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AN IMPLICIT HEATING PROGRAMME TO MINIMIZE THE EFFECT OF THE DIFFERENCE BETWEEN THE SAMPLE TEMPERATURE AND THE PROGRAMMED TEMPERATURE

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An implicit heating programme is suggested for minimization of the effect of the difference between the sample temperature and the programmed temperature in a thermoanalytical set-up.

In a previous paper [1], a heating programme was reported which minimizes the difference between the programmed temperature and the sample temperature during a physical or chemical process followed in a thermoanalytical set-up. The programme was obtained through minimization of the integral

$$I = \int_0^\infty (T_p - T_s)\,\mathrm{d}t \tag{1}$$

where T_p and T_s are the programmed and sample temperatures, respectively, and t is time. To ensure a minimum of the integral (1), a supplementary imposed isoperimetric condition was used.

In the following, we examine the possibility of minimizing integral (1) without the above condition, and finally suggest another minimization criterion.

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Considerations concerning the minimization of the integral

$$J = -I$$

Instead of I, the integral J, defined by

$$J = \int_0^\infty (T_s - T_p)\,\mathrm{d}t \tag{2}$$

will be considered for minimization. In order to see whether the minimization is possible or not, the following approximations have to be taken into account:

1. the heat capacity of the sample C_s is constant (it does not change during the transformation);
2. the total heat of reaction ΔH does not change with the temperature T and the conversion degree α (ΔH = const.).

In isothermal kinetics, the physical or chemical change undergone by a sample is described by the differential equation:

$$\frac{\mathrm{d}\alpha_s}{\mathrm{d}t} = Af(\alpha_s)\,e^{-\frac{E}{RT}} \qquad (T = \text{const.}) \tag{3}$$

$$(A = \text{const};\ E = \text{const.})$$

which, accepted as a P–PIDKE and with the application of the classical nonisothermal change (CNC) [2–4], turns into a nonisothermal differential kinetic equation.

The programmed and sample temperatures, respectively are given by the relationships [4]:

$$T_p = h(t) \tag{4}$$

$$T_s = h(t) - \frac{\Delta H}{C_s}\alpha_s + T_1 \tag{5}$$

where T_1 is the term corresponding to the heat transfer between the sample and the heating block, and $h(t)$ is the heating programme which has to be obtained. No matter what its explicit form, the programme has to fulfil the obvious initial condition:

$$h(t = 0) = T_0 \tag{6}$$

where T_0 is the initial temperature of the sample.

The following differential equation describes the evolution of T_1 in time:

$$\frac{dT_1}{dt} = -\frac{K}{C_s}\left(-\frac{\Delta H}{C_s}\alpha_s + T_1\right) \tag{7}$$

where K = const. is the heat transfer coefficient between the sample and the heating block.

We shall accept that the whole sample at a given moment is characterized by the temperature given by (4). All the further calculations will be performed by considering that the process which occurs in the sample is exothermic, $\Delta H < 0$, and thus $T_s \geqslant T_p$. The endothermic case could be treated in the same way merely by changing the sign.

Equation (4) for the particular condition $K=0$, when, according to (6):

$$T_1 = 0 \tag{8}$$

turns into:

$$T_s = h(t) = \frac{\Delta H}{C_s}\alpha_s \tag{9}$$

Through the CNC [3, 4], Eq. (2) takes the form:

$$\frac{d\alpha_s}{dt} = Af(\alpha_s)e^{-\frac{E}{RT_s}} \tag{10}$$

For the considered case, taking condition (2) into account, it turns out that:

$$J_1 = \int_0^{\infty} -\frac{\Delta H}{C_s}\alpha_s\,dt \tag{11}$$

It is seen from Fig. 1, that the value of J_1 is ∞, and thus its minimization is meaningless.

