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REMARKS ON THE SUITABILITY OF THE ZIVKOVIC AND DOBOVISEK METHOD

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ABSTRACT

The method proposed by Zivkovic and Dobovisek for the kinetic study of solid state reactions using a section of a TG or DTA curve is analysed.

It is demonstrated that the procedure cannot be used to determine accurately the activation energy of a reaction.

Zivkovic and Dobovisek [1] have suggested a new method for performing the kinetic analysis of DTA and TG curves based on a relation between the first order reaction rate and the Arrhenius equation.

Using the idea of Chatterjee [2], Zivkovic and Dobovisek have defined a method for the determination of kinetic parameters from the equation

$$\ln\left(\frac{a}{a-x}\right) = kt \tag{1}$$

where a is the initial concentration of the reactants, x the concentration of the starting material reacting after time t, and k is the rate constant dependent on the temperature according to the Arrhenius equation

$$k = A\ \exp(-E/RT) \tag{2}$$

where k is the universal gas constant, E the activation energy and A the pre-exponential Arrhenius factor.

In order to describe solid state reactions it would be more suitable to rearrange eqn. (1) in the form

$$\ln\left(\frac{1}{1-\alpha}\right) = kt \tag{3}$$

where $\alpha(=x/a)$ is the reacted fraction.

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It is very well known [3] that eqn. (3) is obtained by integrating the theoretical expression of the reaction rate for first order kinetics

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-\alpha) \tag{4}$$

By substituting eqn. (2) into eqn. (3) and taking logarithms we get

$$\log\frac{\ln[1/(1-\alpha)]}{t} = \log A - \frac{E}{2.3RT} \tag{5}$$

If the process is observed up to a maximum rate, eqn. (5) may be adjusted to

$$\log\frac{\ln[1/(1-h_t/h_{\max})]}{t} = \log A - \frac{E}{2.3RT} \tag{6}$$

where $h_{\max}$ is the height of the TG curve at maximum reaction rate, and h_t is the height of the TG curve after time t.

A plot of the left-hand side of eqn. (6) against $1/T$ would yield a straight line whose slope gives the activation energy of the process.

The aim of this work is to demonstrate that the use of eqn. (6) leads to serious errors in the determination of the activation energy and thus it must not be used for performing the kinetic analysis of a solid state reaction. This is because, as shown in previous papers [4,5], eqn. (5) is not suitable for performing the kinetic analysis of non-isothermal data. The reason for this is that eqn. (5) is obtained from eqn. (4) assuming that k remains constant over the whole α-range. If the temperature changed during the experiment a mathematical function relating temperature with time would be necessary in order to perform the integration of eqn. (4).

In the case of a TG curve recorded at a heating rate $\beta = \mathrm{d}T/\mathrm{d}t$, the following expression is obtained from eqns. (1) and (2)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{A}{\beta}\exp(-E/RT)(1-\alpha) \tag{7}$$

hence, by integration

$$\ln\left(\frac{1}{1-\alpha}\right) = \frac{A}{\beta}\int_0^T \exp(-E/RT)\mathrm{d}T \tag{8}$$

A number of approximations to eqn. (8) have been reported in the literature. The method of the third rational approximation developed by Senum and Yang [6] allows integration of the Arrhenius equation with an accuracy of $> 10^{-2}\%$ for E/RT values higher than 5, and leads to the expression

$$\ln\left(\frac{1}{1-\alpha}\right) = \frac{AE}{\beta R}\,\frac{\exp(-x)}{x}\,\frac{x^2+10x+18}{x^3+12x^2+36x+24} \tag{9}$$

where $x = E/RT$.

It is noteworthy that there are two additional drawbacks to the method of Zivkovic and Dobovisek. Firstly, the reacted fraction α (or the concentration x) must be determined previously with regard to the total amount reacted (or the starting concentration) as determined from a complete DTA or TG curve; in other words, it is wrong to select arbitrarily any other point on the curve as a reference for determining α (or x). Secondly, to the best of our knowledge, it is not evident that first order kinetics is a general model for describing solid state reactions.

