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Note

Rapid estimation of the activation energy for the decomposition of a solid using isothermal data

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Numerous procedures are available for the estimation of the activation energy (E) for the thermal decomposition of a solid[1]. However, most methods make assumptions about the kinetic laws which are debatable. A method independent of any such assumption would be ideal for kinetic estimations for those solids which decompose through a complex process or for those where the kinetic order is not known. Recently, we have used a method (equally applicable both for isothermal and dynamic operations) for kinetic estimations which does not make any assumption about the kinetic laws[2]. A few other methods free from kinetic assumptions are also available in the literature. Amongst them the most widely used method, which can also be used with rapidity, is the one developed by Jacobs and Kureishy[3]. The purpose of the present note is to critically examine this method and present a simpler and more rapid method for kinetic estimations.

Jacobs and Kureishy have used the rate equation of the following general form

$$F(\alpha) = kt \tag{1}$$

where, k is the rate constant and α is the fraction decomposed at any time t. They arrive at the following equations at different temperatures by fixing two arbitrary α values. At T_1 °C,

$$F(\alpha_{n+1}) - F\alpha_n = k(t_{n+1} - t_n) \tag{2}$$

and at T_2 °C

$$F(\alpha_{n+1}) - F\alpha_n = k(t'_{n+1} - t'_n) \tag{3}$$

From eqns (2) and (3) it can be shown that the plot of $\log(t_{n+1} - t_n)$ versus $1/T$ will yield E. The order of reaction has not been considered in eqn (1). There are many examples of reactions where the kinetic behaviour itself changes with temperature and therefore any attempt to make kinetic estimations un before using this equation that the order of reaction does not change in the temperature region of interest. Generally, reduced-time plots[4] are used to examine the kinetic behaviour at different temperatures where the α versus time curves are superimposed on each other to get the points on a master curve. A mathematical justification of such reduced-time plots, however, is not available in the literature.

Let us start with the following general separable kinetic law which represents the extent of thermal decomposition as a function of time

$$\frac{d}{dt} = k(1-\alpha)^n \tag{4}$$

where the terms have their usual meaning. n is the order of reaction. It may be noted that aqn (4) can attain the form of eqn (1) in case either n is constant or has a value equal to one. On integration, eqn (1) becomes

$$\frac{(1-\alpha)^{1-n}-1}{n-1} = kt \tag{5}$$

On applying the condition that $t = t_{1/2}$ when $\alpha = 0.5$, eqn (5) becomes

$$\frac{C_n}{n-1} = kt_{1/2} \tag{6}$$

where

$$C_n = [(0.5)^{1-n}-1] \tag{7}$$

$t_{1/2}$ will be a function of temperature of the experiment. On dividing eqn (5) by eqn (6) we get

$$\frac{(1-\alpha)^{1-n}-1}{C_n} = \frac{t}{t_{1/2}} = t_r \text{ (reduced time)} \tag{8}$$

or

$$(1-\alpha) = [1+C_n t_r]^{1/1-n} \tag{9}$$

Eqn (9) can be written at different temperatures. At T_1 °C,

$$(1-\alpha_{p_1}) = [1+C_{n_1} t_{r_1}]^{1/1-n_1} \tag{10}$$

and at T_2 °C,

$$(1-\alpha_{p_2}) = [1+C_{n_2} t_{r_2}]^{1/1-n_2} \tag{11}$$

A typical plot of α_p versus t and α_p versus t_r at different temperatures of RDX are shown in Figs. 1 and 2. The curves at different temperatures superimpose on each other showing thereby, that for any value of t_r (at temperatures T_1 and T_2) the values of α are the same (i.e., $\alpha_{p_1} = \alpha_{p_2}$). Under such a

