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A NEW METHOD FOR THE DETERMINATION OF REACTION KINETICS FROM DTA AND TG CURVES. PART I.

DEFINITION OF THE METHOD

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ABSTRACT

Starting from the expression for the reaction rate under non-isothermal conditions, a method is defined for the determination of kinetic parameters from data available from DTA and TG curves with the application of a computer. The method makes possible the determination of kinetic parameters from one non-isothermal curve, with the condition that a function characterising the reaction mechanism is successfully determined from isothermal data.

INTRODUCTION

Several methods have been defined for the determination of reaction kinetics under non-isothermal conditions from data available from thermal methods. They are often defined in accordance with a thermal analysis method, but may be generally applied to all measurement techniques because they all interpret the same starting data (the rate or the transformation degree). The accuracy of a particular method depends upon the reaction data analysed as well as upon the limitations that are introduced during their development. From the point of view of mathematical interpretation, these methods may be divided differently. Our opinion is that they may be most favourably divided into methods that use one heating rate [1–5] and methods that use different heating rates [6–8].

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The largest number of authors [9–11], in their papers for the analysis of kinetics of particular chemical reactions under non-isothermal conditions, describe the possibility of applying particular methods with special attention being paid to their limitations. Because of this, no special consideration of these will be given in this paper.

In recent literature [9], the combined use of isothermal and non-isothermal methods for kinetic determinations, with the objective of the elimination of some of their particular limitations, is described. Although non-isothermal methods offer particular advantages [12] for the kinetic determination of chemical reactions in the solid phase as compared with isothermal methods, we consider that, for the complete analysis of the kinetics of a chemical reaction, it is necessary to use both these methods. Isothermal methods are more efficient for the identification of the reaction mechanism [13], while non-isothermal methods, based upon these facts, would be used for all kinetic determinations. This is suggested in the practical part of this paper. This consideration is suggested because of the fact that, in both cases, in the expression for the rate there exists the function f(α) (which characterises the reaction mechanism) in the same form, i.e. the consideration is given that a non-isothermal process may be treated as a boundary case of the sequences of isothermal intervals.

Based upon the considerations given above, a computer method was designed for the determination of reaction kinetics from one TG or DTA curve.

BASIC ASSUMPTIONS OF THE METHOD

According to the literature data for the majority of chemical reactions under non-isothermal conditions, the reaction rate is described by the expression

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\tau} = \mathrm{f}(\alpha) \cdot K[T(\tau)] \tag{1}$$

where $\mathrm{d}\alpha/\mathrm{d}\tau$ is the reaction rate and $\mathrm{f}(\alpha)$ and $K[T(\tau)]$ are temperature-dependent functions. Since the function $K[T(\tau)]$ is almost always generally expressed by the Arrhenius equation, eqn. (1) assumes the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\tau} = A \exp\left[-\frac{E}{RT(\tau)}\right]\mathrm{f}(\alpha) \tag{2}$$

Our opinion is that the transformation degree, α, should be used as a starting condition and that is why we have carried out a separation of variables in eqn. (2), to give the expression

$$\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = A \exp\left[-\frac{E}{RT(\tau)}\right]\mathrm{d}\tau \tag{3}$$

Apart from the kinetic parameters, the unknown variables in eqn. (3) are the functions f(α) and $T(\tau)$. The function f(α) characterises the reaction mechanism, i.e. the mechanism of the limiting degree and reaction topochemistry. Investigations made so far in non-isothermal kinetics show that the majority of authors accept or assume the reaction mechanism, i.e. the function f(α). In order to avoid assumptions, we consider that the reaction mechanism may be established by closely monitoring reactions under isothermal conditions, as also suggested by other authors [9,13], because an accurately determined reaction mechanism represents the basis in the investigation of kinetics of all reactions.

Table 1 gives the currently recognised and accepted functions f(α) as well as their integrated forms, F(α), which are used for describing the reaction kinetics of the decomposition process of solid components [14]. By using the values given in the table of the functions f(α) which are represented in the system $\alpha = \mathrm{f}(\tau/\tau_{0.5})$ and experimental curves shown in the same system, the right function f may be readily identified.

In order to avoid possible deviations, which appear in the identification of f(α) in the way previously described, we suggest a generalised division of the mathematical expressions into groups, depending upon the process that limits the total rate, viz. diffusion-controlled (D_1, D_2, D_3, D_4), decomposition reaction at phases boundary (R_2, R_3), and reactions forming the centres of the new phase (F_1, F_2, F_3). The correct values of the constants appearing in the general expression would be determined by a working model.

