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ON THE KINETIC ANALYSIS OF THERMOANALYTICAL DIAGRAMS OBTAINED WITH THE "QUASI-ISOTHERMAL" HEATING TECHNIQUE

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ABSTRACT

A comparative study of "*n*-order", Avrami–Erofeev and diffusion-controlled reactions has been carried out using thermoanalytical data, calculated by assuming a "quasi-isothermal" heating technique. The results reported support the hypothesis that a single diagram obtained with this technique allows the discernment of Avrami–Erofeev, "*n*-order" and diffusion-controlled reactions. This does not occur when a linear heating program is used, as was reported in previous papers. In addition, it is shown that a single thermoanalytical curve obtained with a "quasi-isothermal" heating program does not permit the determination of the actual value of *n* of those reactions following "*n*-order" kinetics. On the other hand, it is proved that the kinetic analysis of two thermoanalytical curves obtained with a linear heating program and a "quasi-isothermal" heating technique, respectively, would provide an excellent procedure for discerning the proper mechanism of solid-state reactions.

INTRODUCTION

The kinetic analysis of TG data obtained under a linear heating program has been largely performed in literature[1] by means of the Coats and Redfern equation[2]

$$\ln g(\alpha) - 2\ln T = \ln \frac{AR}{E\beta} - \frac{E}{RT} \tag{1a}$$

where $g(\alpha)$ is a function depending on the reaction mechanism; β is the heating rate and the other parameters have their usual meanings.

When the reaction kinetics are interpreted in terms of an Avrami–Erofeev mechanism, eqn. (1a) becomes

$$\ln \frac{1}{1-\alpha} - 2m \ln T = m \ln \frac{mRA^{1/m}}{E\beta} - \frac{E}{RT} \tag{1b}$$

where m is a constant related to the growth nuclei. The most usual values of m are

2 and 3 (A_2^* and A_3^*).

The plot of the left-hand side of eqn. (1a) or (1b) against $1/T$ would be a straight line, whose slope gives the activation energy of the process.

In previous papers[3, 4], we have shown that ln g(α) functions of Prout and Tompkins and Avrami–Erofeev (A_2, A_3) mechanisms are linearly correlated with ln g(α) of a first-order reaction (F_1). In a similar way, it has been proved[5] that the logarithmic forms of the functions g(α) of the one-dimensional (D_1) and two-dimensional (D_2) diffusion mechanisms are linearly correlated with those corresponding to the zero-order (R_1) and 1/2-order (R_2) kinetics, respectively. Linear correlations between the logarithmic forms of the kinetic functions of reactions following 2/3-order kinetics (R_3) and those corresponding to the three-dimensional diffusion mechanisms of Jander (D_3) and Ginstling-Brounshtein (D_4), respectively, have also been reported[5].

The above considerations show that a single TG diagram obtained under a linear heating program does not allow the determination of whether a solid decomposition reaction is of "*n* order" or follows the Prout and Tompkins, the Avrami–Erofeev or a diffusion mechanism.

The scope of the present paper is, firstly, to compare the equations developed for the kinetic analysis of TG diagrams obtained with the "quasi-isothermal" heating technique in order to test if they permit the discernment of the above mechanisms. Secondly, we try to verify the conclusions obtained by analyzing theoretical thermoanalytical curves calculated for assumed kinetic parameters and a particular reaction mechanism, after considering both a linear heating program and a "quasi-isothermal" heating technique, respectively.

THEORETICAL

The "quasi-isothermal" heating technique was first developed by J. and F. Paulik. This method programs the reaction temperature in such a way that the decomposition rate of the sample is kept constant at a particular value arbitrarily selected. Rouquerol[7] has described the kinetic analysis of TG curves of "*n*-order" reactions obtained by this procedure.

The general expression of the reaction rate of a heterogeneous reaction is

$$\frac{d\alpha}{dt} = A\,e^{-E/RT}\,f(\alpha) \qquad (2)$$

where f(α) is a function depending on the reaction mechanism and, as is well known, connected with the function g(α) of eqn. (1) through the expression

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \qquad (3)$$

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[*] The symbols of Sharp et al.[8] have been used.

