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A critical appraisal of the Dixit and Ray method for the analysis of non-isothermal kinetic data

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Abstract

A critical appraisal of the suitability of a method proposed by Dixit and Ray for analysis of non-isothermal thermogravimetric (TG) kinetic data has been made by applying it both to computer-simulated and experimental TG data. It is pointed out that this method leads to considerable errors in the determination of activation energy and the error depends on the kinetic order (n) of the reaction.

Keywords: Activation energy; Computer simulation; Dixit and Ray method; Non-isothermal kinetic data; TG

1. Introduction

Dixit and Ray [1] proposed a method for the analysis of non-isothermal kinetic data obeying the kinetic law

$$d\alpha/dt = A \exp(-E/RT) f(\alpha) \quad (1)$$

where α is the fraction of the reaction completed in time t , E is the activation energy, A is the pre-exponential factor and n the order of the reaction; $f(\alpha)$ is a function whose appropriate form depends on the reaction mechanism. Thermogravimetry (TG) measurements are generally performed with a constant heating rate, β , so that

$$T = T_0 + \beta t \quad (2)$$

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where T_0 is the initial temperature and T is the temperature at time t . Eqs. (1) and (2) can be combined to arrive at the basic kinetic equation given by

$$g(\alpha) = \int_0^\alpha d\alpha/f(\alpha) = (A/\beta) \int_{T_0}^T \exp(-E/RT') dT' \quad (3)$$

for the analysis of TG data. One commonly used form of $f(\alpha)$ is

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

Dixit and Ray [1] considered a heating profile of the type

$$1/T = a - bt \quad (5)$$

where a and b are constants. They show that for a heating profile of the type given by Eq. (5) the plot of $\ln [g(\alpha)]$ against $1/T$ will give the activation energy E . They also point out that the method can be used for a linear heating profile if the temperature range considered is small and the initial temperature is high.

In the present paper we show that if their method is used it will give rise to considerable errors in the determination of the activation energy; we also test our findings by applying them to some experimental cases.

2. Theoretical

It is well known that the evaluation of the integral

$$I(T, E) = \int_0^T \exp(-E/RT') dT' \quad (6)$$

popularly known as the temperature integral, is not straight forward. In recent work Gartia et al. [2] have shown that

$$I(T, E) = (E/R)E_2(u)/u \quad (7)$$

where $E_2(u)$ is the second exponential integral [3]. Using Eq. (7), Eq. (3) can be written as

$$g(\alpha) = (AE/\beta R)(E_2(u)/u) \quad (8)$$

Dixit and Ray [1] showed that for a heating profile of the type represented by Eq. (5) one can write

$$g(\alpha) = (AR/bE) \exp(-E/RT) \quad (9)$$

From Eq. (9) we see that the plot of $\ln [g(\alpha)]$ against $1/T$ will give the activation energy E . We note that asymptotically [3]

$$E_2(u) \approx (\exp(-u)/u)G(u) \quad (10)$$

with

$$G(u) = 1 - \frac{2!}{u} + \frac{3!}{u^2} - \frac{4!}{u^3} + \dots \quad (10a)$$

If u is such that $E_z(u)$ is approximated by the first term of the asymptotic series, i.e.,

$$E_2(u) \approx (\exp(-u)/u) \quad (11)$$

One readily finds that Eq. (9) represents the case of a conventional linear heating profile. From Eqs. (8) and (11) one gets

$$g(x) = (AE/\beta R)(\exp(-u)/u) \quad (12)$$

For a heating profile of the type represented by Eq. (5) the instantaneous rate of heating is given by

$$\beta = \frac{dT}{dt} = bT^2 \quad (13)$$

It is evident that if we write $u = E/RT$ and use Eq. (13), Eq. (12) reduces to Eq. (9). So we observe that the crucial parameter controlling the approximation of a linear heating profile (Eq. (2)) by a heating profile of the type given by Eq. (5) is $u = E/RT$, i.e., it is decided not only by the values of initial temperature and temperature range, as shown by Dixit and Ray [1], but also by the magnitude of activation energy, which is not usually known.

