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KINETICS OF DEVITRIFICATION AND DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

A quantitative relationship between kinetic parameters and DTA curves has been derived for devitrification reactions which are described by a Johnson–Mehl–Avrami equation.

Both activation energy, *E*, and reaction order, *n*, can be derived from DTA curves and related to the probable reaction mechanism.

Experimental results and isothermal literature data are consistent.

INTRODUCTION

The usual method of obtaining kinetic data involves a series of experiments carried out under isothermal conditions at different temperatures. This process is laborious and considerable interest exists in the study of reaction kinetics by a dynamic method such as differential thermal analysis (DTA).

Since the classic works of Murray and White on clay dehydration kinetics[1–3], DTA has been used by several workers[4–14] to characterize complex chemical reactions. These investigations meet with the following difficulties:

(a) A previous knowledge of reaction order is required[9].

(b) The numerical integration of DTA data carried out by a computer[12], needs a laborious device.

(c) The range of reaction temperatures is restricted by the use of a differential scanning calorimeter (DSC)[10].

The aim of this work is to show a simple method of evaluation of both kinetic parameters, activation energy and reaction order in devitrification process from DTA curves.

To test the proposed equations the crystallization kinetics of $Li_2O \cdot 2SiO_2$ glass was chosen.

EXPERIMENTAL

Samples of glass with $Li_2O \cdot 2SiO_2$ composition were prepared by melting pure reagents at 1400°C in a Pt crucible in an electric oven and casting them in Fe molds at high cooling rates.

Differential thermal analysis (DTA) at heating rates of 1, 2, 5, 10, 20 and 50°C $\min^{-1}$ in air of 85 mg powdered glass were carried out; the particles were $-170 +230$ mesh and the reference material was Al_2O_3. A Netzsch differential thermal analyzer, Model 404M, was used.

THEORETICAL CONSIDERATIONS AND RESULTS

The process of nucleation and crystal growth in a glass can be formally described by a Johnson–Mehl–Avrami (JMA) equation[15–17]

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

where y is the volume fraction of crystallised phase at time t, n the reaction order and k depends on temperature according to an Arrhenius type equation

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where the temperature coefficient E represents the overall kinetic barrier to nucleation and crystallization.

The most probable mechanisms of crystallization and related n values are reported in Table 1.

TABLE 1

Reaction mechanism		n
Crystal growth controlled by interfacie	Constant nucleation rate	4
	Fixed number of nuclei	3
Crystal growth controlled by diffusion	Constant nucleation rate	5/2
	Fixed number of nuclei	3/2

The method proposed to calculate the activation energy E and the reaction order n from DTA curves is based on two assumptions:

(a) In a DTA curve the temperature differential ΔT at any given instant can be approximated as being proportional to the instantaneous reaction rate[6–7]

$$\Delta T = C_1\frac{dy}{dt} \tag{3}$$

(b) During a DTA run the time of heating t at each temperature can be taken to be proportional to the reciprocal of the heating rate h, if the latter is linear[9]

$$t = C_2\frac{1}{h} \tag{4}$$

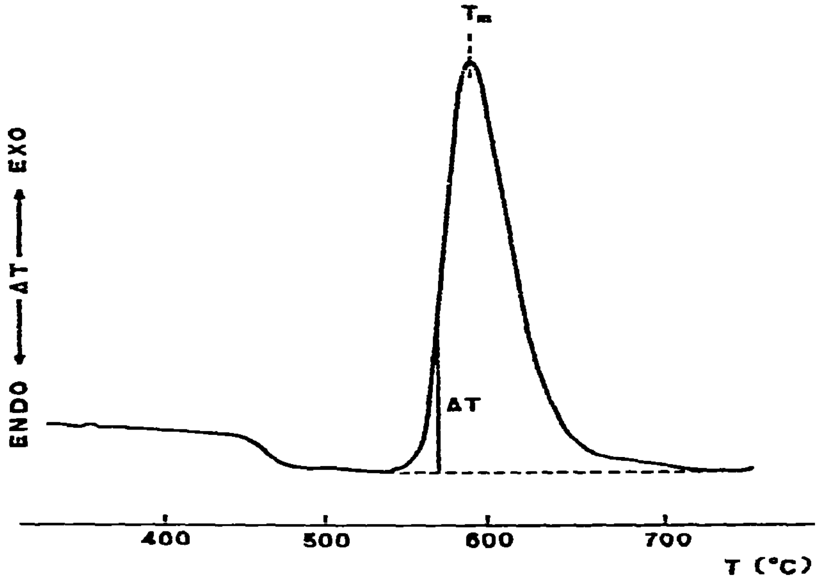

Fig. 1. Crystallization peak of $Li_2O.2SiO_2$ glass detected by DTA.