The algebraic expression of the functions f(α) and g(α) corresponding to the mechanisms more commonly used in the literature for thermal decomposition reactions of solids, have been summarized in previous papers[5, 9].

If the thermoanalytical curve is obtained at a constant decomposition rate, $C = \mathrm{d}\alpha/\mathrm{d}t$, eqn. (2), after taking logarithms and rearranging, can be written as

$$\ln \frac{1}{\mathrm{f}(\alpha)} = \ln \frac{A}{C} - \frac{E}{RT} \tag{4}$$

If studying a particular reaction, the function f(α) has been properly selected, a plot of the left-hand side of eqn. (4) against $1/T$ should be a straight line whose slope gives the activation energy. Therefore, only those reaction mechanisms whose corresponding functions ln 1/f(α) are not linearly correlated can be discerned.

Taking into account that in the case of "n-order" reactions

$$\mathrm{f}(\alpha) = (1 - \alpha)^n \tag{5}$$

it is very easy to deduce the following expression

$$\ln \frac{1}{(1 - \alpha)^{n_1}} = \frac{n_1}{n} \ln \frac{1}{(1 - \alpha)^n} \tag{6}$$

where n_1 and n refer to particular reaction orders.

Equation (6) shows that solid-state reactions following n_1-order kinetics with an activation energy E_1, necessarily fit any kinetic equation of "n order", giving an activation energy $E = (n/n_1)\, E_1$.

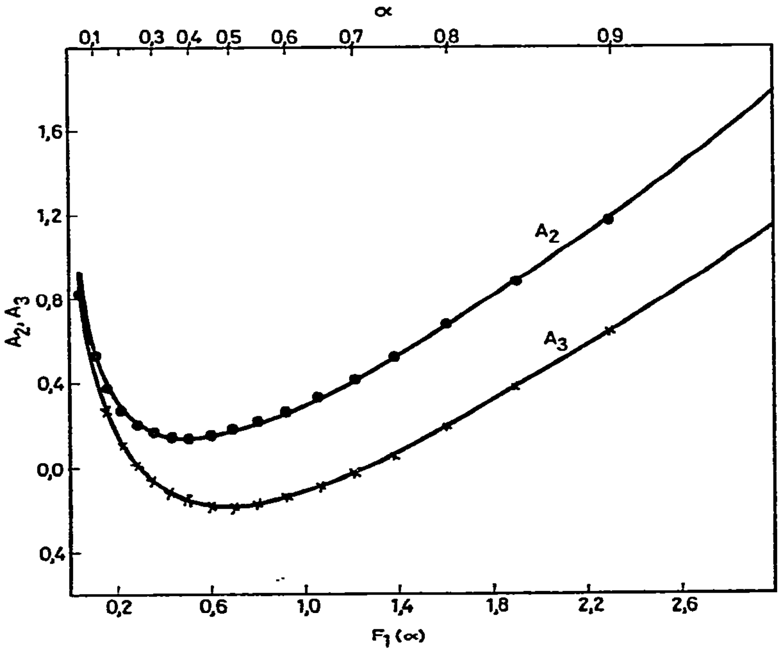
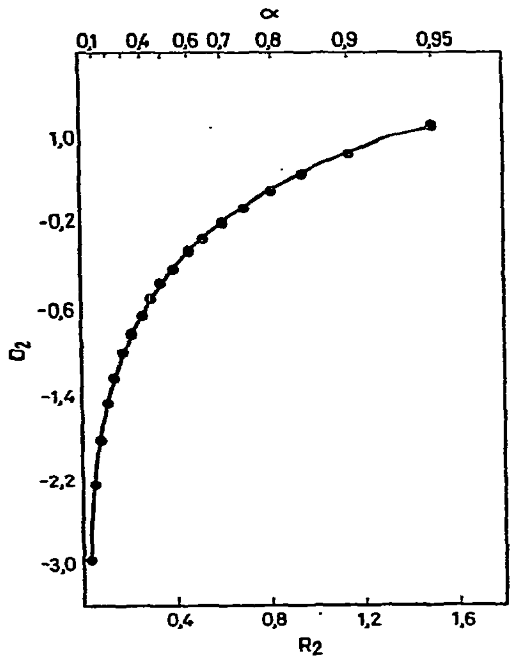


Fig. 1. Relationship between the logarithmic forms of the 1/f(α) functions for the mechanisms A_2 and A_3 and F_1.