Actually, it would be more correct to minimize the integral J_2 given by

$$J_2 = \int_0^{t_2} -\frac{\Delta H}{C_s}\alpha_s\,dt \tag{12}$$

where t_2 is the time corresponding to almost the completion of the process which occurs in the sample (for instance, t_2 should be taken as corresponding to $\alpha_s = 0.99$). Since t_2 depends on the heating programme, relationship (12) cannot be recomanded for minimization.

If T_s is given by relationship (5), one has to minimize the integral J_3 given by:

$$J_3 = \int_0^{\infty}\left(-\frac{\Delta H}{C_2}\alpha_s + T_1\right)dt \tag{13}$$

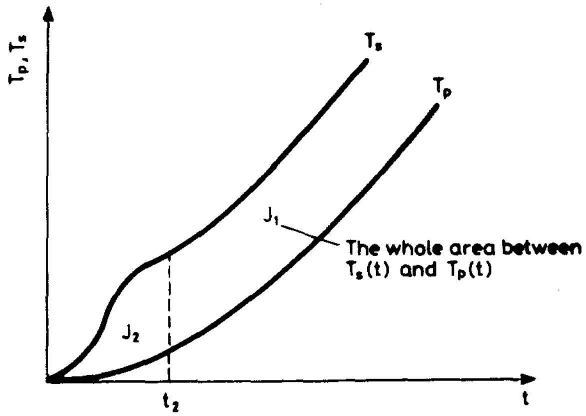

Fig. 1 Temperatures T_s and T_p *vs.* time (T_s given by Eq. (9))

Introducing the notation:

$$-\frac{\Delta H}{C_s}\alpha_s + T_1 = \Delta T(t) \tag{14}$$

the integral J_3 can be written briefly as:

$$J_3 = \int_0^\infty \Delta T(t)\,\mathrm{d}t \tag{15}$$

From (14), through differentiation, one obtains:

$$-\frac{H}{C_s}\mathrm{d}\alpha_s + \mathrm{d}T_1 = \mathrm{d}\Delta T(t) \tag{16}$$

where, taking condition (6) into account:

$$-\frac{\Delta H}{C_s}\mathrm{d}\alpha_s - \frac{K}{C_s}\Delta T(t)\,\mathrm{d}t = \mathrm{d}\Delta T(t) \tag{17}$$

From (17), through integration for $\alpha_s \in [0, 1]$ and $t \in [0, \infty]$, it turns out that:

$$-\frac{\Delta H}{C_s} = \int_0^\infty \left(-\frac{K}{C_s}\right)\Delta T(t)\,\mathrm{d}t = 0 \tag{18}$$

or

$$\int_0^\infty \Delta T(t)\,\mathrm{d}t = -\frac{\Delta H}{K} = J_3 \tag{19}$$

This result is shown graphically in Fig. 2.

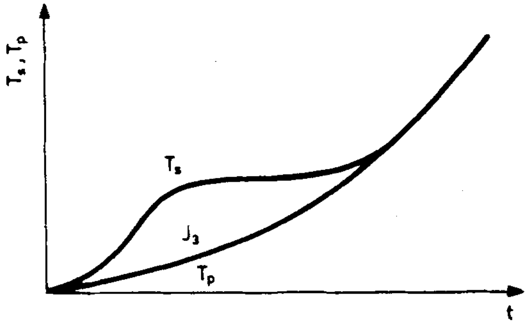

Fig. 2 Temperatures T_s and T_p *vs.* time (T_s given by Eq. (5))

Thus, no matter what the heating programme, the value of the integral J_3 is constant, i.e. the total area under the curve $T(t)$ is invariant to the heating programme if C_s, ΔH and K are constant.

Since these results show that criterion (1) fails under the considered conditions, another minimization criterion must be suggested.

Let us suppose that in a thermoanalytical set-up the reference crucible contains a compound which undergoes a reaction with the same kinetic parameters as in the sample, but without any thermal effect.

This hypothetical compound will be denoted by s^*.