In the function f(α), there appears the transformation degree, the values of which should be known. In TG measurements under non-isothermal conditions, according to literature data [15] the loss of substances, ω, is proportional to the height, h, of the deviation from the zero line so that the transformation degree, α, is given by

$$\alpha = \frac{\omega}{\omega_\infty} = \frac{h}{h_\infty} \tag{4}$$

where the subscript ∞ denotes values at the end of the process.

The calculation of the transformation degree for DTA results is more complex and requires certain assumptions for the solution of equations in order to avoid complex expressions. In that sense, the theoretical assumptions of Borchardt and Daniels [2] were used, which have shown that the number of moles, n, at any time τ for a DTA curve may be calculated by the expression

$$n = n_0 - \frac{n_0}{CS}\left(C_p\,\Delta T + CS_\tau\right) \tag{5}$$

where n_0 and n are the number of moles at the beginning and at time τ, respectively, C is a proportionality constant, C_p is the specific heat, ΔT is the peak height, S is the total peak area, and S_τ is the peak area at time τ.

TABLE 1

Kinetic equations for the description of thermal decomposition of solid components

Symbol	f(α)	F(α)	Rate-controlling process
D_1	$\frac{1}{2}\alpha$	α^2	One-dimensional diffusion
D_2	$-\frac{1}{\ln(1-\alpha)}$	$(1-\alpha)\ln(1-\alpha)+\alpha$	Two-dimensional diffusion; cylindrical symmetry
D_3	$\frac{3}{2}\frac{(1-\alpha)^{2/3}}{1-(1-\alpha)^{1/3}}$	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion; spherical symmetry; Jander equation
D_4	$\frac{3}{2}\frac{1}{(1-\alpha)^{-1/3}-1}$	$(1\frac{2\alpha}{3})-(1-\alpha)^{2/3}$	Three-dimensional diffusion; spherical symmetry; Ginstling and Brounstein equation
F_1	$(1-\alpha)$	$-\ln(1-\alpha)$	Random nucleation; only one nucleus on each particle.
A_2	$2\text{-}[\ln(1-\alpha)^{1/2}](1-\alpha)$	$[-\ln(1-\alpha)]^{1/2}$	Random nucleation; Avrami I equation
A_3	$3[\text{-}\ln(1-\alpha)^{2/3}](1-\alpha)$	$[-\ln(1-\alpha)]^{1/3}$	Random nucleation; Avrami II equation
R_2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$	Phase boundary reaction; cylindrical symmetry
R_3	$(1-\alpha)^{2/3}$	$3\{1-(1-\alpha)^{1/3}\}$	Phase boundary reaction; spherical symmetry

Using the definition of the transformation degree, one obtains

$$\alpha = \frac{c_p \Delta T}{CS} + \frac{S_\tau}{S} \tag{6}$$

Values of S and S_τ may be determined from the DTA curve by graphical integration, ΔT is measured from the curve and the ratio from the cooling curve [16]. However, for the majority of reactions, the product $C_p \Delta T$ is much lower than the product CS, so that the first term in eqn. (6) may be ignored and the transformation degree becomes

$$\alpha = \frac{S_\tau}{S} \tag{7}$$

The possibility of the use of eqn. (7) is greater if the experimental conditions are close to the theoretical assumptions.

The function $T(\tau)$, which appears in the expression $K|T(\tau)|$, is chosen by the investigator. Our investigations were based upon a linear program which is given by the expression

$$T = T_0 + \Phi\tau \tag{8}$$

where T_0 is the starting temperature and Φ is the heating rate.

By using the knowledge of the functions $f(\alpha)$ and $T(\tau)$, we have tried to determine kinetic parameters from one non-isothermal DTA curve as well as one non-isothermal TG curve.

