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DISCRIMINATION OF CONVERSION FUNCTIONS USING TG AND DTG CURVES

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ABSTRACT

A simple method for testing the analytic form of conversion functions using TG and DTG curves recorded under isokinetic conditions was developed. The method was checked using the dehydration of solid $Ca(COO)_2 \cdot H_2O$.

INTRODUCTION

One of the most important problems connected with the non-isothermal kinetics of solid–gas decompositions consists of finding the conversion functions consistent with the true reaction mechanism. Special emphasis was given to this problem in refs. 1–5. In our previous paper [5], a general method for testing various kinds of conversion functions was given. The major disadvantage of the method is the necessity of a complex temperature programmer, which allows the TG curve to be recorded in isokinetic conditions ($d\alpha/dt = \text{constant}$) for all the values of the degree of conversion ($0 \leqslant \alpha \leqslant 1$). In this paper a simple method which uses the data from TG and DTG curves recorded with constant heating rate is described. The advantages of simultaneous recording of TG and DTG curves have already been made use of in non-isothermal kinetics [6–10].

THE PRINCIPLE OF THE METHOD

In the general rate equation

$$\frac{d\alpha}{dt} = A\, e^{-B/T} f(\alpha) \tag{1}$$

where α stands for the degree of conversion, $f(\alpha)$ for the conversion function, t for the time, A for the pre-exponential factor and $B = E/Rm$, m being a constant factor, E the activation energy and R the gas constant, the elimina-

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tion of t can be performed taking into account that for every value of the reaction rate $(d\alpha/dt)_i$ in the acceleration period ($T_0 < T_i < T_{max}$) there is a corresponding equal value $(d\alpha/dt)_{i'}$, in the decay period ($T_{max} < T_{i'} < T_f$). T_0, T_{max} and T_f stand for the initial temperature, the temperature corresponding to the maximum rate, and the final temperature of the reaction respectively; T_i and $T_{i'}$ represent variable values of the temperature.

To put in evidence the points corresponding to the isokinetic condition

$$\left(\frac{d\alpha}{dt}\right)_i = \left(\frac{d\alpha}{dt}\right)_{i'} \tag{2}$$

a family of straight lines parallel to the base line of the DTG curve were plotted (Fig. 1).

Equation (1) with condition (2) leads to

$$e^{-B/T} f(\alpha) = e^{-B/T'} f(\alpha') \tag{3}$$

or

$$\log\frac{f(\alpha)}{f(\alpha')} = \frac{B}{2.303}\left(\frac{1}{T} - \frac{1}{T'}\right) \tag{4}$$

Thus, a conversion function consistent with the true reaction mechanism should lead to a linear plot of $\log[f(\alpha)/f(\alpha')]$ v.s. $(1/T - 1/T')$. From the slope of the resultant straight line the activation energy can be evaluated.

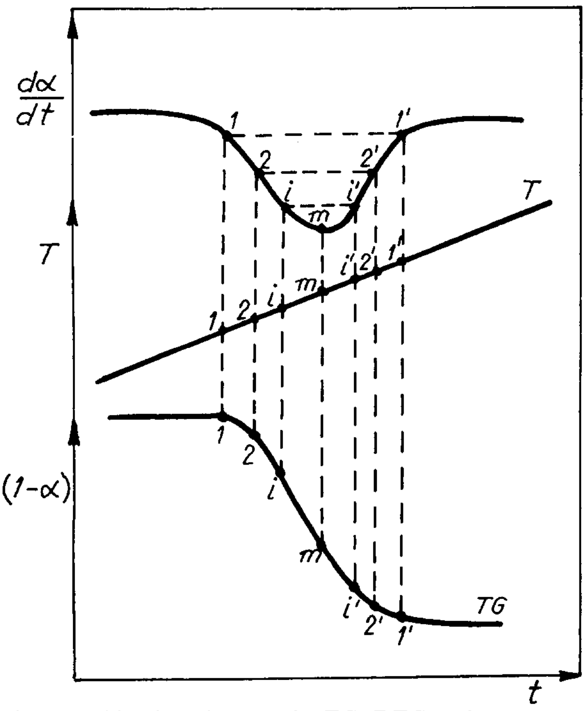

Fig. 1. Isokinetic points on the TG, DTG and T curves.

RESULTS AND DISCUSSION

To check the validity of the method, the dehydration of $CaC_2O_4 \cdot H_2O$ has been chosen. The TG and DTG curves were recorded by a MOM derivatograph (Budapest) of Paulik–Paulik–Erdey type. An air atmosphere was used with $\beta = 10$ K min^{-1} and $\beta = 2.5$ K min^{-1}. The sample weight was 0.117 g.

