Thermochimica Acta, 16 (1976) 382–387

Note

Defects of thermogravimetric analysis for discerning between first order reactions and those taking place through the Avrami-Erofeev's mechanism

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(Received 12 January 1976)

Most papers[1] concerned with the kinetic analysis of TG data consider that the decomposition rate of a solid has the general equation:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

where α is the decomposed fraction of solid after a time t; n, the reaction order and k the rate constant given by the equation:

$$k = A\,e^{-E/RT} \tag{2}$$

A and E being the Arrhenius preexponential factor and the activation energy, respectively.

Sharp and Wentworth[2] and several other authors[3] have pointed out the shortcoming of eqn (1) when applied to solid thermal decomposition and they state that only in the case of organic decompositions with partial or full liquefaction setting in during decomposition, the process might take place under conditions approaching homogeneity and eqn (1) could be applicable .In the most common case of solid decompositions involving reaction interface mechanisms as those of Prout and Tompkins, Avrami-Erofeev, etc. might be held.

In order to provide non-isothermal methods for performing the kinetic analysis of solid state reactions, several authors[4–6] have developed kinetic equations which allow the analysis of TG data of reactions taking place according to the above mechanisms. However, it must be pointed out that the large majority of TG data reported in the literature seem to follow equations like (1). This could be understood if the functions deduced from the above mechanisms and used for performing the kinetic analysis of TG data could be fitted by some of the kinetic equations available for "n order reactions".

Thus, in a previous work[7] we have proved that the TG data of any reaction following the Prout and Tompkins' mechanism must necessarily hold the integral equation of a first order reaction within a decomposed fraction range of $0.2<\alpha<0.8$. However, this is not true when an isothermal curve is used for the kinetic analysis.

With regards to the reactions following the Avrami-Erofeev's mechanism it is well known[8] that they follow the kinetic equation:

$$\ln\frac{1}{1-\alpha} = kt^{m} \tag{3}$$

that can be written:

$$\left[\ln\frac{1}{1-\alpha}\right]^{1/m} = \int_{0}^{t} k^{1/m}\,\mathrm{d}t \tag{4}$$

where m can take the values 2, 3, 4, 5 or 6, but $m=3$ is the most usual in the kinetic data reported in the literature.

Using a linear heating rise $\beta = \mathrm{d}T/\mathrm{d}t$ to perform the kinetic analysis, it is obtained from equations (2) and (4):

$$\left[\ln\frac{1}{1-\alpha}\right]^{1/m} = \int_{0}^{T} A^{1/m}\cdot \mathrm{e}^{-E/mRT}\cdot \mathrm{d}T \tag{5}$$

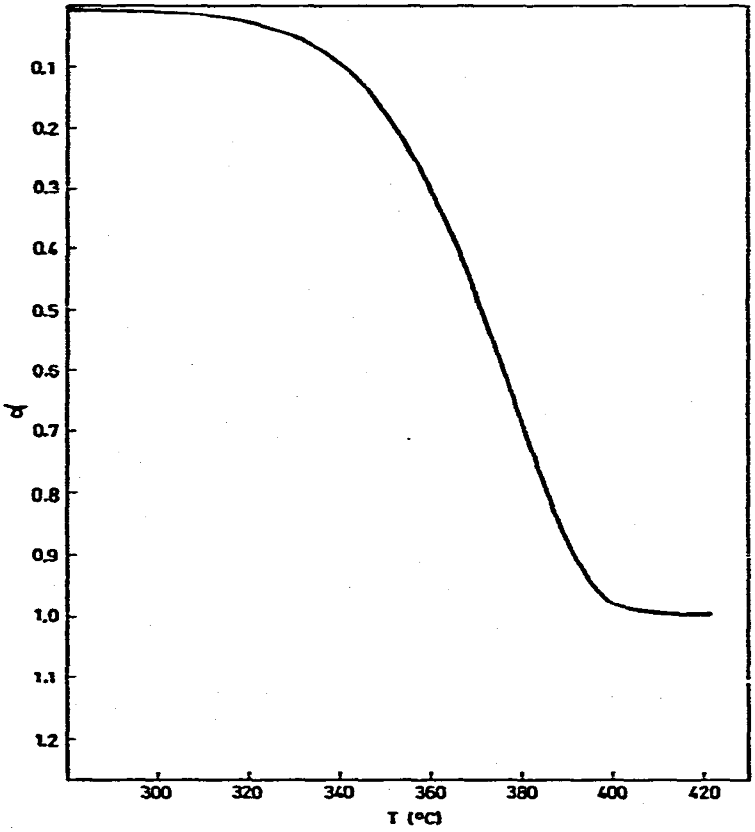

Fig. 1. TG diagram get from eqn (6). $m=3$; $A^{1/m}=10^{4}$ min^{-1}; $E=42$ kcal mol and $\beta=10$ °C min^{-1}.

