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Note

A NEW METHOD FOR THE DETERMINATION OF THE ORDER OF REACTION FOR A SOLID STATE REACTION FROM THE DYNAMIC DTA CURVE

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The concept of an order of reaction in the solid state has a limited significance compared with reactions in other phases. However, it is essential to calculate the so-called "order of reaction" for the purpose of calculating other kinetic parameters such as activation energy, frequency factor, specific reaction rate, etc.

Kissinger's shape index method [1] is usually used to determine the order of reaction from the DTA curve, but it has been recently pointed out that this method is not applicable for higher order reactions [2]. Further, the simplest method suggested by Piloyan et al. [3] for evaluating the activation energy does not include any consideration for the evaluation of the order of reaction. A new simple method, therefore, is suggested for the evaluation of the activation energy as well as the order of reaction from the same plot of log ΔT vs. $1/T$ used for the Piloyan et al.'s [3] evaluation.

The rate of reaction is given by the usual relationships

$$\frac{d\alpha}{dt} = KC^{\eta} \tag{1}$$

or

$$\frac{d\alpha}{dt} = \frac{KC^{\eta}}{\beta} \tag{1a}$$

where C is the concentration, generally expressed in terms of the fraction remaining unreacted $(1 - \alpha)$, $d\alpha/dt$ or $d\alpha/dT$ is the reaction rate, K is the specific reaction rate constant, β is the heating rate, and η is the order of reaction.

Substituting $K = Ze^{-E/RT}$ (Arrhenius equation) in eqn. (1a) and taking logarithms, this relation becomes

$$\log\frac{d\alpha}{dT} = \log\frac{Z}{\beta} - \frac{E}{2.303RT} + \eta\log(1 - \alpha) \tag{2}$$

where Z is the frequency factor, E the activation energy, and T the temperature (K).

Differentiating eqn. (1a) with respect to T

$$\frac{d^2\alpha}{dT^2} = \frac{Z}{\beta} e^{-E/RT}(1-\alpha)^{\eta-1}\left[-\eta\frac{d\alpha}{dT} + \frac{E}{RT^2}(1-\alpha)\right] \quad (3)$$

At the point of inflexion, $d^2\alpha/dT^2 = 0$ and hence

$$E = \frac{\eta RT^2_{max}}{(1-\alpha)_{max}} \frac{(d\alpha)}{(dt)_{max}} \quad (4)$$

Substituting eqn. (4) into eqn. (2) gives

$$\log\frac{d\alpha}{dT} = \log\frac{Z}{\beta} - \eta\left[\frac{T^2_{max}}{(1-\alpha)_{max}} \frac{(d\alpha/dT)_{max}}{2.303T} - \log(1-\alpha)\right] \quad (5)$$

Experimentally, it is observed that $T^2_{max}(d\alpha/dT)_{max}/[(1-\alpha)_{max}\ 2.303T] >> \log(1-\alpha)$ (Table 1) and hence omitting $\log(1-\alpha)$ in the equation

$$\log\frac{d\alpha}{dT} = \log\frac{Z}{\beta} - \frac{\eta T^2_{max}(d\alpha/dT)_{max}}{(1-\alpha)_{max}\ 2.303T} \quad (6)$$

$\log Z/\beta$ is a constant for all practical purposes.

The plot of $\log(d\alpha/dT)$ vs. $T^2_{max}(d\alpha/dT)_{max}/[(1-\alpha)_{max}\ 2.303T]$ gives a straight line, the slope of which gives the order of reaction, η, and the intercept gives $\log Z/\beta$. The plot of $\log(d\alpha/dT)$ vs. $1/T$ also gives a straight line.

This slope, if divided by $T^2_{max}(d\alpha/dT)_{max}/[(1-\alpha)_{max}]$, gives η, the order of reaction.