The kinetic equations tested were:

(a) the equation of the reaction order

$$\frac{d\alpha}{dt} = A\ e^{-E/RT}(1-\alpha)^n \tag{5}$$

with

$$B = \frac{E}{R} \text{ and } f(\alpha) = (1-\alpha)^n \tag{6}$$

(b) the Prout–Tompkins equation [11]

$$\frac{d\alpha}{dt} = A\ e^{-E/RT}\alpha(1-\alpha) \tag{7}$$

with

$$B = \frac{E}{R} \text{ and } f(\alpha) = \alpha(1-\alpha) \tag{8}$$

(c) the equation used by Johnson and Mehl [12], Avrami [13], Erofeev [14] and Kolmogorov [15] (JMAEK) in its integral form

$$-\ln(1-\alpha) = kt^m \tag{9}$$

and differential form

$$\frac{d\alpha}{dt} = kp(1-\alpha)t^{m-1} \tag{10}$$

From eqs. (9) and (10) it follows that

$$\frac{d\alpha}{dt} = A'\ e^{-E/RT}(1-\alpha)[-\ln(1-\alpha)]^n \tag{11}$$

where $A' = A^{1/m}m$ and $n = (m-1)/m$ so that for a reaction whose kinetics are described by the JMAEK model B and $f(\alpha)$ are given by

$$B = \frac{E}{mR} \text{ and } f(\alpha) = (1-\alpha)[-\ln(1-\alpha)]^n \tag{12}$$

Equation (4) with conditions (6), (8) and (9) leads to

$$\log\frac{1-\alpha}{1-\alpha'} = \frac{E}{2.303\ Rn}\left(\frac{1}{T} - \frac{1}{T'}\right) \tag{13}$$

for the reaction order model

$$\log\frac{\alpha(1-\alpha)}{\alpha'(1-\alpha')} = \frac{E}{2.303R}\left(\frac{1}{T} - \frac{1}{T'}\right) \tag{14}$$

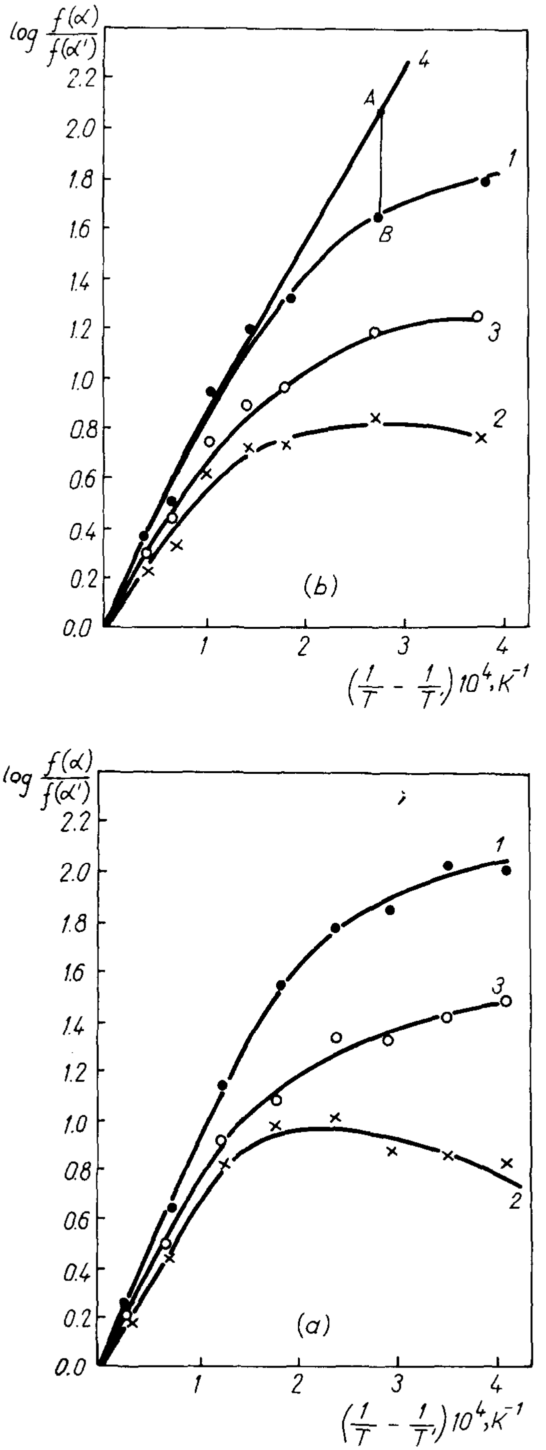

Fig. 2. Plots of log[f(α)/f(α')] vs. ($1/T-1/T'$) according to (1) eqn. (13); (2) eqn. (14); (3) eqn. (15) for dehydration of Ca(COO)$_2$·H$_2$O. (a) $\beta = 10$ K min^{-1}; (b) $\beta = 2.5$ K min^{-1}.

for the Prout–Tompkins model, and

$$\log\frac{1-\alpha}{1-\alpha'}+n\log\frac{\log(1-\alpha)}{\log(1-\alpha')}=\frac{E}{2.303Rm}\left(\frac{1}{T}-\frac{1}{T'}\right) \tag{15}$$

for the JMAEK model, respectively.