If eqn. (8) is introduced into eqn. (3), one obtains

$$\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = A \exp\left[-\frac{E}{R(T_0 + \Phi\tau)}\right] \mathrm{d}\tau \tag{9}$$

By integrating eqn. (9) over α [which appears in a particular form of the function $\mathrm{f}(\alpha)$] from zero to one, and over τ from zero to τ, and by using the starting condition that $\tau = 0$ and $\alpha = 0$, one obtains

$$\mathrm{F}(\alpha) = A \frac{E}{R\Phi} \left\{ \mathrm{I}\left[\frac{R(T_0 + \Phi\tau)}{E}\right] - \mathrm{I}\left[\frac{RT_0}{E}\right] \right\} \tag{10}$$

Integration of the right-hand side of eqn. (9) was carried out in the following way.

$$\int_0^\tau A \exp\left[-\frac{E}{R(T_0 + \Phi\tau)}\right] \mathrm{d}\tau$$

replacement

$$y = \frac{R(T_0 + \Phi\tau)}{E}; \; \tau = \frac{Ey}{\Phi} - T_0; \; \mathrm{d}\tau = \frac{E}{R\Phi} \, \mathrm{d}y$$

$$\tau = 0 => y = \frac{RT_0}{E} = y_1$$

$$\tau = \tau => y = \frac{R(T_0 + \Phi\tau)}{E} = y_2$$

By replacement into the previous equation, one obtains

$$\int_0^{\tau} A \exp\left[-\frac{E}{R(T_0+\Phi\tau)}\right] \mathrm{d}\tau = \frac{E}{R\Phi}\int_{y_1}^{y_2} \mathrm{e}^{-1/y}\,\mathrm{d}y$$

$$= \frac{E}{R\Phi}\left(\int_0^{y_2} \mathrm{e}^{-1/y}\,\mathrm{d}y - \int_0^{y_1} \mathrm{e}^{-1/y}\,\mathrm{d}y\right) = \frac{E}{R\Phi}[\mathrm{I}(y_2)-\mathrm{I}(y_1)]$$

$$= \frac{E}{R\Phi}\left\{\mathrm{I}\left[\frac{RT_0+\Phi\tau}{E}\right] - \mathrm{I}\left[\frac{RT_0}{E}\right]\right\}$$

The kinetic parameters appearing in eqn. (10) are the process activation energy, E, the pre-exponential factor, A and quantities appearing in the function $\mathrm{F}(\alpha)$, i.e. the reaction mechanism and, most frequently, "the apparent reaction order", n. For the determination of these kinetic parameters, which, compared with the parameters in homogenous reactions, are not unique, we introduce the idea of the "least square method".

Equation (9) and its equivalent eqn. (10) are valid for any time τ so that the condition

$$\mathrm{F}(\alpha) - \frac{EA}{R\Phi}\left\{\mathrm{I}\left[\frac{R(T_0+\Phi\tau)}{E}\right] - \mathrm{I}\left[\frac{RT_0}{E}\right]\right\} = 0$$

is satisfied. Based upon the criterion of the "least square method", we form the function G, which is the function of kinetic parameters, obtained by the equation

$$\mathrm{G} = \sum_{i=1}^{k}\left[\mathrm{F}(\alpha_i) - \frac{EA}{R\Phi}\left\{\mathrm{I}\left[\frac{R(T_0+\Phi\tau)}{E}\right] - \mathrm{I}\left[\frac{RT_0}{E}\right]\right\}\right]^2 \tag{11}$$

The integrals in eqn. (11), denoted by $\mathrm{I}(a)$, are not elementary functions so that it is necessary to approximate them, giving a new function

$$\mathrm{G}_1 = \sum_{i=1}^{k}\left[\mathrm{F}(\alpha_i) - \frac{EA}{R\Phi}\left\{\mathrm{P}\left[\frac{R(T_0+\Phi\tau)}{E}\right] - \mathrm{P}\left(\frac{RT_0}{E}\right)\right\}\right]^2 \tag{12}$$

The solution for the kinetic parameters are those values of the function G at which it attains a minimum.

Approximation of the integral $\mathrm{I}(a)$ in eqn. (11) was carried out according to

$$\mathrm{I}(y) = \int_0^{a} \mathrm{e}^{-1/x}\,\mathrm{d}x;\ a = \frac{E}{R(T_0+\Phi\tau)}$$

Approximation is possible if "a" is less than one, which is most often the case, i.e. the lower the value of "a", the more accurate is the approximation.