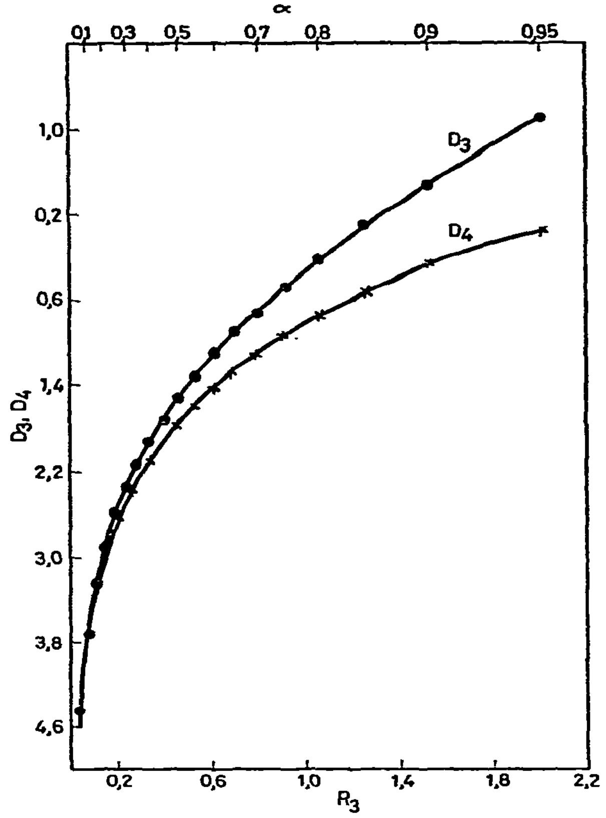


Fig. 2. Relationship between the logarithmic forms of the 1/f(α) functions for the mechanisms D_2 and R_2.

Fig. 3. Relationship between the logarithmic forms of the 1/f(α) functions for the mechanisms D_3 and D_4 and R_3.

With regards to Avrami–Erofeev and diffusion reaction mechanisms, the existence of any correlation between the logarithmic forms of their functions 1/f(α) is not evident. Thus, an empirical study has been carried out in order to correlate the following mechanisms: (i) D_2 and R_2; (ii) D_3 and R_3; (iii) D_4 and R_3, and (iv) A_2 and A_3 and F_1. The results obtained are shown in Figs. 1–3. These data indicate that the functions checked in the previous figures are not linearly correlated. Therefore, reactions taking place either through diffusion or Avrami–Erofeev mechanisms would be clearly distinguished by using a "quasi-isothermal" heating program. This does not occur if a linear heating program is employed, as was proved in previous papers[3–5].

In summary, we conclude from the previous study that when the thermal decomposition of a solid takes place through either an Avrami–Erofeev or a diffusion mechanism, a single TG diagram obtained with a "quasi-isothermal" heating program would permit the determination of the actual reaction mechanism. However, this technique does not allow the discernment of the *n*-value of those reactions following *n*-order kinetics.

In order to prove the above statement and to compare the results with those obtained using a linear heating program, the thermoanalytical curves for a 2/3-order