The kinetics of the processes which occur in the sample and in the reference compound, respectively, are described by the equations:

$$\frac{d\alpha_s}{dt} = Af(\alpha_s)e^{-\frac{E}{R(h(t)-\Delta H/C_s\alpha_s+T_1)}} \tag{20}$$

$$\frac{d\alpha_{s*}}{dt} = Af(\alpha_{s*})e^{-\frac{E}{Rh(t)}} \tag{21}$$

In this case, another criterion of minimization can be suggested by looking for the minimum of the integral:

$$J_4 = \int_0^\infty (\alpha_s - \alpha_{s*})\,dt \tag{22}$$

i.e. one has to minimize the area between the curves $\alpha_s(t)$ and $\alpha_{s*}(t)$ (Fig. 3).

The advantage of such a criterion results from the following theorem, which will be stated without demonstration.

If α_1 and α_2 are the conversion degree at a given moment, corresponding to two heating programmes $T_1 = \theta(t)$ and $T_2 = \theta(t) + \theta_1(t)$ with $\theta_1(t) > 0$, then the curves $\alpha_1(t)$ and $\alpha_2(t)$ satisfy the following two conditions:

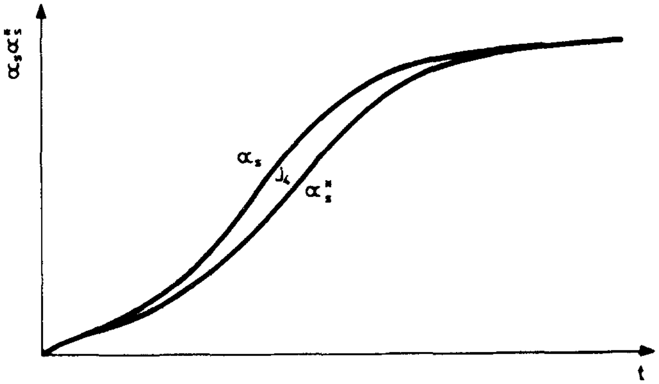

Fig. 3 Conversions α_s and α_{s*} *vs. time*

1. Except for $t=0$ and $t=\infty$, the curves $\alpha_1(t)$ and $\alpha_2(t)$ do not intersect.
2. The area limited by the curves $\alpha_1(t)$ and $\alpha_2(t)$ is a finite quantity which depends on the heating programme.

It is easy to see that $\left(-\frac{\Delta H}{C_s}\alpha_s + T_1\right) > 0$, i.e. the heating programmes (5) and (9) satisfy the above-mentioned conditions.

Conclusions

The minimization of the effect of the temperature difference between the sample and the reference requires a heating programme, $h(t)$, which can be found by considering the equations:

$$\frac{d\alpha_s}{dt} = Af(\alpha_s)e^{-\frac{E}{R(h(t) - \Delta H/C_s\alpha_s + T_1)}}$$

$$\frac{d\alpha_{s*}}{dt} = Af(\alpha_{s*})e^{-\frac{E}{Rh(t)}}$$

$$\frac{dT_1}{dt} = -\frac{K}{C_s}\left(-\frac{\Delta H}{C_s}\alpha_s + T_1\right) \tag{23}$$

$$J_4 = \int_0^\infty (\alpha_s - \alpha_{s*})\, dt - \text{minimum}$$

With regard to the mathematical difficulties, we leave the finding of the explicit form of $h(t)$ from conditions (23) as an open question.

References

1 E. Segal and M. Vlad, Thermochim. Acta, 16 (1976) 115.

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Zusammenfassung — Es wird ein implizites Aufheizprogramm beschrieben, das den Einfluss des Unterschiedes zwischen Probentemperatur und programmierter Temperatur für die Probe minimalisiert.

Резюме — Предложена скрытая программа нагрева с целью свести до минимума влияние различия между температурой образца и запрограммированной температурой в термоаналитической установке.