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ABOUT THE KINETIC EQUATION IN THE DTA STUDY OF THE SILICA GEL TO CRISTOBALITE TRANSFORMATION

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The method suggested by Marotta and Buri for performing the kinetic analysis of the silica gel to cristobalite transformation from the DTA trace is criticized. It is shown that this method does not allow determination of the value of the exponent n in the Avrami-Erofeev law. This is in contradiction with the theoretical deduction made by the above authors.

Marotta and Buri [1, 2] recently proposed that the process of nucleation and crystal growth in a glass can be described by the Johnson-Mehl-Avrami (JMA) law written in the form:

$$-\ln(1-\alpha) = (kt)^n. \tag{1}$$

On differentiation with respect to time, this becomes:

$$\frac{d\alpha}{dt} = nk^n t^{n-1}(1-\alpha) \tag{2}$$

where α is the reacted fraction of the crystallized phase at time t, n a constant concerned with the nucleation-and-growth mechanism, and k the constant rate, that depends on the temperature T according to the Arrhenius equation:

$$k = A \cdot \exp(E/RT) \tag{3}$$

E being the activation energy and A the preexponential Arrhenius factor.

They assume [1, 2] that, during a DTA run at a linear heating rate β, the time is proportional to the reciprocal of β:

$$t = C_1 \frac{1}{\beta}. \tag{4}$$

From Eqns (2), (3) and (4), Marotta and Buri [1] have obtained:

$$\frac{d\alpha}{dt} = nC_1^{n-1} \cdot A^n \left(\frac{1}{ß}\right)^{u-1} (1-\alpha)\exp(-nE/RT) =$$

$$= C_2 \left(\frac{1}{\beta}\right)^{n-1} (1-\alpha)\exp(-nE/RT). \tag{5}$$

After rearrangement in logarithmic form, this becomes:

$$\ln\frac{d\alpha}{dt} = -\frac{nE}{RT} + \ln\left[C_2\left(\frac{1}{\beta}\right)^{n-1}(1-\alpha)\right]. \tag{6}$$

By assuming that in a DTA curve the temperature differential ΔT is proportional to the reaction rate:

$$\Delta T = C_3\frac{d\alpha}{dt} \tag{7}$$

they obtain from Eqns (6) and (7):

$$\ln\Delta T = -\frac{nE}{RT} + \ln\left[C_4\left(\frac{1}{\beta}\right)^{u-1}(1-\alpha)\right]. \tag{8}$$

Marotta and Buri [1] consider, in accordance with Piloyan [3], that the change in temperature has a much larger effect on the change of ΔT (or $d\alpha/dt$) compared with the change in α, and they conclude that Eqn. (8) can be approximated as:

$$\ln\Delta T = \ln\frac{E'}{RT} + \text{Const.} \tag{9}$$

where $E' = nE$ and C is a constant which includes the previous ones.

They also consider [2] that the activation energy could be determined from the Kissinger equation:

$$\ln\frac{\beta}{T_m^2} = -\frac{E}{RT_m} + \text{Const.} \tag{10}$$

T_m being the temperature of the peak of the DTA curve.

Plots of the left hand side of Eqns (9) and (10) against $1/T$ would be straight lines whose slopes give E' and E, respectively (2). Therefore, according to these authors [2], the value of n would be determined from the ratio E'/E.

By way of example, they analyse the DTA curves obtained by Das *et al.* [4] for the silica gel → cristobalite transformation and they report that the values of E' and E (as calculated from Eqns (9) and (10) respectively) are $E' = 453$ Kcal/mole and $E = 150$ Kcal/mol. Furthermore, as the ratio E'/E is equal to 3, they conclude [2] that the reaction follows a JMA law with $n = 3$.

The scope of the present paper is to show the meaningless nature of Marotta and Buri's conclusion. This is due to the fact that Eqn. (2) cannot be used to carry out the kinetic analysis of non-isothermal data. For this purpose it is necessary previously to express the reaction rate as a function of α and temperature as shown in a number of papers [5, 6]. In other words, we must write the kinetic law in the form:

$$\frac{d\alpha}{dt} = k\cdot f(\alpha) = A\exp(-E/RT)\cdot f(\alpha) \tag{11}$$

$f(\alpha)$ being a function depending on the reaction mechanism.