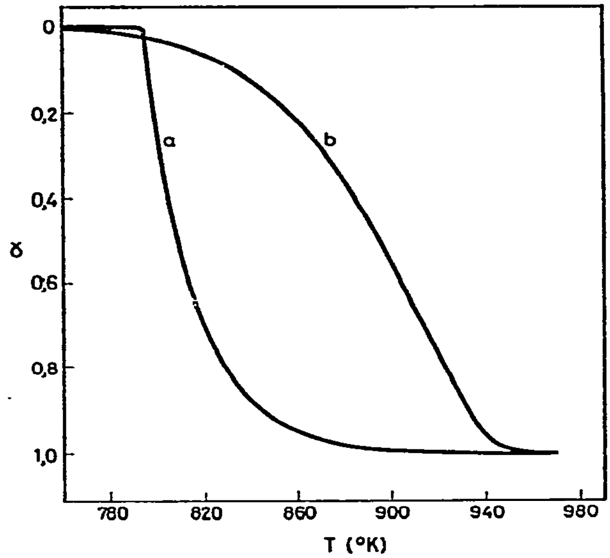


Fig. 4. Diagrams of the thermal decomposition of a solid with the following kinetic parameters: $A = 10^7$ sec^{-1}; $E = 39$ kcal mole^{-1}. a, Constant decomposition rate = 0.01 min^{-1}; b, Linear heating rate = 10 °C min^{-1}.

TABLE 1

NUMERICAL DATA CALCULATED FROM THE ANALYSIS OF CURVES IN FIG. 4 BY ASSUMING DIFFERENT REACTION KINETICS

Mechanism	*Linear heating*			*"Quasi-isothermal" heating*		
	E_a *(kcal mole^{-1})*	A *(sec^{-1})*	*Regression coefficient*	E_a *(kcal mole^{-1})*	A *(sec^{-1})*	*Regression coefficient*
R_2	36.7	$2.2 \cdot 10^6$	−0.9997	29.2	$6.9 \cdot 10^{11}$	−0.9999
R_3	39.0	$9.9 \cdot 10^6$	−1.0000	39.0	$1.0 \cdot 10^7$	−1.0000
F_1	43.8	$1.8 \cdot 10^8$	−0.9992	58.3	$7.8 \cdot 10^{19}$	−0.9999
A_2	40.3	$2.4 \cdot 10^4$	−0.9991	28.6	$4.4 \cdot 10^{11}$	−0.9530
A_3	36.8	$1.6 \cdot 10^0$	−0.9989	18.6	$6.7 \cdot 10^8$	−0.8086
D_1	65.1	$1.3 \cdot 10^{13}$	−0.9965	36.1	$3.4 \cdot 10^{13}$	−0.8807
D_2	81.5	$1.3 \cdot 10^{17}$	−0.9882	40.6	$5.4 \cdot 10^{14}$	−0.6238
D_3	81.3	$3.0 \cdot 10^{16}$	−0.9995	89.3	$1.8 \cdot 10^{27}$	−0.9734
D_4	74.5	$4.8 \cdot 10^{14}$	−0.9992	69.9	$7.6 \cdot 10^{21}$	−0.9581

reaction that are included in Fig. 4 have been theoretically calculated; the following kinetic parameters have been assumed: $A = 10^7$ sec^{-1}; $E = 39$ kcal mole^{-1}. The diagram corresponding to a "quasi-isothermal" heating program has been calculated from eqn. (4), assuming $d\alpha/dt = C = 0.01$ min^{-1}, and taking into account that $f(\alpha) = (1 - \alpha)^{2/3}$. A heating rate of $\beta = 10$ °C min^{-1} has been taken to construct the TG curve corresponding to a linear heating program. The method of theoretically calculating this diagram has been described elsewhere[5].

The kinetic analysis of curves a and b in Fig. 4 has been performed by mean of eqns. (1) and (4), respectively. The results obtained are summarized in Table 1.

The results show that the thermoanalytical curve obtained for a 2/3-order reaction with a "quasi-isothermal" heating technique fit the kinetic equations of "*n*-order" reactions, as previously stated. The regression coefficient calculated for all the other mechanisms are very poor. With regards to the TG diagram calculated under a linear heating program, Table 1 shows that it obeys several kinetic laws simultaneously, giving very good regression coefficients (better than 0.99). However, good agreement between the kinetic parameters determined from both techniques is obtained only when the kinetic equations of the actual reaction mechanism are assumed for performing the calculation. Therefore, the simultaneous kinetic analysis of TG diagrams obtained under both a linear heating program and a "quasi-isothermal" heating technique would provide an excellent procedure for discerning the proper mechanism of solid-state reactions.

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