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Note

THEORETICAL CONSIDERATIONS CONCERNING AVRAMI TRANSFORMATIONS UNDER NON-ISOTHERMAL CONDITIONS

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In recent years, increasing interest has been shown in non-isothermal phase transformations in solids [1—3]. In the particular case of crystallization of amorphous materials, such as polymers or inorganic glasses, Avrami rate equations have been shown to be adequate [4—6]. As shown in ref. 6, starting from the Avrami equation

$$\xi = 1 - \exp[-(kt)^n]$$

the expressions giving the fraction of transformed material, ξ, and its derivative in non-isothermal conditions are

$$\xi = 1 - \exp\left[-\left(\frac{1}{R}\int_0^T K(T)\mathrm{d}T\right)^n\right] \tag{1}$$

and

$$\mathrm{d}\xi/\mathrm{d}T = [K(T)/R](1-\xi)\{\ln(1/(1-\xi))\}^{(n-1)/n} \tag{2}$$

R being the heating rate, and n the Avrami index. The rate constant $K(T)$, is usually found to be of the Arrhenius type

$$K(T) = \nu_0 \exp\{-E/K_B T\}$$

where E is an apparent activation energy for the process and ν_0 is a pre-exponential factor having the dimensions of time^{-1}.

Experiments are commonly performed by DSC or DTA techniques, giving $\mathrm{d}\xi/\mathrm{d}T$ directly, and a number of approximate methods are used in order to obtain the kinetic parameters E, ν_0 and n. However, there has been a lack of systematic analysis of the influence of these parameters on the transformation rate curves. Such results would be useful in order to estimate the errors involved in the approximations, which have been used in some cases without special care.

The aim of this note is to provide a quick method, based upon such an analysis, for obtaining kinetic parameters from experimental data.

Values of $\mathrm{d}\xi/\mathrm{d}T$ have been calculated by means of an HP 2000 computer for different sets of E, ν_0/R, and n, in the temperature range 0—500°C. The

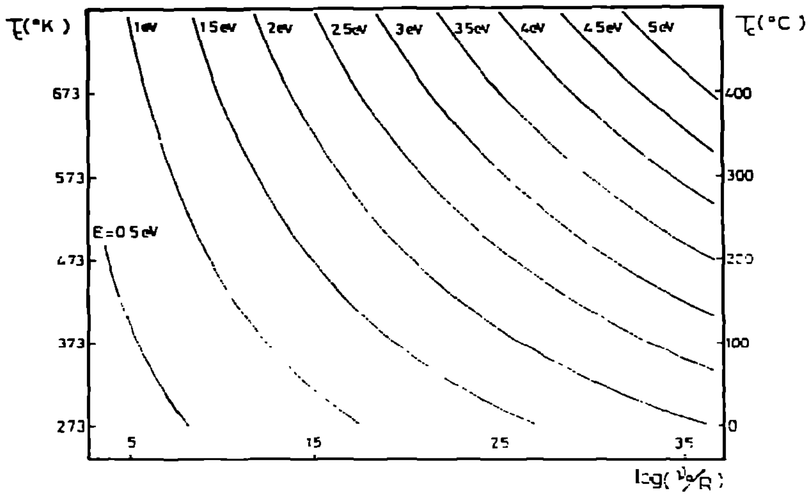

Fig. 1. T_c versus log ν_0/R for some characteristic values of activation energy E.

curves obtained show the following properties:

(a) The temperature, T_c, at which $d\xi/dT$ is a maximum, does not depend on the value of the Avrami index n, but only on E and ν_0/R. This dependence is shown in Fig. 1.

(b) For a given value of T_c, there is a linear relationship between E and $\log(\nu_0/R)$, which can be approximately written as

$$\log(\nu_0/R) \simeq 5.15(10^3 \times E/T_c) - 1.56 \tag{3}$$

(c) The value of ξ at T_c (ξ_c) remains constant irrespective of the values of E, ν_0/R and n, and is approximately equal to 0.62.

(d) The shape of the rate curves can be adequately characterized by the value of $d\xi/dT$ at T_c. This parameter varies with E, ν_0/R and n. However, for constant values of E and ν_0/R, $(d\xi/dT)_{T_c}$ is a linear function of n, as can be deduced from eqn. (2) at $T = T_c$. According to point (c) above, $\{\ln[1/(1-\xi_c)]\}^{(n-1)/n}$ is almost equal to one, irrespective of the value of n, with the result that

$$(d\xi/dT)_{T_c} = nA(E, \nu_0/R) \tag{4}$$

This approximation is also supported by direct computation, and the values of the proportionality factor A, are plotted in Fig. 2.

(e) The Kissinger formula [7]

$$\ln(T_c^2/R) - E/K_BT = \text{constant}$$

can be obtained with some approximations [5,6] from eqns. (1) and (2). The validity of this expression is confirmed, by direct calculation, to within ±2%.

