], are tabulated in Table 1. We can notice a satisfactory agreement between the results obtained with the three methods.

TABLE 1

THE VALUES OF KINETIC PARAMETERS FOR
CALCIUM OXALATE DEHYDRATION

	n	E (kcal mol^{-1})	Z (sec^{-1})
Eqn (15')	0.97	22.9	7.32×10^6
Eqn (16)	0.93	22.4	7.43×10^6
Hyperbolic programme	1	23.5	8×10^6
DTA method	1	21.8	6.23×10^6

The minimal character of the programme was checked up by comparison with a linear reference programme.

We have to make a note concerning the temperature programme. Theoretically, the adjustment parameter E_0 should have a magnitude order of the activation energies (20–30 kcal mol^{-1}). But too high values of the E_0 parameter lead to too high heating rates. These rates cause impediments in the diffusion of the gaseous reaction products. That is why the E_0 parameter has to remain below the value of 8 kcal mol^{-1}.

CONCLUSIONS

An approximate formula has been found for the temperature programme which minimizes the deviation of the sample temperature from the programmed one. In our calculations we started from the validity of the reaction order model. The suggested programme was checked up through the determination of the kinetic parameters of calcium oxalate dehydration. The programme can be used only in the determination of the kinetic parameters, making use of the differential methods.

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