Other equations describing the decomposition kinetics in solid–gas systems can be brought to particular forms of eqn. (4) in the same way. Plots of the right-hand side of eqns. (13)–(15) vs. $1/T - 1/T'$, give the curves shown in Fig. 2, for the dehydration of $CaC_2O_4 \cdot H_2O$ with (a) $\beta = 10$ K min^{-1} and (b) $\beta = 2.5$ K min^{-1}.

In eqn. (15) the value $n = 1/3$, which corresponds to a diffusion-controlled growth mechanism of nuclei, was considered [16].

Inspection of the curves in Fig. 2 shows that none of the equations used describe the dehydration kinetics for all the values of α between 0 and 1. The best linearity is exhibited by eqn. (13) for the reaction order model.

The decrease of the heating rate from 10 K min^{-1} to 2.5 K min^{-1}, leads to a decrease in the slope of the kinetic curves.

To evaluate the kinetic parameters one has to use low heating rates which reduce interferences of chemical reaction due to heat transfer. From the linear portion of curve 1, Fig. 2(b), according to eqn. (13), it turns out that $E/n = 36$ kcal mole^{-1}. The activation energy can be evaluated independently of the particular form of the conversion function using low values of α [17]. In such conditions, due to the slow change of $1 - \alpha$, the conversion function keeps practically a constant value and eqn. (5) can be given as

$$\log\frac{d\alpha}{dt} = -\frac{E}{2.303R}\frac{1}{T} + \text{const} \tag{16}$$

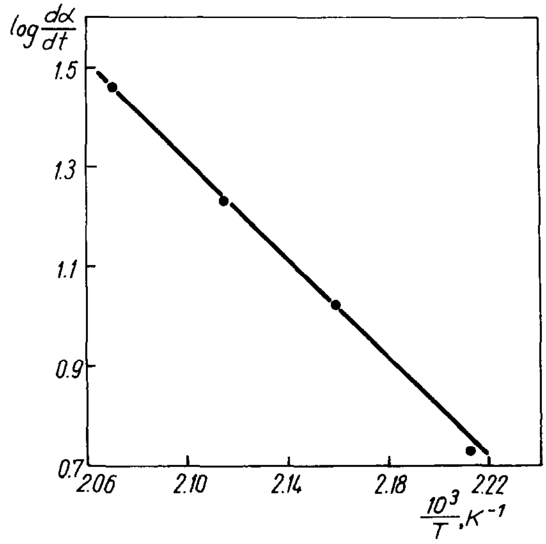

Fig. 3. Plot of log $d\alpha/dt$ (arbitrary units) vs. $1/T$.

The reaction rate values are given in arbitrary units by the ordinates of the DTG curve in its initial portion (Fig. 3). From the slope of the straight line $\log d\alpha/dt$ vs. $1/T$, $E = 23$ kcal mole^{-1}. This value leads to $n = 0.64 \simeq 2/3$, which corresponds to a contracting-sphere value. The values of the activation energy and reaction order given in the literature are in the intervals $20.2 < E < 26.0$ kcal mole^{-1} and $0.4 < n < 1.1$, respectively [18].

The deviation from linearity of curve 1, Fig. 2(b) measured by the variable length of the segment AB, increases with the differences $1/T - 1/T'$ and $T - T'$. The deviation reaches its maximal value for the points $(1 - 1')$ (Fig. 1) located at the extremities of the TG and DTG curves, the difference $T_i - T_{i'}$ being equal to 100 K.

A first explanation of such a deviation could be given taking into account the temperature dependence of the pre-exponential factor. In such conditions eqns. (3), (4) and (13) should be changed to

$$A\,e^{-B/T}f(\alpha) = A'\,e^{-B/T'}f(\alpha') \tag{17}$$

$$\log\frac{f(\alpha)}{f(\alpha')} + \log\frac{A}{A'} = \frac{B}{2.303}\left(\frac{1}{T} - \frac{1}{T'}\right) \tag{18}$$

$$\log\frac{1-\alpha}{1-\alpha'} + \log\frac{A}{A'} = \frac{E}{2.303Rn}\left(\frac{1}{T} - \frac{1}{T'}\right) \tag{19}$$