The plot of $\log T$ vs. $1/T$ is suggested by Piloyan et al. [3] for the evaluation of the activation energy from a DTA curve. The same plot, if used with

TABLE 1

Comparison of $\frac{T^2_{max}(d\alpha/dt)_{max}}{(1-\alpha)_{max}\ 2.303T}$ and $\log(1-\alpha)$ for $CdCO_3$ decomposition

$\frac{T^2_{max}(d\alpha/dT)_{max}}{(1-\alpha)_{max}\ 2.303T}$	$-\log(1-\alpha)$
54.39	0.0019
53.50	0.0075
52.57	0.0180
51.58	0.0356
50.51	0.0631
49.80	0.1073
48.99	0.1801
48.20	0.3032
47.39	0.5219
46.59	1.0342
46.34	1.9322

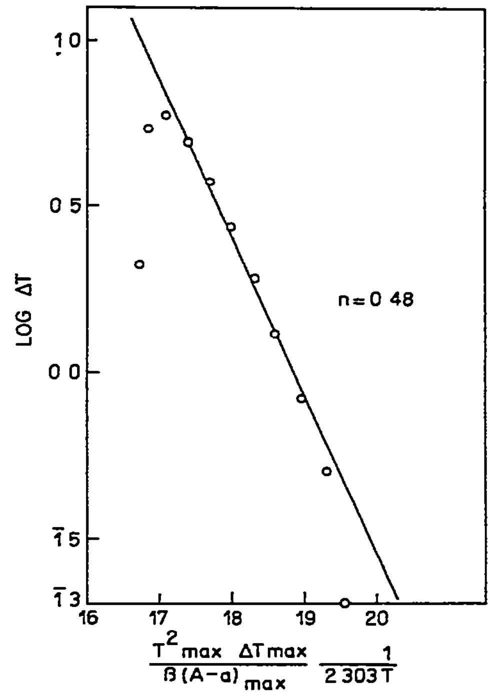

Fig. 1. Plot of log ΔT vs. $T^2_{max}\Delta T_{max}/[\beta(A-a)_{max}2.303T]$.

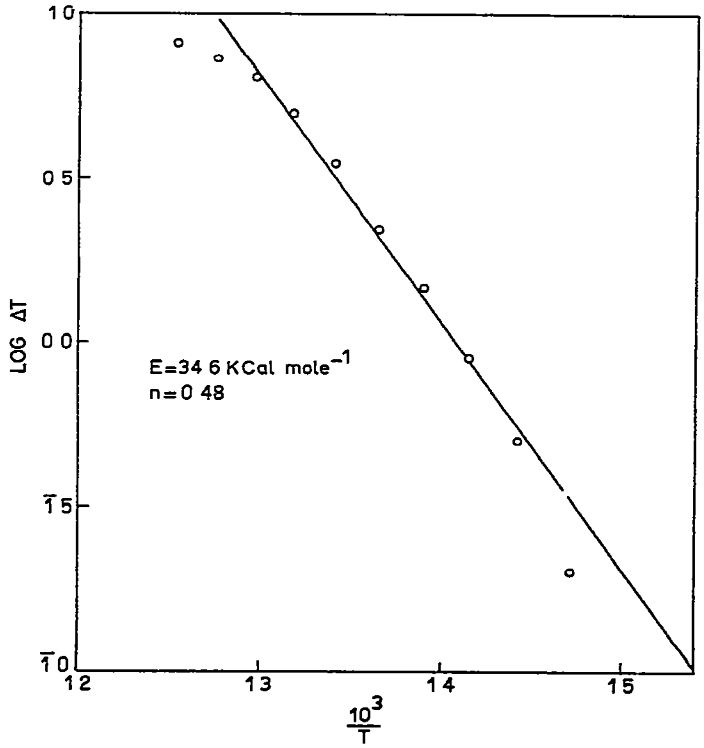

Fig. 2. Piloyan et al.'s method [3] plot for the decomposition of $CdCO_3$.