By integrating the right hand side as Doyle[9] has shown, we obtain:

$$\left[\ln\frac{1}{1-\alpha}\right]^{1/m}=\frac{A^{1/m}\cdot E}{m\beta R}\,\mathrm{p}(x) \tag{6}$$

the p(x) function being:

$$\mathrm{P}_{\mathrm{p}(x)}=\frac{\mathrm{e}^{-x}}{x^2}\left[1-\frac{2!}{x}+\frac{3!}{x^2}-\ldots+\frac{(-1)^n\cdot(n+1)!}{x^n}\right] \tag{7}$$

where $x=E/mRT$.

Taking into account that usually $1/x \ll 1$, eqn (7) becomes:

$$\mathrm{p}(x)\cong\left(\frac{mRT}{E}\right)^2\cdot\mathrm{e}^{-E/mRT} \tag{8}$$

Thus, substituting in eqn (6), taking logs, and rearranging, we get:

$$\ln\ln\frac{1}{1-\alpha}-2m\ln T=m\ln\frac{mA^{1/m}\cdot R}{E\beta}-\frac{E}{RT} \tag{9}$$

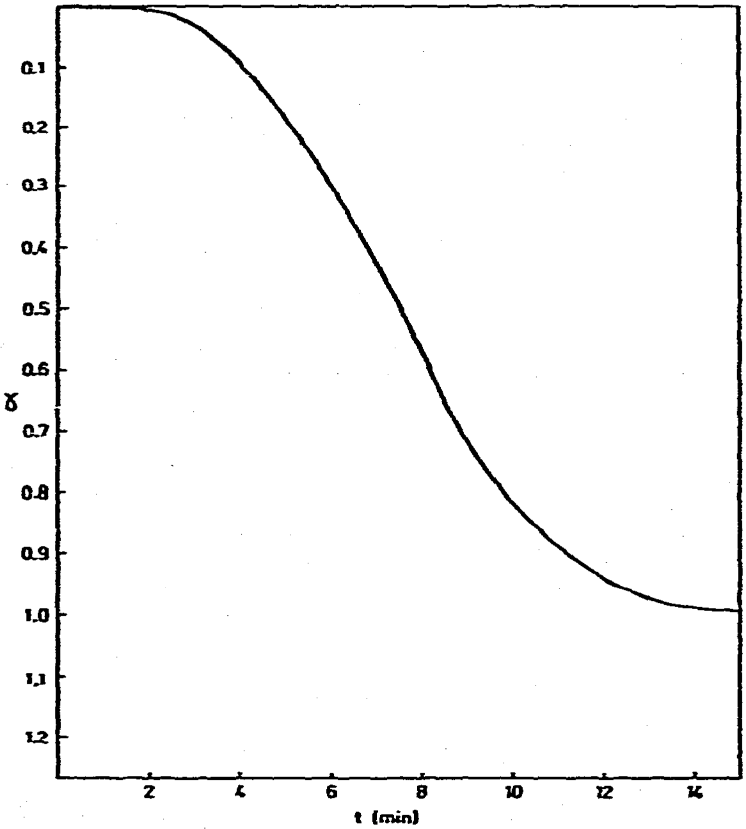

Fig. 2. Isothermal curve obtained at 350 °C from eqn (3) with the same kinetic parameters of Fig. 1.

The plot of the left hand side of eqn (9) against $1/T$ would give a straight line whose slope gives the activation energy of the process.

With regards to the value of m above, it may be assumed that its "best value" would be the one giving the highest linear correlation coefficient. However, as a solid decomposition reaction at programmed temperature usually occurs in a narrow range of temperature, the corresponding values of $\ln T$ would be nearly constant and, therefore, regardless of the value given to m in eqn (9), would lead to a very good correlation coefficient.

Coats and Redfern[1] and other authors[2-10] analyse TG data of first order reactions by means of the equation:

$$\ln \ln \frac{1}{1-\alpha} - 2 \ln T = \ln \frac{AR}{E\beta} - \frac{E}{RT} \tag{10}$$

Comparing eqns (9) and (10), bearing in mind the previous considerations, we can conclude that the reactions following an Avrami–Erofeev's mechanism would be erroneously considered as first order ones by analysing them as if they follow the general equation (1).

