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Note

REMARKS ON THE CRYSTALLIZATION KINETICS IN THE NON-ISOTHERMAL DEVITRIFICATION OF GLASSES

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In a recent paper Marotta et al. [1] carried out the kinetic analysis of the devitrification of samples of $Li_2O \cdot 2\,SiO_2$ glass from DTA traces after considering that the reaction fits an Avrami—Erofeev law written in the form

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

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

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

where E is the activation energy and A is the pre-exponential factor of Arrhenius.

They evaluated [1] the activation energy from a simplified Kissinger's equation

$$\ln\beta = -\frac{E}{R} \times \frac{1}{T_p} + \text{const.} \tag{3}$$

where β is the heating rate, and T_p is the temperature of the DTA peak. Hence, the plot of $\ln\beta$ vs. $1/T$ yields a straight line, the slope of which is proportional to the activation energy.

On the other hand, in order to determine n, Marotta et al. [1] used the equation which they derived in a previous paper [2] by assuming that the time is proportional to $1/\beta$ (i.e., $t = C_1 \times 1/\beta$) and by considering, according to Piloyan et al. [3], that the change in temperature has a much larger effect on the change of the differential temperature, ΔT, compared with the change in α

$$\ln\Delta T = -\frac{nE}{RT} + \text{const.} \tag{4}$$

Therefore, in agreement with Marotta et al. [1] the slope of the straight line obtained by plotting $\ln\Delta T$ vs. $1/T$ yields the value of nE. Moreover, these authors have calculated the values of n from the ratio of the slopes of the straight lines yielded by eqns. (4) and (3), respectively.

However, the above method has been criticized in a previous paper [4] which shows that in order to introduce Piloyan's simplification, the reaction rate must be expressed in the form

$$\frac{d\alpha}{dt} = A\ \exp(-E/RT)\ f(\alpha) \tag{5}$$

where f(α) is a function depending on the reaction mechanism. Thus, in the case of an Avrami—Erofeev mechanism it would be derived from eqns. (1) and (2)

$$\frac{d\alpha}{dt} = A\ \exp(-E/RT)(1-\alpha)[-\ln(1-\alpha)]^{1-1/n} \tag{6}$$

Moreover, bearing in mind that $\Delta T = C_2(d\alpha/dt)$, eqn. (6) becomes

$$\ln \Delta T = -\frac{E}{RT} + \ln\frac{A}{C_2} + \ln[(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}] \tag{7}$$

or

$$\ln\frac{\Delta T}{(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}} = -\frac{E}{RT} + \ln\frac{A}{C_2} \tag{8}$$

If we consider, after Piloyan [3], that the change ΔT is very large compared with the change in f(α), eqn. (6) may be approximated as

$$\ln \Delta T = -\frac{E}{RT} + \text{const.} \tag{9}$$

Hence, the plot of ln ΔT vs. $1/T$ gives a straight line, the slope of which yields the activation energy E instead of nE, as suggested by Marotta and Buri [2].

We conclude, therefore, that the huge difference between the slopes of the straight lines obtained from the plots of DTA data of crystallization of samples of $Li_2O \cdot 2\,SiO_2$ glass by means of eqns. (3) and (9), respectively, is perhaps due to errors involved in the method of calculation used by these authors [1].

In order to prove the above assertion we have analyzed some of the DTA traces included in ref. (1) from eqn. (8) that overcome the simplification introduced by Piloyan's method. The values of α were determined [5] from the expression

$$\alpha = \frac{a_T}{A} \tag{10}$$

where

$$a_T = \int_0^T \Delta T\, dT\,; \qquad A = \int_{T_0}^{T_\infty} \Delta T\, dT$$

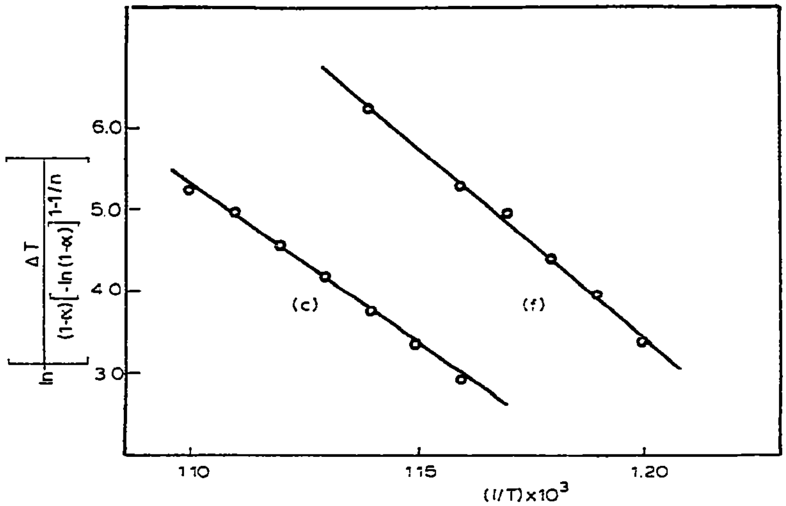

Fig. 1. Plots of DTA data for the crystallization of as-quenched samples of $Li_2O \cdot 2\ SiO_2$ glass (ref. 1) according to eqn. (11), after assuming the same values of n reported by Marotta et al. [1]. c, Coarse powder ($n = 1$); f, fine powder ($n = 1.2$).

Substitution of eqn. (10) into eqn. (8) gives

$$\ln \frac{\Delta T}{\left(1 - \frac{a_T}{A}\right)\left[-\ln\left(1 - \frac{a_T}{A}\right)\right]^{1-1/n}} = \frac{-E}{RT} + \text{const.} \tag{11}$$

Values of the left-hand side of eqn. (11) such are plotted against $1/T$ in Fig. 1 were calculated from the DTA traces of the crystallization of fine and coarse powders of $Li_2O \cdot 2\ SiO_2$ [1]. The activation energies calculated from the slopes of these plots are included in Table 1 together with n and E values reported in ref. 1.

The huge difference between the kinetic parameters calculated from eqn. (11) and those reported by Marotta et al. [1] seems to show the important errors involved in the method of kinetic analysis suggested by Marotta et al. [1], in agreement with our previous statement.

TABLE 1

Kinetic parameters of the crystallization process of as-quenched samples of $Li_2O \cdot 2\ SiO_2$ glass from DTA traces of ref. 1

Sample	n	E (kcal mole^{-1}) Ref. 1	This work
Fine powder	1.2	70	102
Coarse powder	1.0	61	78

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