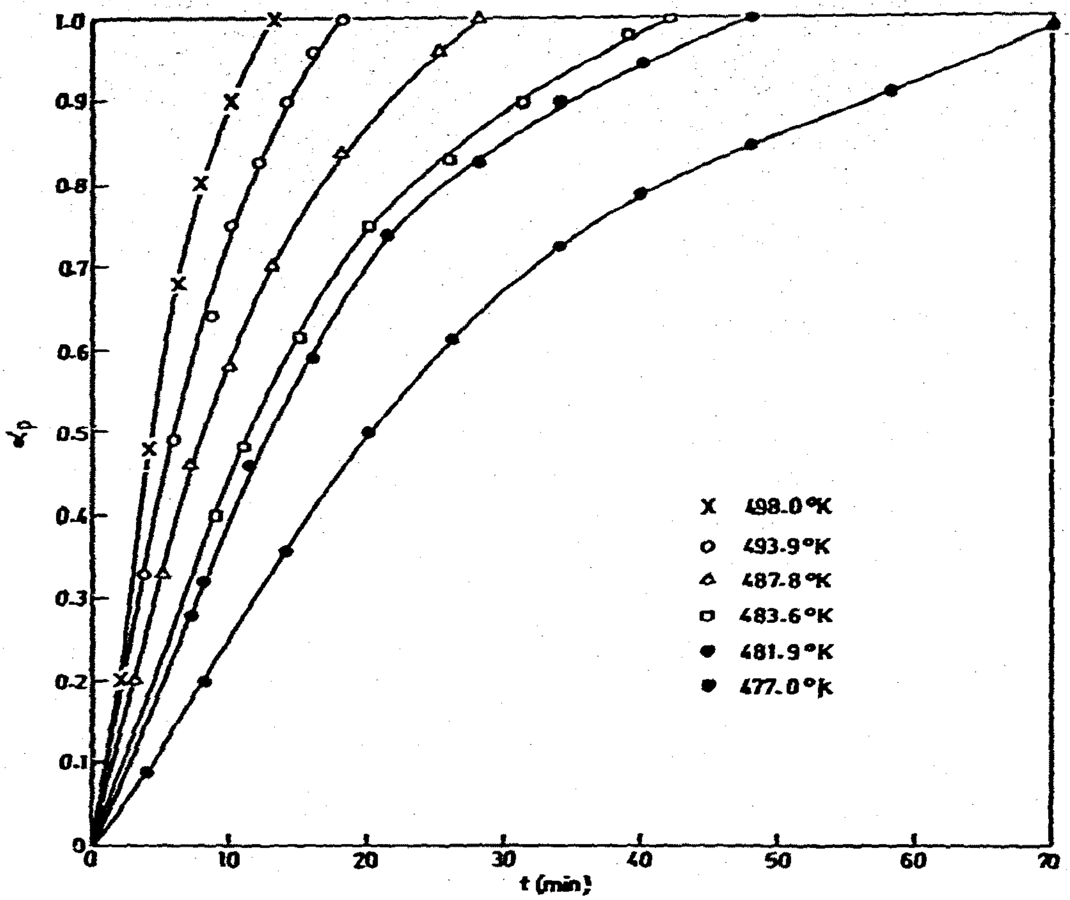

Fig. 1. Plot of the fraction decomposed (α_p) versus time (RDX decomposition).

TABLE 1

ACTIVATION ENERGY DATA OF SOME SOLIDS

Name of the solid	*Activation energy values (kcal mol^{-1})*		
	This method	*Jacobs and Kureishy's method*	*Other methods*
Manganese(II) formate dihydrate	16.0 (70–90 °C)	—	17.2[4], 17.6[5]
Ammonium perchlorate	23.0 (250–300 °C)	26.2	23[2], 19.8[6], 24.8
RDX (hexahydro - 1,3,5-trinito-s-triazine)	40.0 (200–225 °C)	38.0	41[8], 47.5[9], 67.4[10], 45.2[11], 63[12]