For $A = CT^{-r}$, where C and r are constants, eqn. (19) becomes

$$\frac{E}{2.303Rn}\left(\frac{1}{T} - \frac{1}{T'}\right) - \log\frac{1-\alpha}{1-\alpha'} = r\log\frac{T'}{T} \tag{20}$$

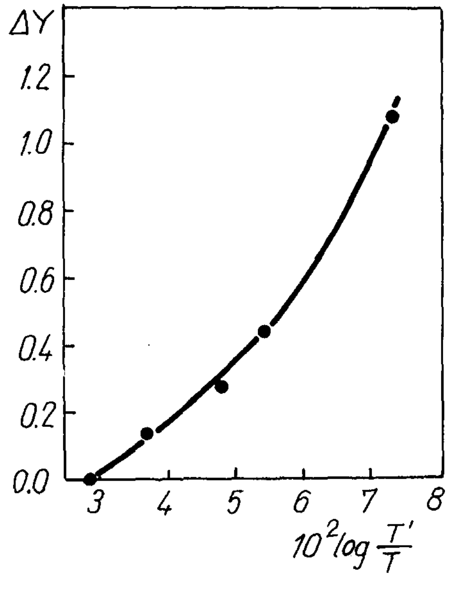

Fig. 4. Plot of ΔY vs. $\log T'/T$.

The left side of eqn. (20) gives the deviation from linearity $\Delta Y = AB$ of curve 1, Fig. 2a such that

$$\Delta Y = r \log \frac{T'}{T} \qquad (21)$$

The plot of ΔY vs. $\log(T'/T)$ is given in Fig. 4. Even in this case the outermost point does not lie on the straight line. From the linear portion of the curve, it turns out that $r = 17.6$, a value with no theoretical meaning. For the exponential temperature dependence of the pre-exponential factor

$$A = C\mathrm{e}^{-aT} \qquad (22)$$

where C and a are constants it turns out that

$$\Delta Y = a(T' - T) \qquad (23)$$

The plot of ΔY vs. $(T' - T)$ is given in Fig. 5. Even in this case the point corresponding to the extremities of the TG and DTG curves does not lie on the straight line. From the slope of the linear portion it turns out that $a = 0.08\ \mathrm{K}^{-1}$.

The exponential decrease of the A factor with temperature is equivalent to a parabolic inrease of the activation energy with temperature. This statement can be demonstrated by introducing condition (22) into the Arrhenius equation, $k = A\ \mathrm{e}^{-E/RT}$. This leads to

$$k = C\,\mathrm{e}^{-(E_0 + aRT^2)/RT}$$

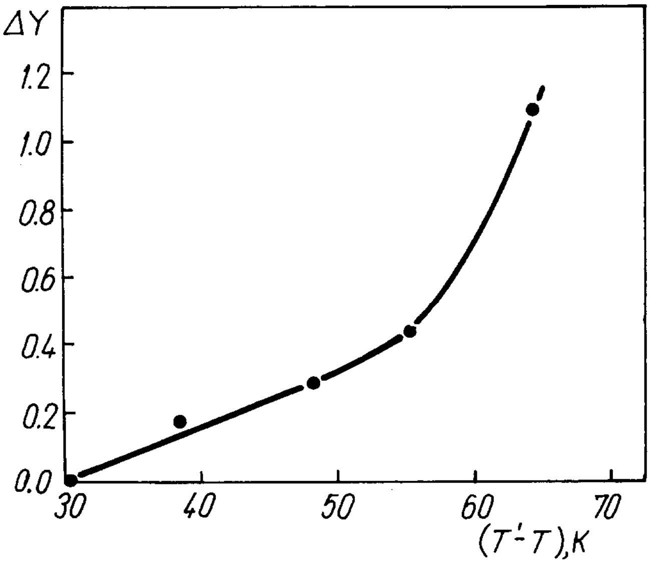

Fig. 5. Plot of ΔY vs. $T' - T$.

such that

$$E = E_0 + aRT^2$$

where E_0 is the part of the activation energy which does not depend on temperature.

From these considerations, the deviation from linearity of curve 1, Fig. 2(a) cannot be explained only by taking into account the temperature dependence of the pre-exponential factor, A. The reasons for such deviations may be found in the different kinetic laws which describe the initial and final periods of the thermal decomposition.

CONCLUSIONS

A testing method in isokinetic conditions for the conversion functions describing the thermal decomposition of solids has been suggested.

According to our testing method eqn. (6) adequately describes the dehydration kinetics of $CaC_2O_4 \cdot H_2O$.

Equations (1), (5) and (7) could not linearize the data corresponding to the extremities of the TG and DTG curves. Consideration of the exponential decrease of the factors, A, with temperature improves but does not remove the deviation from linearity corresponding to the outermost points on the TG and DTG curves.

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