

A CRITICAL STUDY OF THE SUITABILITY OF THE FREEMAN AND CARROLL METHOD FOR THE KINETIC ANALYSIS OF REACTIONS OF THERMAL DECOMPOSITION OF SOLIDS

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ABSTRACT

It is demonstrated that non-isothermal traces of thermal decomposition reactions of solids must fit the equation developed by Freeman and Carroll for performing the kinetic analysis of “*n* order” reactions even if they are following a quite different mechanism. Therefore, it is concluded that this method does not allow one to determine if a reaction is obeying an “*n* order” kinetic law or a different one.

INTRODUCTION

The Freeman and Carroll method [1] is perhaps one of the most widely used in the literature [2–4] for performing the kinetic analysis of reactions that fulfil the kinetic law

$$\frac{d\alpha}{dt} = A e^{-E/RT}(1-\alpha)^n \quad (1)$$

where α is the reacted fraction at the time t , E is the activation energy, A is the pre-exponential factor of Arrhenius and n stands for the reaction order.

By differentiating the logarithmic form of eqn. (1) with respect to $d \ln(1-\alpha)$, Freeman and Carroll obtained

$$\frac{d \ln(d\alpha/dt)}{d \ln(1-\alpha)} = -\frac{E}{R} \frac{d(1/T)}{d \ln(1-\alpha)} + n \quad (2)$$

or

$$\frac{\Delta \ln(d\alpha/dt)}{\Delta \ln(1-\alpha)} = -\frac{E}{R} \frac{\Delta(1/T)}{\Delta \ln(1-\alpha)} \quad (3)$$

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The plots of the left-hand side of eqn. (2) or (3) against $d(1/T)/d \ln(1 - \alpha)$ [or $\Delta(1/T)/\Delta \ln(1 - \alpha)$] should be a straight line with a slope $-E/R$ and an intercept equal to n . Therefore this method allows one to determine simultaneously both the activation energy and the reaction order without a previous knowledge of this last parameter, as required by the majority of the methods proposed in the literature [5,6].

However, it is well known that solid state reactions are often described by kinetic laws quite different from eqn. (1). Heide et al. [7] have developed a differential-differential method similar to Freeman and Carroll's in order to discriminate the actual mechanism of reactions whose rate is not expressed by eqn. (1).

In the present paper we try to determine if the Freeman and Carroll method allows one to discern clearly between solid state reactions fitting an n order kinetic law and those following a different mechanism.

THEORETICAL

It is well known that the rate of a reaction of thermal decomposition of solids can be expressed in the general form

$$\frac{d\alpha}{dt} = A e^{-E/RT} f(\alpha) \quad (4)$$

$f(\alpha)$ being a function depending on the actual reaction mechanism.

If we differentiate the logarithmic form of eqn. (4) with respect to $\ln(1 - \alpha)$, we get

$$\frac{d \ln(d\alpha/dt)}{d \ln(1 - \alpha)} = -\frac{E}{R} \frac{d(1/T)}{d \ln(1 - \alpha)} + \frac{d \ln f(\alpha)}{d \ln(1 - \alpha)} \quad (5)$$

By taking increments in the logarithmic form of eqn. (4) and dividing by $\Delta \ln(1 - \alpha)$, we may also write

$$\frac{\Delta \ln(d\alpha/dt)}{\Delta \ln(1 - \alpha)} = -\frac{E}{R} \frac{\Delta(1/T)}{\Delta \ln(1 - \alpha)} + \frac{\Delta \ln f(\alpha)}{\Delta \ln(1 - \alpha)} \quad (6)$$

On the other hand, if the temperature of the sample is increased at a constant rate $\beta = dT/dt$, eqn. (4) may be integrated

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{-E/RT} dT \quad (7)$$

So that, after taking logarithms and considering Doyle's approximation [8] for integrating the Arrhenius equation, this becomes

$$\ln g(\alpha) \approx \ln \frac{AE}{\beta R} - 5.34 - 1.05 \frac{E}{RT} \quad (8)$$