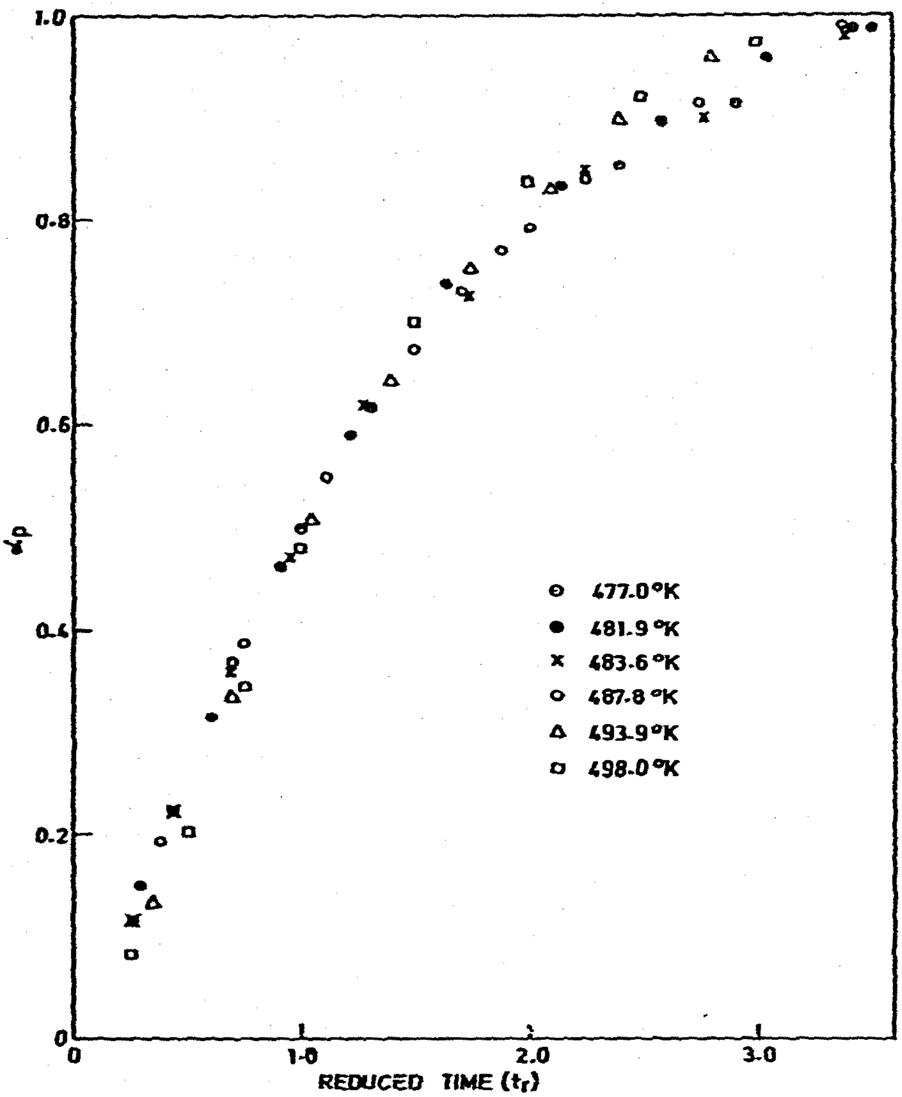

Fig. 2. Plot of the fraction decomposed (α_p) versus reduced time (t_r) (RDX decomposition).

similar at different temperatures (i.e., $n_1 = n_2$). In other words, when the curves at different temperatures superimpose under α versus t_r plot, the order of reaction at different temperatures remains unchanged.

For any decomposition process when it established that n remains constant at different temperatures, it may be useful to estimate E with a very simple method using eqn (6). This equation can be written as follows:

$$kt_{1/2} = \frac{C_n}{n-1} = r \text{ (constant)} \qquad (12)$$

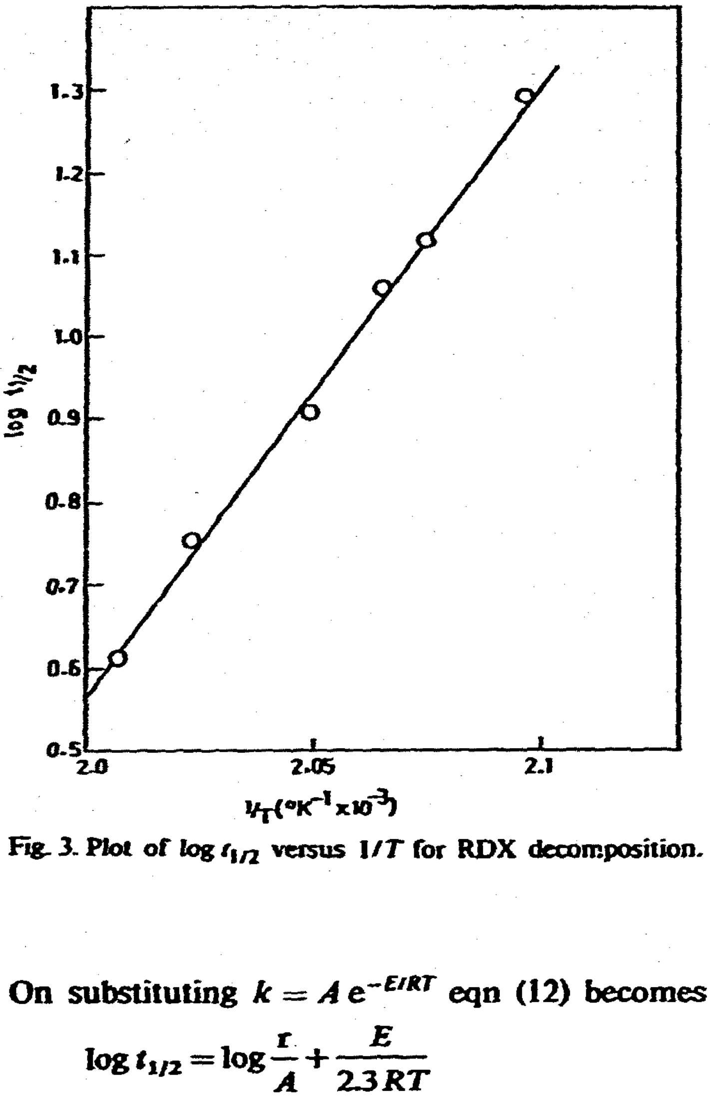

Fig. 3. Plot of log $t_{1/2}$ versus $1/T$ for RDX decomposition.

On substituting $k = A\,e^{-E/RT}$ eqn (12) becomes

$$\log t_{1/2} = \log \frac{r}{A} + \frac{E}{2.3RT} \tag{13}$$

The slope of the plot of log $t_{1/2}$ versus $1/T$ will yield the value of E. Such a typical plot of RDX is shown in Fig. 3. Table 1 gives the values of E for RDX and other solids using the above method. Table 1 also shows the comparison of E values using Jacobs and Kureishy's method[3] and other methods. It was observed that α versus t_r plots for other solids mentioned in Table 1 yield a master curve showing thereby that the kinetic behaviour for these solids does not change with temperature.

It may be seen that values of E obtained by this method compare well with Jacobs and Kureishy's method[3] because in all these cases the kinetic behaviour at different temperatures was found to remain same. This shows that if the condition of similar kinetic behaviour at different temperatures is satisfied, both the above methods will give identical results. However, Jacobs whereas the present method will require only one time at a particular value of α and, therefore, the present method is simple as well as much more rapid.

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