3. Results and discussion

To test the validity of the Dixit and Ray method [1] we computed TG curves using both the exact form of Eq. (8) and Eq. (12) corresponding to the Dixit and Ray method. Eqs. (8) and (12) were solved by the Newton–Raphson method [Appendix A]. As a check of our computer program we reproduce the theoretical data of Zuru et al. [4] for $E = 83.68 \text{ kJ mol}^{-1}$, $A = 1.0 \times 10^{12} \text{ min}^{-1}$, $\beta = 5^\circ\text{C min}^{-1}$, $n = 1$. We also computed the TG curve using Eq. (12) for the Dixit and Ray (DR) method. In Fig. 1(A) we show the theoretical α - T curves for $n = 0.5$, $E = 83.68 \text{ kJ mol}^{-1}$, $A = 1.0 \times 10^{12} \text{ min}^{-1}$ and $\beta = 5^\circ \text{ min}^{-1}$ obtained by use of Eqs. (8) and (12).

We observe that the TG curves computed by the DR method differ from exact TG curves for all values of temperature (T) and always lie above the exact curves. In Figs. 1B–1D we show the theoretical TG curves for other values of the kinetic order (n) namely $n = 1, 1.5$ and 2 ; values of n between 0.5 and 2 have been reported in a number of thermal studies [5–7]. In all cases the TG curves as computed by the DR method differ from the exact ones, thereby demonstrating that the DR approximation affects the entire TG curve.

We have computed the proportional percentile error $\delta_{\text{DR}} = 100(E - E_{\text{DR}})/E\%$ in order to calculate the error in the determination of the activation energy by the DR

method (E_{DR} is the activation energy evaluated by the DR method and E is the input value of activation energy) as a function of order of kinetics (n) for theoretical TG data generated by using $E = 83.68 \text{ kJ mol}^{-1}$, $A = 1.0 \times 10^{12} \text{ min}^{-1}$ and $\beta = 5^\circ\text{C min}^{-1}$ [4]. The plot of δ_{DR} as a function of n is depicted in Fig. 2 δ_{DR} increases almost linearly with n and varies from 6.69 to 6.90% as n changes from 0.5 to 2. We also observe that E_{DR} is

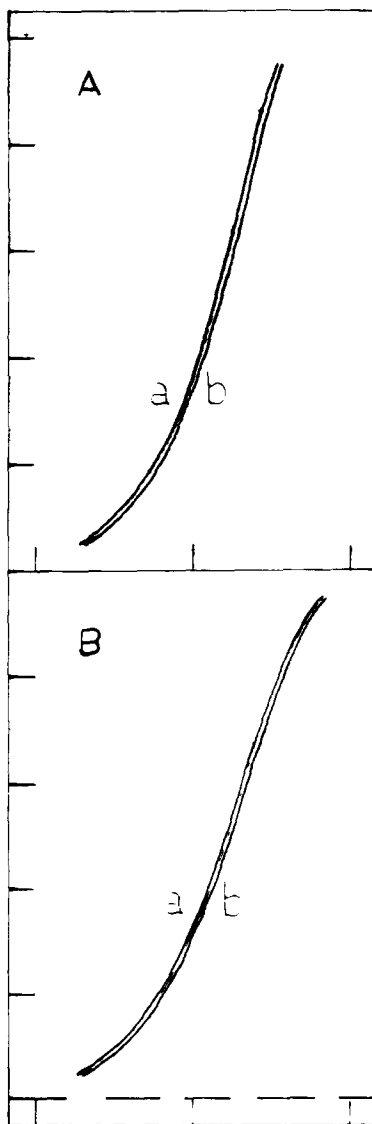


Fig. 1. Numerically computed TG curves using the Dixit and Ray equation (Eq. (12); curves a) and the exact equation (Eq. (12); curves b) for $E = 83.68 \text{ kJ mol}^{-1}$, $A = 1.0 \times 10^{12} \text{ min}^{-1}$, $\beta = 5^\circ\text{C min}^{-1}$. A, $n = 0.5$; B, $n = 1$; C, $n = 1.5$; D, $n = 2$.

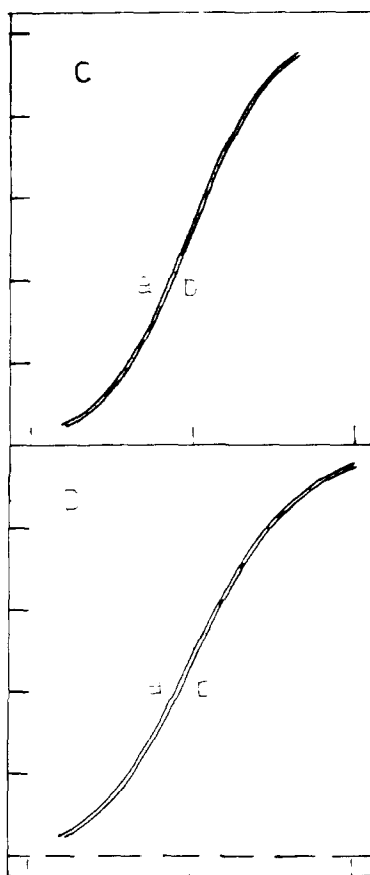


Fig. 1. (Continued).

always larger than E , i.e. the DR method overestimates the activation energy. Since, even for theoretical TG data, the DR method leads to an error of about 7% in the determination of the activation energy, it is expected that for experimental TG curves the error will be greater.