In order to check the validity of the above considerations we have constructed from eqn. (9) the series of TG curves in Fig. 1 for different values of E/RT (9–40) by assuming first order kinetics and different kinetic parameters.

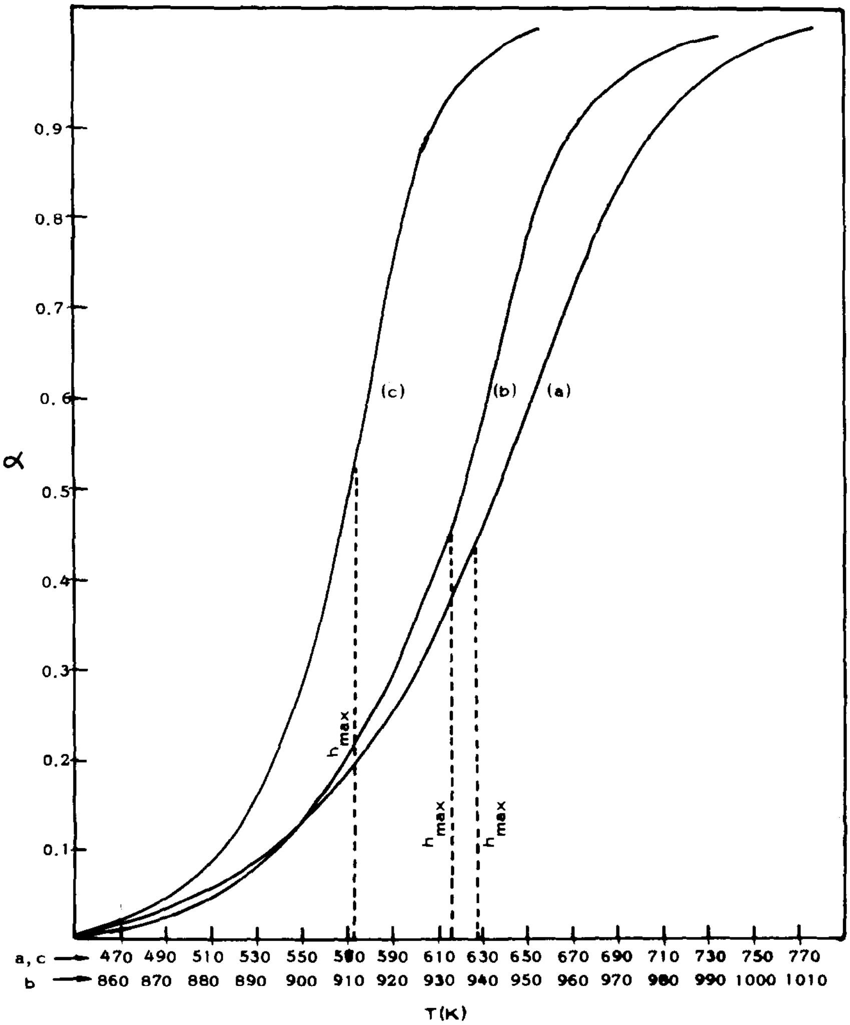

Fig. 1. Series of TG curves constructed for different values of E/RT, by assuming a first order kinetic model.

From Fig. 1, values of α, $h_{\max}$, h_t, t and T were taken and the corresponding values of $\log\{\ln[1/(1-h_t/h_{\max})]/t\}$ were calculated and plotted in Fig. 2 against $1/T$. From the slope of these linear plots the values of the activation energy may be calculated from eqn. (6) and the error yield defined as follows

$$\epsilon = \frac{E_{\text{real}} - E_{\text{cal}}}{E_{\text{real}}} \times 100(\%) \tag{10}$$

these values are shown in Table 1.

The time at which the weight change is observed has been taken as $t_0 = 0$.