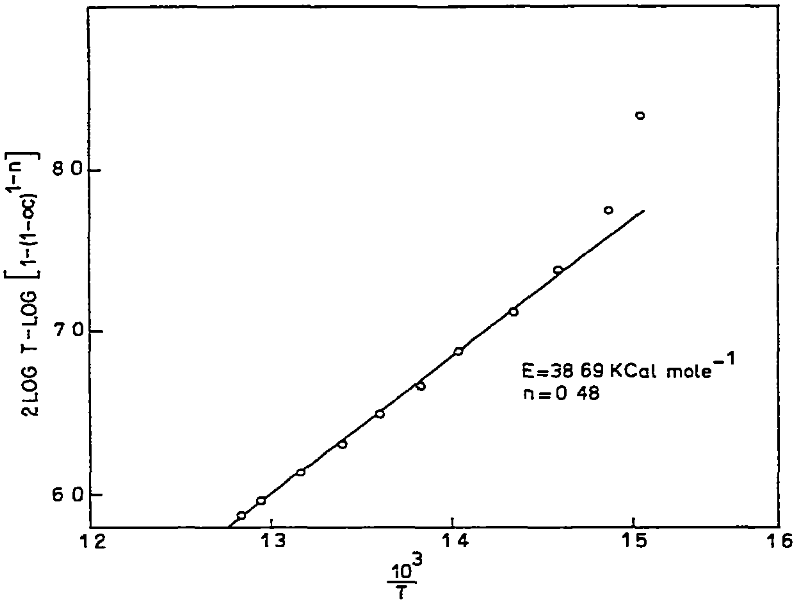

Fig. 3. Coats and Redfern's method plot [4] for the decomposition of $CdCO_3$.

proper multiplying factors, gives the activation energy and order of reaction simultaneously.

The rate of reaction $d\alpha/dt$ or da/dt obtained from DTA curves where a is the area under the DTA peak (total area A) is equivalent to ΔT and the relation $\Delta T = da/dt$ or $A(d\alpha/dt)$ holds good.

Substituting this relation in eqn. (6) and replacing $\alpha = a/A$, where a is the area under the DTA peak at a particular point, A gives the relation

$$\log \Delta T = \log ZA - \frac{\eta}{\beta} \frac{T_{\max}^2 \, \Delta T_{\max}}{(A-a)_{\max} \, 2.303T} \qquad (7)$$

where β is the heating rate.

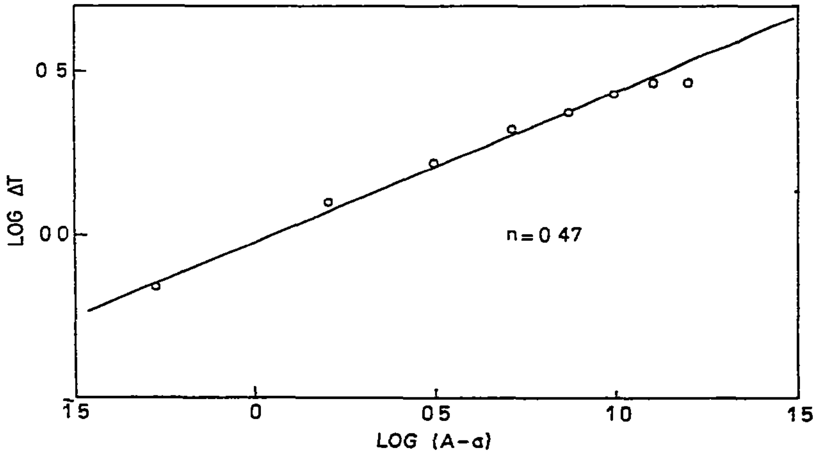

Fig. 4. Log ΔT vs. $\log(A - a)$ plot for the isothermal decomposition of $CdCO_3$ at 703 ± 1 K.

TABLE 2

Order of reaction values calculated from different methods for $CdCO_3 \rightarrow CdO + CO_2$

Kissinger's method	0.48
Isothermal method	0.47
This method	0.48

A plot of log ΔT vs. $T^2_{max}\Delta T_{max}/\beta(A - a)_{max}2.303T$ (Fig. 1) gives a straight line, the slope of which will be η, the order of reaction. The plot of log ΔT vs. $1/T$ also gives a straight line, the slope of which if divided by $T^2_{max}\Delta T_{max}/[\beta(A - a)_{max}2.303T]$ (whose ΔT is expressed in temperature scale) will give the order of reaction (Fig. 2).

This relation was tested for the decomposition $CdCO_3 \rightarrow CdO + CO_2$ and the order of reaction was found to be 0.48. The value determined from Kissinger's slope index method [1] was 0.48. Using this reaction order value, the activation energy value calculated by Coats and Redfern's method [4] for 0.5 order was found to be 38.69 kcal mole^{-1} (Fig. 3), which is comparable with the value calculated by the method of Piloyan et al. [3] (Fig. 2) and also by the conventional isothermal method (Fig. 4; Table 2).

It is evident from this that the method is very simple, convenient and easily applicable to solid state reactions.

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