Setting the time derivative of eqn. (1)

$$\frac{dy}{dt} = C_3 k^n \left(\frac{1}{h}\right)^{n-1} (1 - y) = C_4 \left(\frac{1}{h}\right)^{n-1} (1 - y) \exp\left(-\frac{nE}{RT}\right) \tag{5}$$

into eqn. (3) and taking logarithms, the following equation can be obtained

$$\ln \Delta T = -\frac{nE}{RT} + \ln \left[C_5 \left(\frac{1}{h}\right)^{n-1} (1 - y)\right] \tag{6}$$

As in the initial part of the crystallization peak in a DTA curve (Fig. 1), recorded at any usual but constant heating rate (10–40°C min^{-1}), the change in temperature has a much larger effect on the change in ΔT compared with the change in y[11]; the eqn. (6) can be approximated as

$$\log \Delta T = -\frac{E'}{4.57} \frac{1}{T_i} + C \tag{7}$$

where $E' = nE$ and C is a constant which includes all the constants C_1, C_2 ... C_5 of previous equations.

A plot of log ΔT against $1/T$ gave a straight line as shown in Fig. 2; from its slope a value of 114 Kcal mol^{-1} was calculated for E'.

Equation (7) is unable to distinguish the reaction order n from the activation energy E but the latter can be evaluated if several DTA curves are recorded at different heating rates.

The peak temperature (T_m) of a DTA curve (Fig. 1), is obtained by simply setting

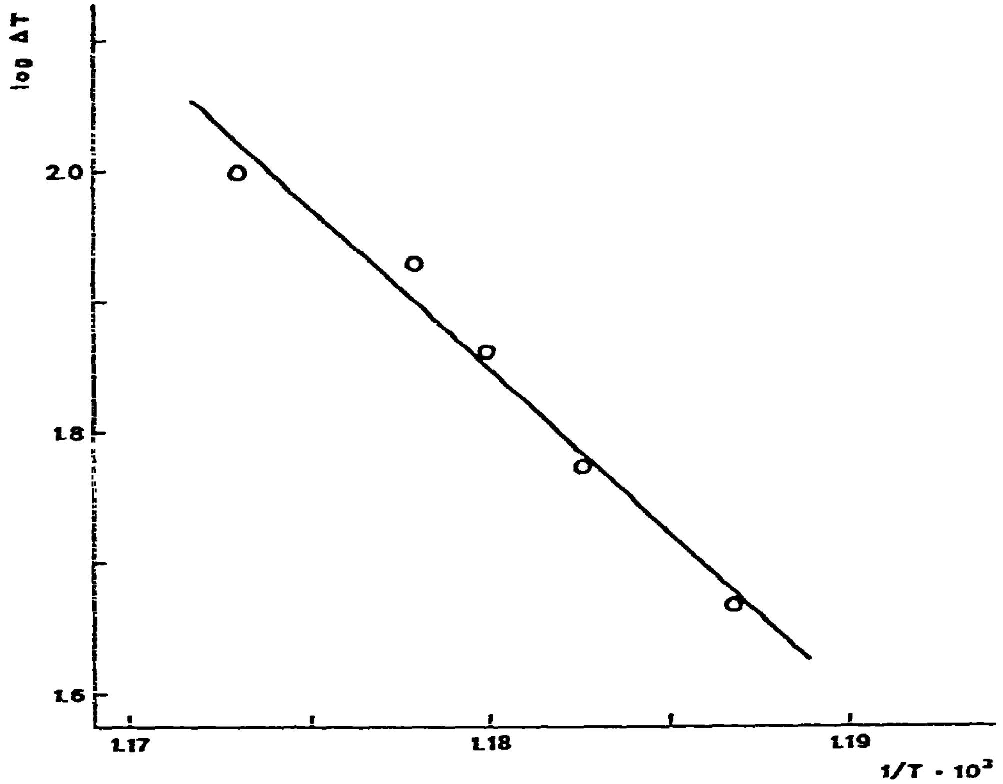

Fig. 2. Plot of log ΔT vs $1/T$ (the values of ΔT and T are derived from a DTA curve recorded at 20°C min^{-1}).

$$\frac{d\Delta T}{dT} = \frac{d}{dT}\left(\frac{dy}{dt}\right) = 0 \tag{8}$$

and solving for T_m. This leads to the following relationship between the exothermic peak temperature T_m and the heating rate h[9]

$$\log h = -\frac{E}{4.57}\frac{1}{T_m} + C' \tag{9}$$

where C' is a constant.