Table 1 shows that the error is independent of the value of $x = E/RT$. In summary the above results clearly demonstrate that eqn. (6), developed by Zivkovic and Dobovisek, does not describe properly the kinetics of solid state reactions carried out under non-isothermal conditions.

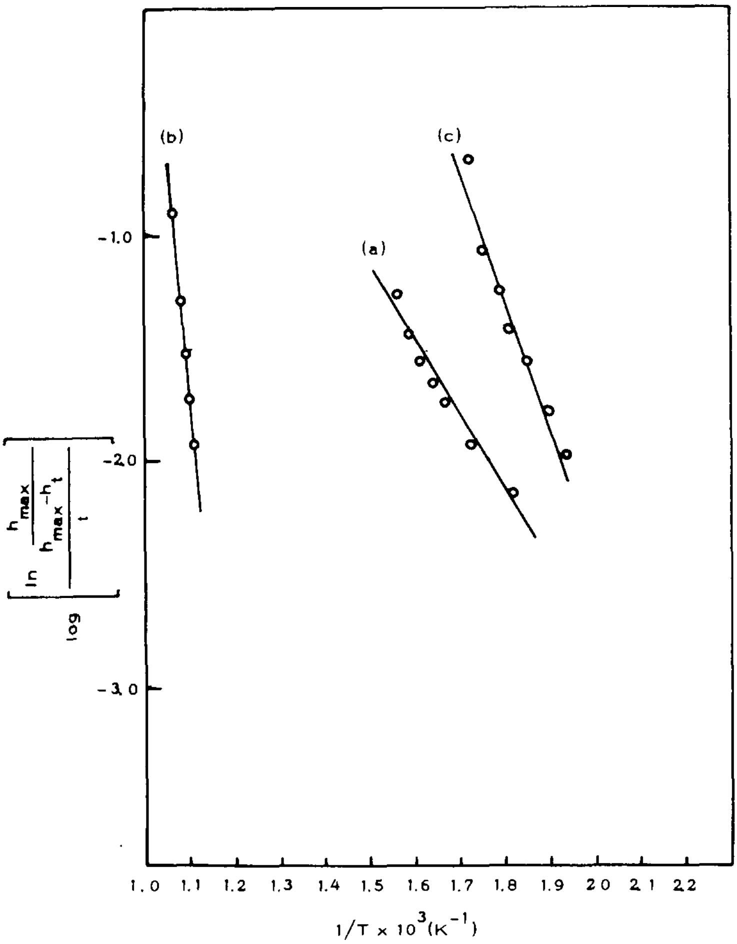

Fig. 2. Plots of data taken from Fig. 1 according to eqn. (6).

TABLE 1

Relative errors in the calculation of the activation energy by the method of Zivkovic and Dobovisek from the experimental data of Fig. 1

E/RT	9	15	40
ϵ(%)	25	30	20

On the other hand, this procedure leads to larger errors in the activation energy than the conventional methods of Coats and Redfern [7], Doyle [8], Gyulai and Greenhow [9], MacCallum and Tanner [10], etc., which do not require complicated calculations in order to evaluate the kinetic parameters.

REFERENCES

1 D. Zivkovic and B. Dobovisek, Thermochim. Acta, 32 (1979) 205.
2 P.K. Chatterjee, J. Polym. Sci., Part A, 3 (1965) 4253.
3 J.H. Sharp and S.A. Wentworth, Anal. Chem., 41 (1969) 2060.
4 J.M. Criado, J. Therm. Anal., 19 (1980) 381.
5 J.M. Criado, Thermochim. Acta, 43 (1981) 111.
6 G.I. Senum and R.T. Yang, J. Therm. Anal., 11 (1979) 445.
7 A.W. Coats and J.P. Redfern, Nature, 208 (1964) 68.
8 C.D. Doyle, J. Appl. Polym. Sci., 6 (1962) 639.
9 G. Gyulai and E. Greenhow, Thermochim. Acta, 6 (1973) 239.
10 J.R. MacCallum and J. Tanner, Eur. Polym. J., 6 (1969) 1033.