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REMARKS ON THE SUITABILITY OF CHATTERJEE'S METHOD FOR THE KINETIC ANALYSIS OF TG TRACES

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It is shown that Chatterjee's method cannot be used at all to determine the value of n in reactions of thermal degradation of solids following n-order kinetics. It has been demonstrated that, if heat and mass transfer effects are avoided, the reaction order obtained from this method will be equal to one whatever the reaction mechanism.

Chatterjee's method [1] has been widely used for the kinetic analysis of TG data. Gupta and Dwarakanath [2] have recently used this method to evaluate the reaction order of the thermal degradation of polystyrene and styrene acrylonitrile copolymer and they have concluded that both reactions follow first-order kinetics.

The scope of the present paper is to analyse whether the above method is an appropriate one for determining the value of the reaction order.

Chatterjee represents the rate of decomposition in the following form:

$$-\frac{dW}{dt} = k \cdot W^n \tag{1}$$

where W is the active weight of the material remaining at time t, n is the reaction order and k is the rate constant.

For the calculation of n by Chatterjee's method, two TG curves from two different initial weights of sample must be recorded, all the other experimental conditions being kept constant. Then, sets of W_1 and W_2 values and the corresponding $(-dW/dt)_1$ and $(-dW/dt)_2$, taken at the same temperature from each diagram, are substituted into the following relationship, derived from Eq. (1):

$$n = \frac{\log(-dW/dt)_1 - \log(-dW/dt)_2}{\log W_1 - \log W_2}. \tag{2}$$

However, we must bear in mind [3, 4] that the rates of thermal decompositions of solids following n-order kinetics must fit the following expression:

$$\frac{d\alpha}{dt} = k_t(1 - \alpha)^n \tag{3}$$

where α is the fraction reacted at time t and k_t is the "true" rate constant of the reaction, given by the Arrhenius law.

Therefore, it is necessary to state the connection between Eqs (1) and (3). If we designate W_∞ as the total weight loss when the reaction is over, we can write:

$$\frac{W}{W_\infty} = 1 - \alpha . \tag{4}$$

After obtaining the first derivative, this becomes:

$$-\frac{\mathrm{d}W}{\mathrm{d}t} = W_\infty \cdot \frac{\mathrm{d}\alpha}{\mathrm{d}t} . \tag{5}$$

By substituting Eqs (4) and (5) into Eq. (1), we obtain:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k \cdot W_\infty^{n-1}(1 - \alpha)^n . \tag{6}$$

From Eqs (3) and (6), we get:

$$k = \frac{k_t}{W_\infty^{n-1}} . \tag{7}$$

Equation (7) means that, unless first-order reactions are concerned, the rate constant of Eq. (1), k, depends not only on the temperature, but also on the sample weight used in the recording of the TG diagrams. Hence, Eq. (5) cannot be used to determine the reaction order.

Moreover, let us consider that the initial sample weights for the two diagrams are in the ratio $W_{i1}/W_{i2} = c$, c being a constant. Accordingly:

$$W_{\infty 1} = c \cdot W_{\infty 2} . \tag{8}$$

If we substitute the values of W_1, W_2 $(-\mathrm{d}W/\mathrm{d}t)_1$ and $(-\mathrm{d}W/\mathrm{d}t)_2$, given by Eqs (4) and (5), into Eq. (2), we get, after considering Eq. (8):

$$n = \frac{\log(\mathrm{d}\alpha/\mathrm{d}t)_1 - \log(\mathrm{d}\alpha/\mathrm{d}t)_2 + \log c}{\log(1-\alpha)_1 - \log(1-\alpha)_2 + \log c} . \tag{9}$$

It must be remembered that, provided that mass and heat transfer effects have been avoided, both α and $(\mathrm{d}\alpha/\mathrm{d}t)$ are quite independent of W_i. Thus, we can conclude that the reaction order obtained from Chatterjee's method will be equal to one whatever the reaction mechanism.

However, if the reaction rate is modified because of mass transfer effects, it is well known [5–7] that an increase in the sample weight gives rise to a movement of the TG curve at higher temperatures, while a broadening of the reaction temperature range takes place. These facts mean that if $W_{i1} > W_{i2}$ (i.e., $c > 1$), the data taken at the same temperature from both TG curves satisfy the relationships:

$$\alpha_1 < \alpha_2;\ (1-\alpha)_1 > (1-\alpha)_2;\ (\mathrm{d}\alpha/\mathrm{d}t)_1 < (\mathrm{d}\alpha/\mathrm{d}t)_2 . \tag{10}$$

Therefore, from Eqs (9) and (10) we can conclude that the higher the influence of the mass transfer phenomenon, the lower the reaction order obtained from Eq. (5). This assertion is in good agreement with the fact that the *n* values determined in [1] for the dehydration of $CaC_2O_4 \cdot H_2O$ and the thermal decomposition of $CaCO_3$, both largely influenced by the mass transport [5, 8], are much lower than 1.

Similar reasoning could be applied with regard to the influence of the heat transfer effect on the value of the reaction order as determined from Eq. (5). In this case *n* would be lower or higher than 1, depending on whether the reaction is endothermic or exothermic.

To summarize, we can conclude from the above considerations that Chatterjee's method cannot be used at all to determine the value of *n* in reactions of thermal degradation of solids following *n*-order kinetics. In turn, this *n* value would be useful as a measurement of the sensitivity of a reaction influenced by heat and/or mass transfer phenomena under the experimental conditions employed.

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