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Note

THE POSSIBILITY OF DETERMINING THE AVRAMI–EROFEEV INDEX FROM NON-ISOTHERMAL MEASUREMENTS

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Recently, a controversy has arisen concerning the possibility of determining the index n of the well known Avrami–Erofeev equation

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

from non-isothermal DSC or DTA data. Here, α is the fraction transformed in time t and K is the rate constant, which is usually assumed to be of the Arrhenius type

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

where A is a pre-exponential factor, E is the activation energy and the other parameters have their usual meanings. This equation is found to apply in a wide range of solid–solid transformations such as the crystallization of glasses.

Marotta et al. [1,2] claimed that a Piloyan plot [3], i.e. a plot of $\ln(\mathrm{d}\alpha/\mathrm{d}T)$ vs. $1/T$ for the initial part of a DTA curve obtained at a constant heating rate β, should have a slope of n times the activation energy E, so that if the latter is known, the Avrami index n can be easily determined. This statement has been criticized by one of the authors, who showed the errors contained in the mathematical derivation [4,5]. As a conclusion, he proposes that the differences in activation energies obtained from a Piloyan plot and other methods such as the Kissinger [6] or Ozawa plots [7] or isothermal measure-

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ments may be due to experimental errors and the Avrami index cannot be determined in this way.

On the other hand, some of the authors have shown, in a recent paper [8] by means of a numerical analysis of the Avrami–Erofeev transformation during heating at a constant rate, that a Piloyan plot for values of α lower than 0.2 actually gives n times the activation energy for the rate constant in eqn. (2). The possibility of an analytical derivation was also suggested. Moreover, several experimental determinations of n have been carried out by this procedure [9,10] and the values obtained are in very close agreement with the isothermal values, which seems to support the above conclusion.

In this note, we wish to discuss this statement as analytically as possible and give some experimental confirmation of it.

The Avrami–Erofeev equation under heating at a constant rate β becomes [8,11]

$$-\ln(1-\alpha)=\left[1/R\int_0^T K(T)\,\mathrm{d}T\right]^n \tag{3}$$

and its derivative

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{nK}{\beta}(1-\alpha)\left(\ln\frac{1}{1-\alpha}\right)^{(n-1)/n} \tag{4}$$

By taking logarithms of both sides and approximating the integral by [11]

$$\int_0^T \exp(-E/RT)\,\mathrm{d}T=(RT^2/E)(1-2RT/E)\exp(-E/RT) \tag{5}$$

which is valid for $E/\mathrm{RT}\geqslant 20$, one obtains

$$\begin{aligned}\ln(\mathrm{d}\alpha/\mathrm{d}T)&=-nE/RT+\ln n(A/\beta)^n+\ln(1-\alpha)\\&\quad+(n-1)\ln\left[(RT^2/E)-(2R^2T^3/E^2)\right]\end{aligned} \tag{6}$$

so that, if the variation of both $\ln(1-\alpha)$ and $\ln[(RT^2/E)-(2R^2T^3/E^2)]$ can be disregarded compared with the variation of nE/RT, the slope of a plot of $\ln(\mathrm{d}\alpha/\mathrm{d}T)$ vs. $1/T$ will give n times the activation energy, the remaining term in eqn. (6) being constant. This assumption restricts us to the initial part of the DTA or DSC curves where $(1-\alpha)$ has a slight variation as Piloyan suggested. This condition is fulfilled when $\alpha\leqslant 0.15$, but good correlation factors are obtained up to $\alpha\simeq 0.4$, although, in such cases, the values of n obtained are about 10% lower than the initial values. This procedure is widely used in other techniques as Thermally Stimulated Depolarization Currents (TSDC), where $n=1$ kinetics applies, in order to obtain the activation energy for the process [12].

In the most general case, however, $n\neq 1$ and the last term in eqn. (6) does not vanish, so that the approximation is only valid if E/RT is high, as assumed in the expression (5) for the integral. Then the errors involved are about, or lower than, 2%. This condition is not a very restrictive one for the activation energy is usually high compared with the temperature of the DTA or DSC peak in most cases, in particular for the crystallization of glasses ($E = 2$–4 eV).

Similar results can be obtained using other approximations in eqn. (3). Bearing in mind the Doyle approximation [13] for the logarithmic form of the integral of the Arrhenius equation

$$\int_0^T \exp(-E/RT)\,\mathrm{d}T = \frac{E}{R}\mathrm{P}(E/RT)$$

with

$$\ln \mathrm{P}(E/RT) = -5.34 - 1.05(E/RT)$$

which is valid for $E/RT > 15$, one obtains

$$\ln(\mathrm{d}\alpha/\mathrm{d}T) = \ln\left[n(A/\beta)^n(E/R)^{n-1}\right] + 5.34(1-n) + \ln(1-\alpha) - (1.05n\text{-}0.05)E/RT \qquad (7)$$

This can be written in the form

$$\ln(\mathrm{d}\alpha/\mathrm{d}T) = \text{constant } - E_a/RT$$

with $E_a \simeq nE$ in the range of α mentioned above.