The expressions of $f(\alpha)$ corresponding to the kinetic laws more commonly used in the literature to fit DTG and DTA data of solid-state reactions have been given in several references [7–9]. The corresponding one for the JMA mechanism is:

$$f(\alpha) = (1 - \alpha)[-\ln(1 - \alpha)]^{1-\frac{1}{n}}. \tag{12}$$

On the other hand, this could very easily be derived from Eqns (1) and (2).

Thus, from Eqns (11) and (12) we get:

$$\frac{d\alpha}{dt} = A \cdot \exp(-E/RT)(1 - \alpha)[=\ln(1 - \alpha)]^{1-\frac{1}{n}} \tag{13}$$

Introducing Eqn. (7) into Eqn. (13) and rearranging after taking logarithms, we obtain:

$$\ln \Delta T = \frac{-E}{RT} + \ln\frac{A}{C_2} + \ln\Big[(1 - \alpha)[-\ln(1 - \alpha)]\Big]^{1-\frac{1}{n}} \tag{14}$$

If we were to consider, after Piloyan (3), that the change in T is very large compared with the change in $f(\alpha)$, Eqn. (14) would be approximated as:

$$\ln \Delta T = -\frac{E}{RT} + \text{Const.} \tag{15}$$

Therefore, according to Eqn. (15), the plot of $\ln \Delta T$ against $1/T$ would be a straight line whose slope gives the activation energy E, instead $E' = nE$ as Marotta and Buri [2] have concluded.

On the other hand, it is necessary to note that although Kissinger [10] obtained Eqn. (10) for reactions following "n order" kinetics (i.e. $f(\alpha) = (1 - \alpha)^n$, just the same equation would be obtained on starting from the JMA law written in the form of Eqn. (1), as we have shown in a previous work [11].

To summarize, we can conclude that both the plot of $\ln T$ against $1/T$ and the plot of $\ln \beta/T_m^2$ as a function of $1/T_m$ give straight lines whose slope is E/R. Therefore, it is a meaningless exercise to try to calculate the exponent n from the ratio of the slopes of these plots as Marotta and Buri [2] suggest.

The huge difference between the activation energies derived by the Piloyan and Kissinger methods from DTA traces of the silica gel → cristobalite transformation would perhaps be due to errors involved in these procedures of kinetic analysis. For instance, it has been pointed out [12–13] that the Kissinger method cannot be used to analyse DTA traces because the maximum reaction rate is not reached at the peak of the curve, as was assumed in the development of this procedure.

With reagard to the Piloyan method, a study about its accuracy is now in progress in our laboratory and will be the subject of a further paper.

References

1. A. Marotta and A. Buri, Thermochim. Acta, 25 (1978) 155.
2. A. Marotta and A. Buri, J. Thermal Anal., 16 (1979) 449.
3. G. O. Piloyan, I. D. Ryabchikov and O. S. Novikova, Nature, 212 (1966) 1229.
4. S. K. Das, S. K. Mookerjee, S. K. Niyogi and R. L. Thakur, J. Thermal Anal., 9 (1976) 43.
5. J. H. Sharp and S. Wentworth, Anal. Chem., 41 (1969) 2060.
6. J. Zsakó, J. Thermal Anal., 5 (1973) 239.
7. D. Dollimore, G. R. Heal and B. P. Krupay, Thermochim. Acta, 24 (1978) 293.
8. K. Heide, W. Holand, H. Golker, K. Seyfarth, B. Müller and R. Sauer, Thermochim. Acta, 13 (1975) 365.
9. J. M. Criado, J. Morales and V. Rives, J. Thermal Anal., 14 (1978) 221.
10. H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
11. J. M. Criado, F. Gonzalez and J. Morales, Ann. Quim., 70 (1974) 787.
12. R. L. Reed, L. Weber and B. S. Gottfried, Ind. Eng. Chem. Fundamentals, 4 (1965) 38.
13. J. H. Sharp, Differential Thermal Analysis (R. C. Mackenzie, Ed.), Academic Press, London, 1970, Vol. 2, p. 55.