We now apply the DR method to some experimental data [8, 9]. In the cases considered the activation energy has been measured by the Horowitz and Metzger (HM) method [10]. The activation energy as measured by the HM method is denoted by E_{HM} . In Table 1 we tabulate the values of E_{HM} and E_{DR} . If we take the value of the activation energy as determined by the HM method as the standard, the percentile proportional error incurred in the determination of the activation energy for the experimental cases reported in Table 1 turn out to be 17.5, 23.7 and 11.1, respectively. We find that the DR method overestimates the value of the activation energy in accordance with our findings; the errors are within the limits we obtained.

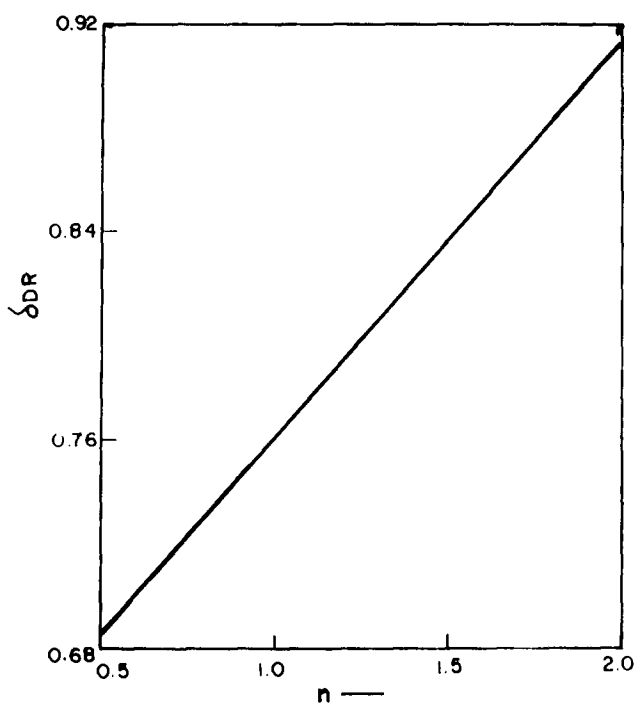


Fig. 2. Percentile proportional error (δ_{DR}) in the determination of the activation energy by the Dixit and Ray method as a function of the kinetic order (n).

Table 1
Determination of the activation energies of some experimental TG curves [8, 9] by the Dixit and Ray [1] method

Process studied	$E_{DR}/(\text{kJ mol}^{-1})$	$E_{HM}/(\text{kJ mol}^{-1})$
$\text{Na}_2[\text{Mn}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O} \rightarrow \text{Na}_2[\text{Mn}(\text{C}_2\text{O}_4)_2]$	148.5	126.4
$\text{Na}_2[\text{Mn}(\text{C}_2\text{O}_4)_2] \rightarrow \text{Na}_2\text{O} \cdot \text{MnO}_2$	131.5	106.3
$[\text{Ni}(\text{mpipz})(\text{NCS})_2] \rightarrow [\text{Ni}(\text{SCN})_2]$	159.1	138.0

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Appendix:

Eq. (8) can be written as

$$H(u) = (cE(u)/u) - g(x) = 0 \quad (\text{A1})$$

with

$$c = (EA/R\beta) \quad (\text{A2})$$

$$g(\alpha) = -\ln(1-\alpha) \quad \text{for } n = 1$$

$$= [1 - (1-\alpha)^n]/(1-n) \quad \text{for } n \neq 1 \quad (\text{A3})$$

$$dH/du = -c[\exp(-u)/u^n] \quad (\text{A4})$$

using the relationships [3]

$$d[E_2(u)]/du = -E_1(u) \quad \text{and} \quad E_2(u) = \exp(-u) - uE_1(u)$$

Eq. (A1) can be solved for different values of α by using the Newton–Raphson method [11] according to which

$$u^{(k+1)} = u^{(k)} - [H(u^k)/(dH/du)_{u=u^k}]$$

where $u^{(k)}$ is the k th approximation to u . If we start with a suitable trial value of u we get rapid convergence. We can solve Eq. (12) in a similar manner.

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