The activation energy $E = 67$ Kcal mol^{-1} was calculated from the slope of the straight line obtained by plotting log h against $1/T_m$ as shown in Fig. 3.

The kinetic parameters thus obtained are in good agreement with those reported in the literature ($E = 60$–120 Kcal mol^{-1}; $n = 1$–2), obtained under isothermal conditions[18].

The value of 1.7 for the exponential factor n suggests a crystal growth controlled by diffusion from a fixed number of nuclei, as reported in Table 1.

This mechanism is consistent with the heating process in a DTA apparatus. In fact, as reported by Hench et al.[9], in a $Li_2O \cdot 2SiO_2$ glass reheated at 480°C, metastable metasilicate ($Li_2O \cdot SiO_2$) particles precipitate because of its structural

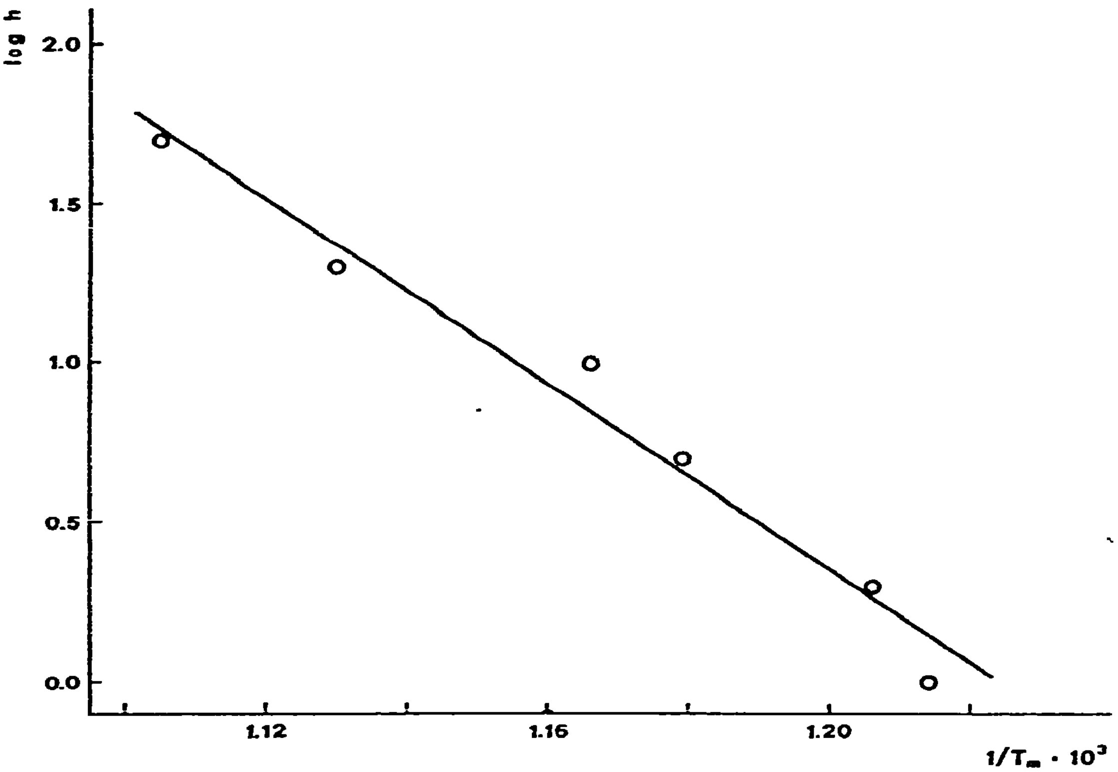

Fig. 3. Plot of log *h* vs 1/*T* (the values of T_m are read on DTA curves recorded at different heating rates *h*).

simplicity relative to the glass structure. At higher temperatures, reaction of metasilicate with the SiO_2-rich matrix, governed by Li^+ ion diffusion, produces the structurally more complex and thermodynamically stable disilicate crystals. In a DTA run the $Li_2O \cdot 2SiO_2$ glass passes through the temperature of high nucleation rate (precipitation of metastable metasilicate nuclei) and then crystallizes at a higher temperature where the formation of new nuclei is very unlikely.

Moreover the value of 67 Kcal mol^{-1} corresponds to the activation energy of crystal growth in a nucleated $Li_2O \cdot 2SiO_2$ glass[20].

CONCLUSIONS

The good agreement between the experimental results and the isothermal data confirms the validity of the described procedure.

The DTA method proposed has many advantages over the isothermal one:

(1). A temperature range can be continuously and quickly studied.

(2). Only a small amount of sample is required.

(3). Both activation energy and reaction order can be easily calculated.

(4). From these kinetic parameters a mechanism of reaction can be derived.

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