By replacement

$$\frac{1}{x} = z; \qquad \mathrm{d}x = -\frac{\mathrm{d}z}{z^2}$$

$$x = 0 => \quad z = +\infty$$
$$x = a => \quad z = 1/a$$
$$\mathrm{I}(a) = \int_{+\infty}^{1/a} -\frac{\mathrm{e}^{-z}}{z^2}\,\mathrm{d}z = \int_{1/a}^{+\infty} \frac{\mathrm{e}^{-z}}{z^2}\,\mathrm{d}z$$

By partial integration, one obtains

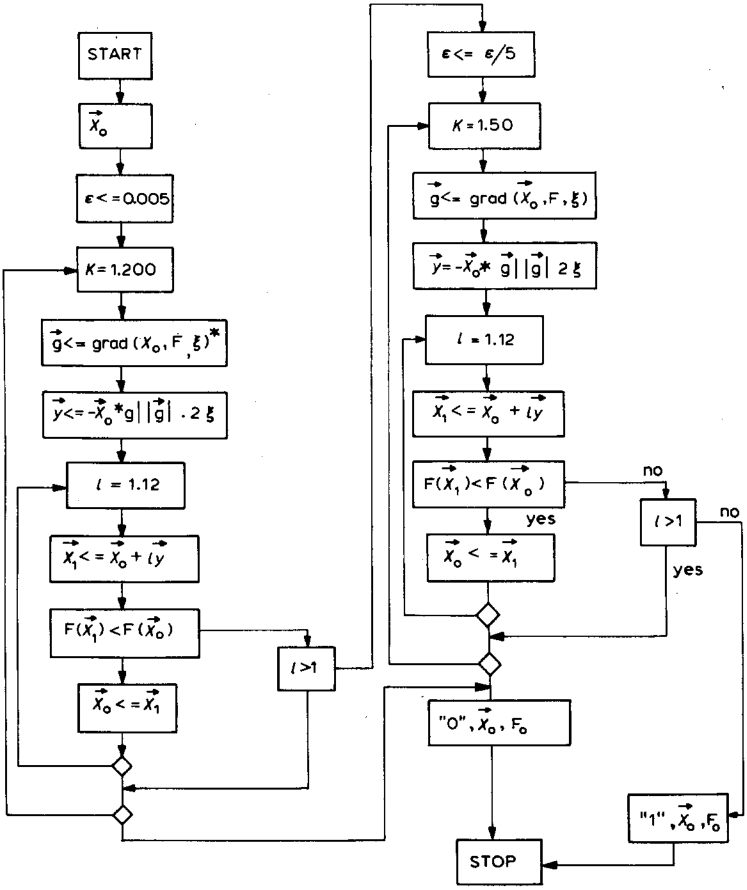
$$\mathrm{I}(a) = -\frac{\mathrm{e}^{-z}}{z^2}\Big|_{1/a}^{+\infty} + \int_{1/a}^{+\infty} \mathrm{e}^{-z}\,\mathrm{d}(1/z^2) = a^2\,\mathrm{e}^{-1/a} - 2\int_{1/a}^{+\infty} \frac{\mathrm{e}^{-z}}{z^3}\,\mathrm{d}z$$

By the same procedure, one obtains in the end

$$\mathrm{I}(a) = \mathrm{e}^{-1/a}(a^2 - 2!a^3 + 3!a^4 - 4!a^5 + \ldots) = \mathrm{e}^{-1/a}a^2 \sum_{k=0}^{+\infty} (-1)^k (k+1) a^k$$

TABLE 2

Block diagram for solution of the model proposed



*grad ($\vec{X}$,F,ξ) - statistical gradient of the function F at point $\vec{X}$ with the relative log ξ.

Quite sufficient accuracy is obtained up to the fourth member so that $|(a)$ may be written by the function $P(a)$ in the form

$$P(a) = a^2 e^{-1/a}(1 - 2!a + 3!a^2 - 4!a^3)$$

We would like to point out that the minimisation of the function G_1 [eqn. (12)] was carried out by the method of "statistical gradient" [17] using the computer.

The block diagram for the solution of the given model is presented in Table 2. It is general from the point of view of the possibility of usage of any form of the function $F(\alpha)$, which characterises the reaction mechanism. For the solution of the model, the modifications (a) that the step is different for each variable and (b) that the change of the length of step is regulated during iterations were introduced. Bearing in mind that the input data are approximate numbers, the estimate of the operation error was established, i.e. the accuracy was established by which the computer carries out mathematical operations and it was shown that the error may be ignored (less than 0.1%).

The suggested method enables determination of the reaction kinetics by one curve under isothermal conditions for identification of the reaction mechanism and one curve under non-isothermal conditions for determination of kinetic parameters on condition that the time when the reaction mechanism change takes place is known.

The discussion of concrete applications of the method for the analysis of the kinetics of particular chemical reactions will be given in Part II [18].

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