By differentiating eqn. (8) with respect to $\ln(1 - \alpha)$, one obtains

$$\frac{d \ln g(\alpha)}{d \ln(1 - \alpha)} \approx -1.05 \frac{E}{R} \frac{d(1/T)}{d \ln(1 - \alpha)} \quad (9)$$

If the following relationship can be established

$$\frac{d \ln f(\alpha)}{d \ln(1-\alpha)} = a \frac{d \ln g(\alpha)}{d \ln(1-\alpha)} + b \quad (10)$$

(a and b being constants) from eqns. (5), (9), and (10) one obtains

$$\frac{d \ln(d\alpha/dt)}{d \ln(1-\alpha)} = -\frac{E'}{R} \frac{d(1/T)}{d \ln(1-\alpha)} + b \quad (11)$$

where $E' = (1 + 1.05a)E$.

By comparing eqns. (2) and (11) it can be seen that if eqn. (10) applies then the reaction would be seen to obey an n order kinetic law in spite of really following a quite different mechanism. In this case, an apparent reaction order $n = b$, and an apparent activation energy $E' = (1 + 1.05a)E$ would be obtained.

In order to see if the above assumptions work, we have collected in Table 1 the mathematical expressions of the functions $d \ln g(\alpha)/d \ln(1-\alpha)$ and $d \ln f(\alpha)/d \ln(1-\alpha)$ corresponding to some of the mechanisms of thermal decomposition found in the literature, and have used eqn. (10) to obtain values of a and b which are shown in Table 1, together with their linear correlation coefficients.

It must be noted that in the case of reactions following the Avrami-Erofeev mechanism there is no agreement in the literature with regard to a method of defining the specific reaction rate for the reaction. Some authors [7,9,10] express the isothermal kinetic law in the form

$$\left[\ln \frac{1}{1-\alpha} \right]^{1/m} = kt \quad (12)$$

m being a constant depending on the nucleation and growth mechanism. (This factor is usually quoted as n , but is called m here to distinguish from the previous use of n .)

The results included in Table 1 are obtained from the kinetic analysis of eqn. (12) under a linear heating rate.

However, we must point out that the Avrami-Erofeev kinetic law would be more properly written as [11-13]

$$\left[\ln \frac{1}{1-\alpha} \right]^{1/m} = k^{1/m} t \quad (13)$$

or in differential form

$$\frac{d\alpha}{dt} = mk^{1/m}(1-\alpha) \left[-\ln(1-\alpha) \right]^{1-(1/m)} \quad (14)$$

and that under non-isothermal conditions this becomes

$$\frac{d\alpha}{dt} = mA^{1/m} e^{-E/mRT} (1-\alpha) \left[-\ln(1-\alpha) \right]^{1-(1/m)} \quad (15)$$

By taking logarithms and differentiating with respect to $\ln(1-\alpha)$, eqn. (15) becomes

$$\frac{d \ln(d\alpha/dt)}{d \ln(1-\alpha)} = -\frac{E}{mR} \frac{d(1/T)}{d \ln(1-\alpha)} + [1 - (1/m)] \left[\frac{-1}{\ln(1-\alpha)} \right] + 1 \quad (16)$$

TABLE I

Values of a and b calculated by correlating the functions $d \ln f(\alpha)/d \ln(1-\alpha)$ and $d \ln g(\alpha)/d \ln(1-\alpha)$ according to eqn. (10): leading to apparent order and E'/E