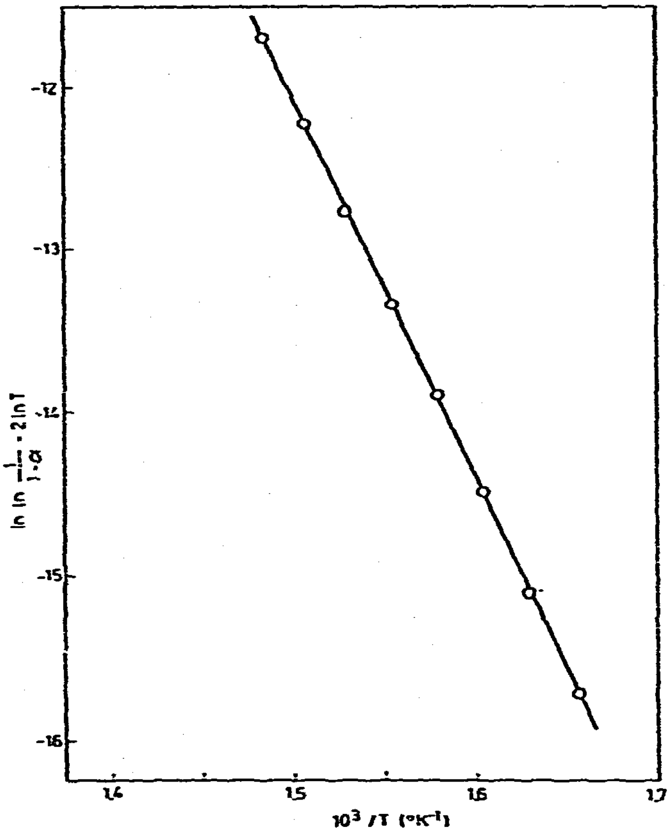

Fig. 3. Plot of the data of Fig. 1 according to eqn (10).

In order to check the previous statements, first of all both an isothermal and a TG curve of a hypothetical reaction following the Avrami–Erofeev's mechanism have been calculated. Secondly, the results obtained performing the kinetic analysis of both curves as if the reactions were of first order have been compared.

Figure 1 shows a TG diagram obtained by using eqn (6) with $m = 3$ after giving to the kinetic parameters the arbitrary values: $A^{1/m} = 10^4$ min^{-1} and $E = 42$ kcal/mol^{-1}. In the calculation, a heating rate of 10°C min^{-1} has been assumed and the values of the p(x) function tabulated by Szako[11] have been used.

Figure 2 shows the isothermal curve at 350°C (in the decomposition range recorded in Fig. 1), obtained from eqn (3) after substituting the same activation energy and Arrhenius preexponential factor used there. Thus, a rate constant $k^{1/m} =$ 0.118 min^{-1} was determined.

From the diagram of Fig. 1, values of between 0.05 and 0.95 were taken and the corresponding values of ln ln $(1/1-\alpha) - 2 \ln T$ were calculated and represented in Fig. 3 against $10^3/T$, according to eqn (10). An activation energy of 46 kcal mol^{-1} has been obtained from the slope of the plot. Although such a value is somewhat higher than the 42 kcal mol^{-1} that would be obtained from eqn (9), the correlation coefficient of Fig. 2 ($r = 0.99997$) is very good. These results demonstrate that TG data of reactions following the Avrami–Erofeev's mechanism also fit closely a first order kinetic equation, as we had previously deduced.

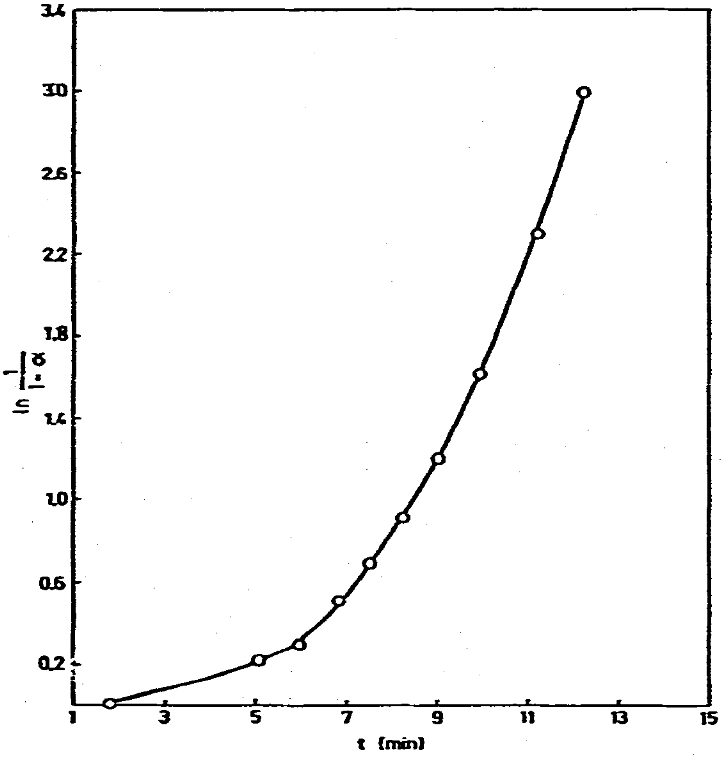

Fig. 4. Plot of the data of Fig. 2 according to the isothermal kinetic equation of a first order reaction.

On the countrary, the isothermal data of Fig. 2, that have been calculated by assuming an Avrami–Erofeev's mechanism do not fit a first order kinetic equation as shown in Fig. 4.

In summary, the data reported in the present work seem to support that a single TG diagram does not allow to determine whether a solid decomposition reaction is of first order or follows the Avrami–Erofeev's mechanism. However, the analysis of both a single TG diagram and a single isothermal curve would be a quick and proper way for discerning the kinetic parameters of the reaction.

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