(f) Equation (2) can be written as

$$\ln(d\xi/dT) = -E/K_BT + \ln(\nu_0/R) + \ln g(\xi)$$

$g(\xi)$ being the last term of eqn. (2). It has been assumed [8] that the temperature variation of ln $g(\xi)$ can be disregarded for low values of ξ. In this

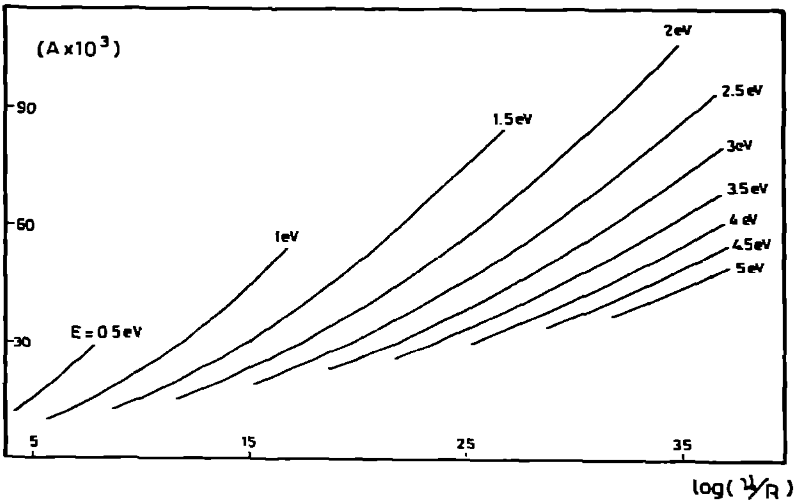

Fig. 2. A [eqn. (4)] as a function of log ν_0/R. Values of E are given on the curves.

assumption, the slope of a plot of ln(dξ/dT) versus $1/T$ should give the activation energy for the process, as first suggested by Piloyan [9]. However, a numerical analysis (Fig. 3), shows that the value actually obtained is $n \times E$, so that the Piloyan method is valid only for $n = 1$. This result can also be

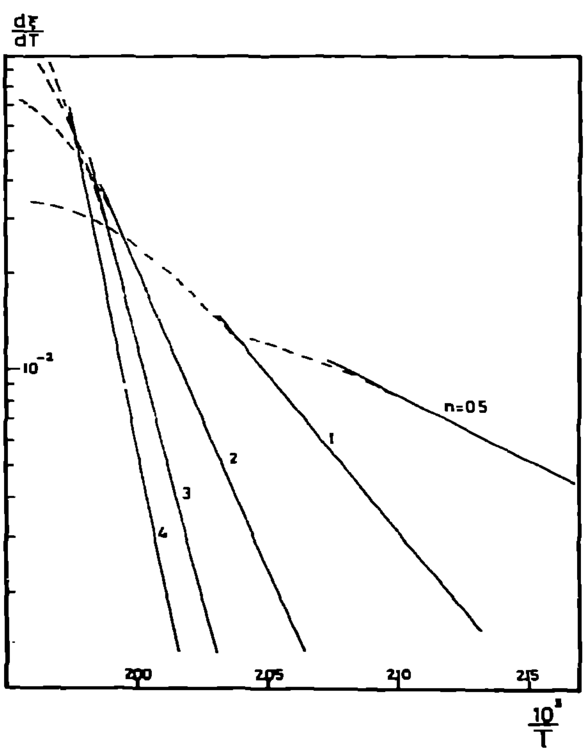

Fig. 3. Plot of ln(dξ/dT) versus $1/T$, for E = 2 eV, $\nu_0/R = 5 \times 10^{18}$, and different values of n. If $\xi < 0.2$, the curves appear to be straight lines, the slope being proportional to n, as observed.

analytically derived, but the derivation would require lengthy further discussion.

The data contained in Figs. 1 and 2 provide a quick method for obtaining kinetic parameters from experimental curves of $(d\xi/dT)$. For this method, the activation energy, E, must be previously known. The aforementioned Kissinger method is valuable for this task. E can also be obtained from a plot of $\ln\{R(d\xi/dT)_{T_c}\}$ versus $1/T_c$ for different scan rates, as can be easily derived from eqn. (2).

Now, ν_0 can be read in Fig. 1 from the experimental value of T_c at a given scan rate R, or approximately calculated using eqn. (3). Figure 2 gives the value of A corresponding to E and ν_0/R. The Avrami index, n, is then obtained from the experimental value of $(d\xi/dT)_{T_c}$ by means of expression (4). This value of n can also be obtained by using Piloyan's method if the value of E is already known, although this latter method requires great precision in the measurement of experimental DSC or DTA curves.

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