Mechanism (symbol) ^a	$\frac{d \ln g(\alpha)}{d \ln(1-\alpha)}$	$\frac{d \ln f(\alpha)}{d \ln(1-\alpha)}$
Avrami-Erofeev ^b	$\frac{-1}{m \ln(1-\alpha)}$	$(1-\frac{1}{m}) \frac{-1}{\ln(1-\alpha)} + 1$
Undimensional diffusion (D ₁)	$\frac{-2(1-\alpha)}{\alpha}$	$\frac{1-\alpha}{\alpha}$
Two-dimensional diffusion (D ₂)	$\frac{(1-\alpha) \ln(1-\alpha)}{(1-\alpha) \ln(1-\alpha) + \alpha}$	$\frac{-1}{\ln(1-\alpha)}$
Three-dimensional diffusion (Jander mechanism) (D ₃)	$-\frac{2}{3} \frac{(1-\alpha)^{1/3}}{1-(1-\alpha)^{1/3}}$	$\frac{1}{3} \frac{(1-\alpha)^{1/3}}{1-(1-\alpha)^{1/3}} + \frac{2}{3}$
Three-dimensional diffusion (Ginstling-Brounshtein mechanism) (D ₄)	$\frac{-2[(1-\alpha)^{-1/3}-1](1-\alpha)}{3[1-(2\alpha/3)-(1-\alpha)^{2/3}]}$	$\frac{(1-\alpha)^{-1/3}}{3[(1-\alpha)^{-1/3}-1]}$

^a Symbols of Sharp et al. [15] have been used.

^b If the kinetic law is written in the form $[-\ln(1-\alpha)]^{1/m} = kt$.

On the other hand, integrating eqn. (15) taking into account the Doyle's approximation, we get

$$\ln[-\ln(1-\alpha)]^{1/m} = \ln \frac{A^{1/m} E}{m\beta R} - 5.34 - 1.05 \frac{E}{mRT} \quad (17)$$

which on differentiation with respect to $\ln(1-\alpha)$ can be rearranged to

$$\frac{-1}{\ln(1-\alpha)} = -1.05 \frac{E}{R} \frac{d(1/T)}{d \ln(1-\alpha)} \quad (18)$$

By substituting eqn. (18) into eqn. (16) we obtain, after collecting terms

$$\begin{aligned} \frac{d \ln(d\alpha/dt)}{d \ln(1-\alpha)} &= - \left(1.05 - \frac{0.05}{m} \right) \frac{E}{R} \frac{d(1/T)}{d \ln(1-\alpha)} + 1 \\ &\approx - \frac{E}{R} \frac{d(1/T)}{d \ln(1-\alpha)} + 1 \end{aligned} \quad (19)$$

From the comparison of eqns. (2) and (19) we can conclude that employing the Freeman and Carroll's method for performing the kinetic analysis of a reaction

a	$1 + 1.05a \approx E'/E$	Apparent order $n \approx b$	Correlation coefficient (r) ($0.05 \leq a \leq 1.0$)
$m-1$	$1.05m - 0.05$ $\approx m$	1.00	1.00000
-0.500	0.475	0.00	1.00000
-0.503	0.472	0.30	0.99999
-0.500	0.475	2/3	1.00000
-0.501	0.474	0.43	0.99999

taking place through an Avrami–Erofeev mechanism it would be erroneously interpreted as first order. This is true whatever the way of defining the rate constant. Moreover, the apparent activation energy obtained from eqn. (2) coincides with the actual one if we take into account that the proper rate constant is defined by eqn. (13). However, if eqn. (12) is considered, a ratio E'/E very close to m would be obtained as shown in Table 1.

The results in Table 1 and the above considerations seem to show that the equation developed by Freeman and Carroll for carrying out the kinetic analysis of n order reactions is fulfilled whatever the reaction mechanism of thermal decomposition of solids. (Note in the above equations $d\alpha/dt$ may be substituted by $d\alpha/dT$ with the same result.)

In order to test the validity of the above considerations we have constructed both the TG and the DTG curves included in Fig. 1 by assuming a Ginstling–Bronshtein diffusion mechanism (D_4) and the following kinetic parameters: $E = 30 \text{ kcal mole}^{-1}$ ($125.4 \text{ kJ mole}^{-1}$), $A = 10^{13} \text{ sec}^{-1}$ and a heating rate = $10^\circ\text{C min}^{-1}$. The integration of the Arrhenius equation was performed by a third order rational approximation developed by Senung and Yang [14] with an accuracy better than $10^{-2}\%$.

$$\int_0^T e^{-E/RT} dT = \frac{E \exp(-x)}{R} \frac{x^2 + 10x + 18}{x^3 + 12x^2 + 36x + 24} \quad (20)$$