It is noteworthy that a straight line could also be obtained from the Piloyan plots at different α ranges. For instance, it can be demostrated that for α in the range $0.2 < \alpha \leqslant 0.5$, eqns. (6) or (7) lead to an apparent activation energy, E_a, of $\simeq 0.6nE$.

In order to check the validity of the above considerations, we have constructed from eqns. (3) and (4) the $\mathrm{d}\alpha/\mathrm{d}T$ vs. $1/T$ curve by assuming an Avrami–Erofeev index, n, of 2 and the kinetic parameters $E = 25$ kcal mole^{-1}, $A = 10^8$ min^{-1} and $\beta = 10$ K min^{-1}. The Arrhenius equation has been integrated by means of the 4th degree rational approximation proposed by Senung and Yang [14], which involves an error of less than 10^{-3}%.

The kinetic analysis of this theoretical curve has been carried out using the Piloyan method. The apparent activation energies calculated from the plots

TABLE 1

Values of the activation energy calculated for the theoretical example given in the text by means of the Piloyan plots in different α ranges. A comparison of the E_a/E ratios ($E = 25$ kcal mole^{-1}) with the theoretical approximated values $(E_a/E)_t$.

α range	E_a (kcal mole^{-1})	Regression coefficient	E_a/E	$(E_a/E)_t$
0 –0.2	49.3	−0.9996	1.972	$n=2$
0 –0.5	43.8	−0.9947	1.750	$n=2$
0.2–0.5	29.7	−0.9921	1.188	$0.6n=1.2$

of ln $(d\alpha/dT)$ vs. $1/T$ in the ranges $0 < \alpha < 0.2$, $0 < \alpha < 0.5$ and $0.2 < \alpha < 0.5$, respectively, are included in Table 1, together with the ratio between these values and the actual value of 25 kcal $mole^{-1}$. We can see that the results obtained are in very good agreement with those expected from eqns. (6) and (7).

We can conclude from the above results that in order to obtain reliable data of the n index from the ratio between the apparent activation energy obtained from the Piloyan plot and that derived from the Ozawa or the Kissinger methods, it is necessary to make a careful selection of the range in which the corresponding values of $\ln(d\alpha/dT)$ will be taken and plotted against $1/T$.

With the aim of checking the above assertion, we present here, as an example, the application of the Piloyan method to the determination of the n index of the second crystallization step of $Al_{23}Te_{77}$ glasses. It was stated in a previous work [15], from both isothermal methods and computer fitting of the whole DSC curve, that this process follows an Avrami–Erofeev mechanism with $n = 4$ and an activation energy $E = 67$ kcal $mole^{-1}$. The values of $d\alpha/dT$ taken from the DSC curve included in ref. 15 are plotted in Fig. 1 as a function of $1/T$. An activation energy $E_a = 261$ kcal $mole^{-1}$ has been calculated from the slope of this plot, which leads to an index $n = E_a/E = 3.9$, in very good agreement with the value previously reported for the same sample [15].

In summary, we conclude that the Avrami–Erofeev index can be easily

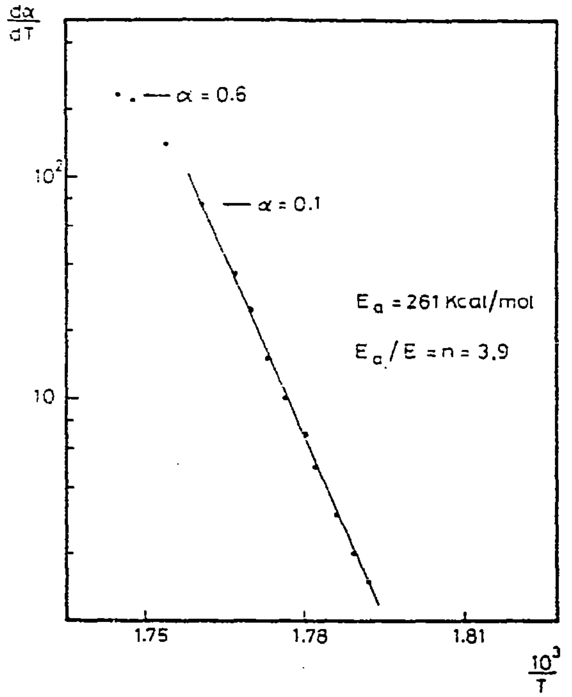

Fig. 1. Piloyan plot of the second DSC peak of the crystallization of $Al_{23}Te_{77}$ glasses.

obtained from a Piloyan plot if the activation energy is known. This result was derived by Marotta et al. [1,2] in a rather irregular way. Their procedure can only be legitimized by an explicit statement of the negligible variation of the "equivalent isothermal time" t^* appearing in their expression

$$d\alpha/dt = K''t^{*n-1}(1-\alpha)$$

in the temperature range of application. Such a statement, however, must be justified by a rigorous anaiysis as done in this work.

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