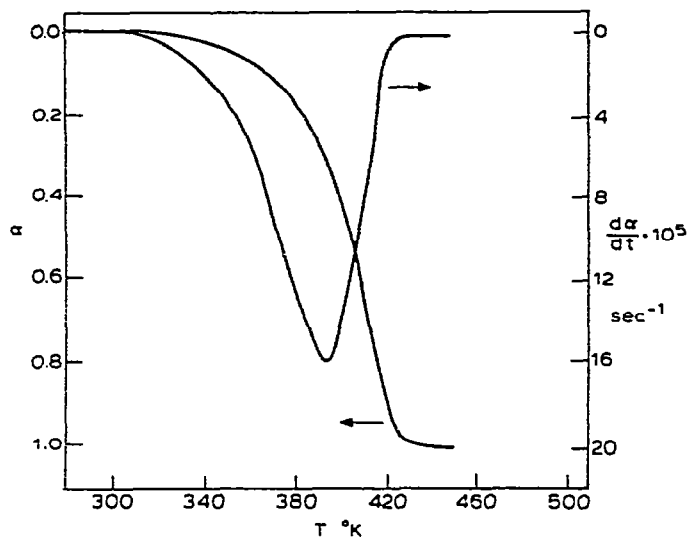


Fig. 1. Plots of the values of α and $d\alpha/dt$ calculated as a function of the temperature by assuming a D_4 mechanism and the following kinetic parameters: $E=30$ kcal mole $^{-1}$ (125.4 J mole $^{-1}$); $A=10^{13}$ sec $^{-1}$; $\beta=10^\circ\text{C min}^{-1}$.

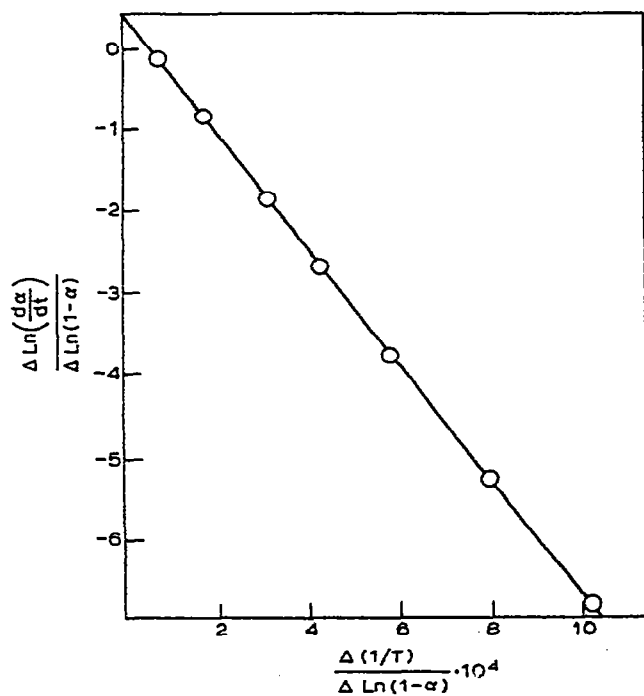


Fig. 2. Plots of data taken from Fig. 1 according to eqn. (3). Results obtained: $E=14.25$ kcal mole $^{-1}$ (59.5 kJ mole $^{-1}$) (i.e., $E'/E=0.475$); $n=0.432$; correlation coefficient $r=-0.99999$.

The results of the kinetic analysis of data in Fig. 1 according to eqn. (3) are included in Fig. 2. The values of the kinetic parameters calculated from this Figure are $E' = 14.24 \text{ kcal mole}^{-1}$ ($59.5 \text{ kJ mole}^{-1}$) (i.e., $E'/E = 0.475$) and $n = 0.432$. These results are in excellent agreement with those previously calculated in Table 1.

In summary, we conclude that the Freeman and Carroll method cannot be used for determining if a solid state reaction is following an " n order" kinetic law because, as we have shown, eqns. (2) and (3) must be fulfilled in spite of the reaction following a quite different mechanism.

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